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Army Materials Research:

Transforming Land Combat Through New Technologies

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Editorial: Adapting to a Changing Battlefield

Regular readers of the *AMPTIAC Quarterly* will have noticed that we've published several 'special issues' over the past few years. The common aim of these publications has been to highlight topics of special interest to targeted technological communities. Examples include our issues on nanotechnology (May 2002) and blast mitigation (*Protecting People at Risk*, February 2003). Both issues were well received by our readers but for different reasons: Nanotechnology represents an exciting and unexplored frontier with intense scientific interest; while protecting people and structures from explosions has gained national attention, especially since 9/11. This current issue addresses perhaps an even more important topic: the development of new technologies to enable our ground troops to become more effective in the war against terror as well as other emerging global threats.

All one has to do is follow the news reports to appreciate the major technological hurdles now facing the Army. Gone are the days when we faced large standing armies, consisting of heavily armored units employing traditional tactics much like our own. Today, we face adversaries that seemingly have no qualms at sacrificing their lives or those of innocent bystanders in an attempt to inflict damage on our troops. Through a mix of conventional and unconventional weapons (such as improvised explosive devices or IEDs) these fanatics have forced us to adopt new tactics while relying upon our existing weaponry and equipment.

To be totally effective against our new and other possible future enemies, the Army must transform from a force relying on heavy armor to one employing a broad spectrum of lightweight, yet survivable systems and equipment that will enhance their ability to fight. In this context, the word 'transform' means to change doctrine, tactics, and assets to respond rapidly to the environments of the new battlefield. The challenge for our community is to develop the advanced materials that will provide the Army improved effectiveness across the full spectrum of operational environments. To make things even more complex, researchers must address additional 21st Century requirements beyond mere system performance. They must give greater consideration for 'green' solutions that reduce the generation or introduction of toxic materials into the environment during production, training, deployment, or other military operations.

Much recent work has been undertaken to improve the survivability of vehicles and their occupants subjected to fire from ballistic weapons as well as blast and fragmentation from mines, Rocket-Propelled Grenades (RPGs), and IEDs. Discussed in this publication are several of the emerging materials that will enable improved yet lighter armor for future systems. Included are ceramic, metal, and composite material research programs that show tremendous promise. Past armor research has yielded the effective but heavy systems we employ today. Becoming more effective against insurgents requires lighter armored vehicles employing innovative materials including transparent armor for windshields and visors. Armor research has been and continues to be a significant activity at the Army Research Laboratory.

Other subjects of significant interest are those related to ordnance materials, including propellants, projectiles, and even the systems used to shoot them. One area of concern lately has been to find replacements for lead bullets and depleted uranium (DU) kinetic energy penetrators. Environmental concerns are the primary reasons for finding alternative materials for these applications, and several of the articles here discuss the programs addressing the problem.

One approach to reduce the weight and complexity of systems is to develop multifunctional materials that perform two or more primary functions. Army researchers have many programs underway that are leading to technologies that exploit this concept and several of them are mentioned here. A multitude of other technology development efforts are also being examined to develop the new generation of lighter, higher performance materials needed to improve warfighting effectiveness.

The twenty separate articles contained in this issue of the *AMPTIAC Quarterly* will provide you with a glimpse at some of the technologies that will enable the Army to transform into a more mobile, survivable, and lethal force while simultaneously becoming a better steward of the environment. There are numerous technical challenges yet to be overcome, but as the reader will notice the Army Research Laboratory's Weapons and Materials Research Directorate (ARL/WMRD) is actively pursing those technologies necessary for the Army to transform the face of the new battlefield.

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Issue Focus:

Army Transformation

Section I: New Approaches for a Changing Army

The US Army is undergoing a transformation that will enable it to better protect the Nation throughout the 21st Century. Advanced materials will be pivotal in achieving the Army's Future Force characteristics of responsiveness, deployability, agility, versatility, lethality, survivability, and sustainability.

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About the Cover and Acknowledgements

The cover represents how new materials – from the nanoscale up to the macroscopic, are being harnessed to deliver the systems necessary to make the Future Force a reality. We would like to thank Ms. Amy Kehring of ARL for creating it. We would also like to thank the following personnel for their support and guidance in the preparation of this issue: Dr. Bruce Fink, Chief of Ordnance Materials; and Dr. James McCauley, ARL Fellow; both of the Army Research Laboratory at Aberdeen Proving Ground. Lastly, AMPTIAC would like to extend our sincere appreciation to all our authors and contributors who helped to make this issue the best yet!

Materials, Disruption, and Revolution

New Materials Will Benefit Tomorrow's Soldier

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Throughout the history of warfare, materials technologies have had a significant impact on land-combat force capabilities. Today, materials scientists and engineers from government laboratories, industry, and academia are working diligently to achieve a common goal of transitioning advances in materials research to improved warfighting capabilities for the Soldier. Research is being performed at the Army's corporate materials laboratory within the Army Research Laboratory (ARL); at several Army Research, Development, and Engineering Centers (RDECs); and other laboratories, such as the Army Corps of Engineers and the US Military Academy. This special issue of the *AMPTIAC Quarterly* highlights a number of the critical materials technologies currently being explored and developed within these laboratories. This article aspires to describe to non-materials scientists and engineers, some of the toughest problems facing the materials and processing community as we strive to enable the Army's vision of rapidly deployable, lethal, and survivable fighting systems.

A fundamental attribute of materials technologies is their inherently disruptive nature.

Materials, as a technical discipline, is by nature horizontal in its scope – meaning that it horizontally feeds and serves as the basis for vertically-integrated technologies such as munitions, cannons, and ground vehicles. As research programs are defined to impact a number of technologies, both basic and applied research programs in materials are inherently capable of feeding multiple vertically-integrated technologies. Hence, there can also be multiple methods to realize the benefits of materials research; whether embodied in engineered materials, new processing capabilities that reduce the cost of commodity, or in new analytical and computational models that enable the design of engineered systems through advanced materials. Even though specialty materials may have been developed for a singular purpose, they are quite often serendipitously relevant and thus may be suitable for myriad alternate applications; many of which were not considered or even dreamed of during the original research effort.

As an example, consider the evolution in our understanding of the mechanics and processing of thick-section advanced carbon-fiber composite materials; developed for and used in the design and fielding of the Army's M829A2 kinetic energy projectile sabot (described in more detail later in this issue) in the late 1980s and early 1990s. Analytical and computational models were developed, validated, maintained, and improved over the next decade, and were subsequently used to develop the Army's lightweight composite armors for the Future Combat Systems. Similarly, electromagnetic induction-based heating of carbon fibers (developed for the repair of thermoplastic-based thin-section composites on rotorcraft) was adapted to process the sabots for the M829A3 projectile, resulting in substantial cost-reductions. These are just two examples of how materials technology, unlike many other fields, can be timeless. That is, materials-related technologies do not become obsolete. Instead, they often find practical (performance plus cost benefits) application in systems far different than those for which they were originally developed.

A fundamental attribute of materials technologies is their inherently disruptive nature. Acclaimed author and Harvard economist Clayton Christiansen defines disruptive innovation as *products or systems that create entirely new markets*. The Army materials community has long embraced this concept. Disruptive technologies can also be thought of, in part, as a new understanding of existing materials and techniques; which in turn may be used to synthesize and process them into new and useful forms, thus creating new opportunities to be exploited for previously unanticipated yet critical applications (i.e., new markets). Luckily for Army materials experts, the Soldier "marketplace" is quite broad and its future is wide open.

Consider the following. If a specific solution path were pre-defined to attack a certain problem, it is less likely that engineers would be able to take advantage of any disruptive technologies, since they would need to rely on commodity

The Army Materials Centers of Excellence: A New Model for Government-University Collaborations

In 1996, the Army created the Materials Centers of Excellence (MCOE) program at to work with leading materials research universities and corporations. In contrast to “knowledge driven” basic research, the approach of these Centers is to conduct high risk, large potential payoff, strategically focused basic research and exploit the development of new materials and related materials technologies for future Army applications; they are basically science-driven, problem-directed Centers.

Strategically focused, linked, and agile collaborations involving equipment, people, and publications are established creating seamless and synergistic teams between personnel from Army laboratories and their University partners including equipment, people, and publications. Using cooperative agreements instead of traditional contracts or grants, each institution collaborates with Army scientists and engineers to create programs that are redefined annually, where projects can be modified, terminated, enhanced and new ones started at any point in time. Additional funding, if available, is easily added to enhance or start new work. The close connections to ongoing work in the Army also allow for the rapid transition of breakthroughs. Centers are nationally competed every 3-5 years and the current centers are described below.

COMPOSITES:

The Army Center of Excellence in Composite Materials Research (CMR) began in 1996 at the world-renowned Center for Composite Materials at the University of Delaware (UD-CCM). The program has produced over 100 journal publications and 14 patents with more than half of these being a joint effort between University and Army researchers. UD-CCM has hosted dozens of Army researchers including several full-time Army research staff members in residence at the Center’s Newark, Delaware facility. Notably, research from this program has resulted in receiving two of the last three biennial Army Siple Memorial Medals, which is the highest award for science and engineering in the Army.

In 2000, the Army instituted a sister program at UD-CCM called the Composite Materials Technology (CMT) Program. CMT is an applied research program designed to accelerate the transition of basic research efforts developed under CMR to the Soldier. The program is funded by multiple Army laboratories including the Army Research Laboratory (ARL), the Tank-Automotive Research, Development and Engineering Center (TARDEC), the Armament Research, Development and Engineering Center (ARDEC), and the Aviation Missile Research, Development and Engineering

materials that could be engineered into the desired solution. Therefore, if one were to say: “There is a ceramic-based armor for ground vehicles, and I need a ceramic with certain properties and performance characteristics to be able to mitigate this defined threat,” we would be asking for an evolutionary approach and an incremental solution. This approach is often warranted, but requires a vast knowledge of materials and extraordinary expertise in the art and science of armor design and optimization. However, because revolutionary advances in warfighting capability only come about through broadly enabling advances in science or technology (and materials advances are historically the most profound agents of change in technology), we need to ask the question differently: “There is a need to protect soldiers from these defined threats.” This is the same requirement stated in a very different way – but now it has the opportunity to capitalize on novel engineered solutions that take advantage of a spectrum of materials and technologies, whether they are commodity, engineered, or synthesized.

> **Materials-related technologies do not become obsolete ...they often find practical application in systems far different than those for which they were originally developed.**

Interlaced throughout this special issue are examples of the insertion of new materials, development of engineered materials, and the creation of new classes of materials for Army applications. Predictably, yet not without ingenuity and difficulty, engineered composites are applied to pull back the center of gravity of steel cannons, commodity ceramics are applied to composite armors, and synthesized organic nanomaterials are specifically designed to improve the energy absorbing capabilities of composite structures. On the other hand and quite unpredictably, ferromagnetic nanoparticles designed for rapid curing of adhesives are poised to revolutionize treatment of cancerous tumors; advances in ceramic processing and statistical failure analysis techniques are enabling hotter propellants and longer-lasting gun tubes; and alumina-based metal matrix composites (originally designed for high-tension power lines) may turn out

Center (AMRDEC). The combination of these programs has resulted in several major technologies, including the design and testing of a lightweight composite-overwrapped gun barrels, the field-testing of composite wheeled vehicle components, and the development of building-block structural design protocols for lightweight armors.

METALS AND CERAMICS:

In 2001, MCOE programs were established at Johns Hopkins and Rutgers Universities. The program at the Johns Hopkins "Center for Advanced Metallic and Ceramic Systems" focuses on the dynamic behavior of non-crystalline and nano-structured metallic systems, while a Rutgers – Johns Hopkins team focuses on the high fidelity design and processing of high performance structural ceramics. The underpinning technical philosophy consists of integrating processing and characterization with the visualization, identification, modeling, and simulation of dynamic failure and damage mechanisms within metallic and ceramic systems. The primary technical focus in the Johns Hopkins program is on shear band formation in nano-structured metals and bulk amorphous metals during largely compressive loadings. In the Rutgers – Johns Hopkins ceramic program, the technical focus is on the quantification of the effects of processing defects, identification of high strain rate damage and failure mechanisms, and the control of grain size and macrostructures to mitigate high strain rate failure.

POLYMERS:

The Army Center of Excellence in Polymeric Materials was established in 2001. Serving as the core institution, the University of Massachusetts at Amherst has partnered with a number of other institutions, including the University of Tennessee and Amherst College, focusing on the development of new concepts in polymer materials technology. Currently, this program has two overarching thrusts. The first is to develop functional polymeric materials through the combination of novel polymer chemistry and self-directed assembly processes. At the foundation of this research has been the development of nanostructured templates materials with ordered nanoscopic patterns using block copolymer technology, the continued optimization of which has resulted in materials with unique optical, electrical, and magnetic properties. On-going research in this thrust area includes the chemical modification of carbon annotates nanotubes and quantum dots to allow for controlled incorporation of these materials into polymers, and the development of new polymeric materials for applications such as fuel cells, flexible displays, and photovoltaic cells. The second thrust of this Center is to develop technologies capable of enhancing the performance of polymeric materials used in Army applications. Examples of on-going research efforts in this thrust area include the development of sprayable coatings systems with antimicrobial activity, (i.e., that are self-decontaminating with regard to biological agents); the use of organosilicate nanoparticles for enhancing the mechanical performance of polymers used in transparent armor applications; and the control of surface topology for tailoring interfacial interactions between dissimilar materials.

to be the critical enabling technology for high-stiffness, high-conductivity electromagnetic gun tubes.

Each step in our quest to understand materials, and to apply that knowledge judiciously toward improved warfighting capability for the Soldier, can take us down many alternative paths – both ultimately fruitful trails and frustrating dead ends. As the Army materials community, our daily responsibility is to move forward without trepidation or doubt, but with eager resolve and continuous focus on the Soldier. Just as together we will often fail, we will also often succeed. Failure is, in fact, an integral part of ultimate success. As surely as our soldiers in uniform risk life and limb, we must heed their example by taking intellectual risks. Only by accepting that risk of failure will we truly revolutionize warfighting capabilities through the application of advanced materials. The Soldier depends on that.

REFERENCE

Clayton Christiansen, *The Innovator's Dilemma*, HarperCollins Publishers Inc, New York NY, 2003

Dr. Bruce K. Fink received his BS in Civil Engineering in 1985 and his MS in Applied Mechanics in 1987, both at the University of Nebraska-Lincoln; and his PhD in Materials Science and Engineering in 1991 from the University of Delaware. Dr. Fink has 20 years of service with the Army, including 10 years as a Combat Engineer Officer. He is currently serving as Chief of Ordnance Materials at the Army Research Laboratory.

Meeting New Challenges:

Advanced Materials Aid the Army's Transformation

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INTRODUCTION

As threats to the United States become more asymmetric, the US Army is transforming itself by adapting its operational strategies to better protect the Nation. In *The Way Ahead – Our Army at War – Relevant and Ready*,[1] General Peter J. Schoomaker, Chief of Staff of the United States Army lays out a vision of a more relevant and ready Army. This vision is grounded in the Army's longstanding core competency, i.e., training and equipping soldiers and growing leaders, and providing "relevant and ready land power capability." *The Way Ahead* clearly articulates that the Army must transform for operations different from those it has been traditionally structured to face. In order to defeat new threats such as the largely transnational terrorist organizations with worldwide infrastructure, resources and sponsors, a "capabilities-based modular, flexible and rapidly employable Joint-Army team" capable of controlling the battlefield and dominating the enemy is required.[1] This article highlights the role of advanced materials in the Army's transformation, and the challenges inherent in developing and implementating of new materials in combat systems.

Cross-cutting characteristics of Army transformation include responsiveness, deployability, agility, versatility, lethality, survivability, and sustainability. These characteristics fully support the "Future Joint Force Attributes"[2] to achieve "Full Spectrum Dominance." On-going capability gap analyses are being carried out for the Current and Future Force by TRADOC, the Army's Training and Doctrine Command.

In many, if not most of the cross-cutting characteristics and identified gaps, new and improved materials used in innovative designs offer significantly enhanced, and in some applications, revolutionary capabilities. Advanced materials are the enabling underpinning for the evolutionary improvement of the Current Force, as well as for the revolutionary invention of weapon systems for the Future Force. However, as suggested in *Alternative Approaches to Army Transformation*,[3] the tradeoffs on mobility, survivability, and lethality that result from "reducing the weight of single platforms presents the greatest challenge to transformation." Advanced materials and structures, incorporating multi-functionality, can significantly improve Army capabilities by providing lighter weight, stronger and more durable materiel but not without additional challenges.[3]

Future Joint Force Attributes

- ➢ Fully Integrated
- ➢ Expeditionary
- ➢ Networked
- ➢ Decentralized
- ➢ Adaptable
- ➢ Decision Superior
- ➢ Lethal

CHALLENGES IN DEVELOPING AND IMPLEMENTING ADVANCED MATERIALS

Throughout human existence, people have used natural (e.g. stone arrow heads) and synthetic (e.g. steel Samurai swords) materials as means of preserving their security. In these two examples, the importance of the materials used in the weapons was obvious and visible. As weapon platforms have become more complex, it has become increasingly more difficult to appreciate the importance of materials to the performance and capabilities of the system. All engineering systems require certain material properties for performance. As a result of this complexity, materials decisions become further removed from total system decisions, as illustrated in Figure 1. Thus, it is extremely difficult for materials scientists and engineers to convince the decision makers at the component and full system levels of the advantages of advanced materials technology without extensive data bases and prototype experiences.

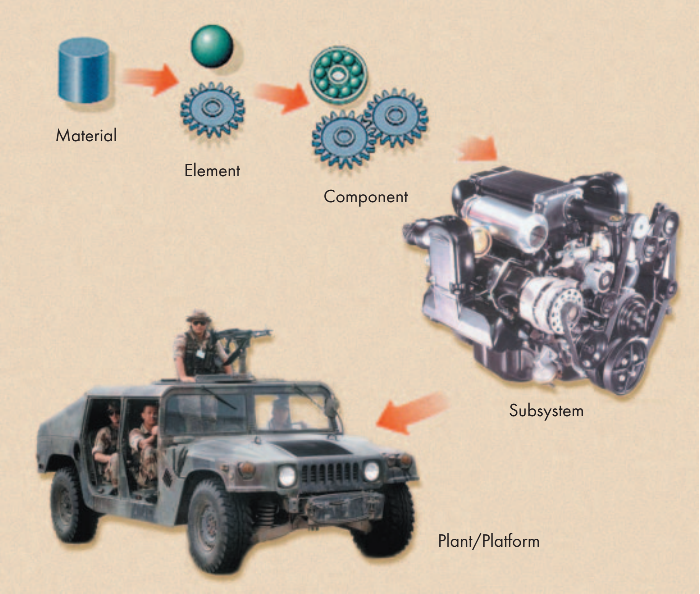

Figure 1. **Scale Progression of the Composition of a System[4].**

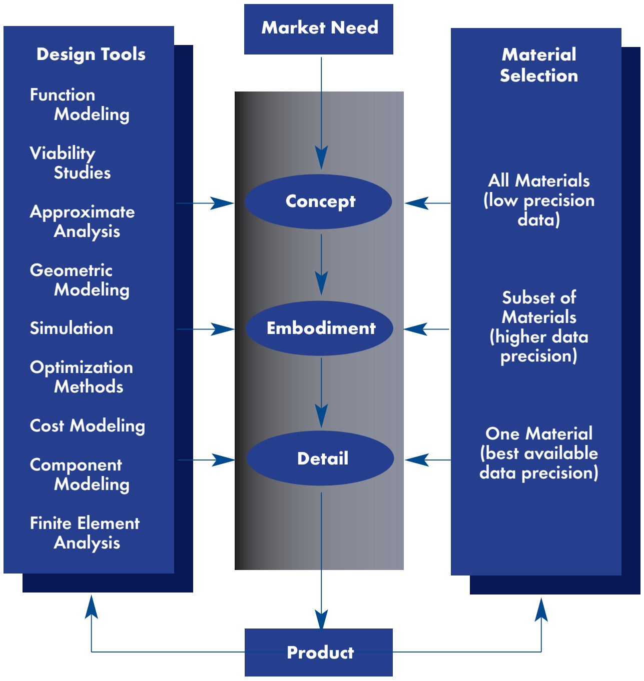

Figure 2. **Materials Selection Process in the Various Stages of Design[5].**

The utilization of advanced materials in the early design stages (Figure 2) of the acquisition cycle has always been problematic. To minimize risk, design engineers typically utilize commercial, off-the-shelf materials rather than advanced materials with limited property data. From a materials perspective, this results in fielded systems being obsolete almost from the day they roll off the production line. Figure 3 illustrates this ongoing problem for materials. As seen in the figure, it often takes 20-30 years to mature a material to the point of widespread commercialization or use in engineering systems.

THE ARMY'S PROCESS FOR MATERIALS DEVELOPMENT

It is useful for people who are not routinely exposed to advanced materials to have working definitions of various aspects of the field: in particular, the relationship between materials science, materials engineering and materials technology.

- **Materials Science** – the creation of new materials and the understanding of the relation of material characteristics (unique signature = chemistry, microstructure, defects) to properties.

  $$\text{Property} = f\,(c, M, PD)$$

  Any material is a population of identifiable constituents (c) in a certain physical array (M) with certain, almost unavoidable defects (PD).
- **Materials Engineering** – the processing/manufacturing of materials with controlled properties and geometries for certain performance. *Materials Figures of Merit (FOM)* are critical links here as they define a quantitative relationship between combinations of properties to desired performance.

  $$\text{Performance} = f\,(\text{property } 1, \text{property } 2, \text{property } x, \ldots)$$
- **Materials Technology** – the successful or highly likely application of materials science and materials engineering knowledge to the improvement, development and enabling/invention of useful products and systems.

Materials scientists and engineers often work in collaboration with other engineers (mechanical, electrical, aeronautical, civil etc.) in refining or developing engineering systems. This involves a range of activities from selection of the best available material to optimizing existing materials or creating new ones with the desired properties. The process of generating advanced materials technology incorporates the synthesis, processing, characterization, properties, performance and predictive modeling of materials; as well as manufacturing, including miniaturization technologies; and nondestructive testing technologies to reduce the time, risk, and cost of acquiring materials. In addition to these activities, materials scientists and engineers work on processing and manufacturing technology to reduce costs and improve the reproducible quality of existing materials. This usually involves material characterization (determination of the unique signature) by

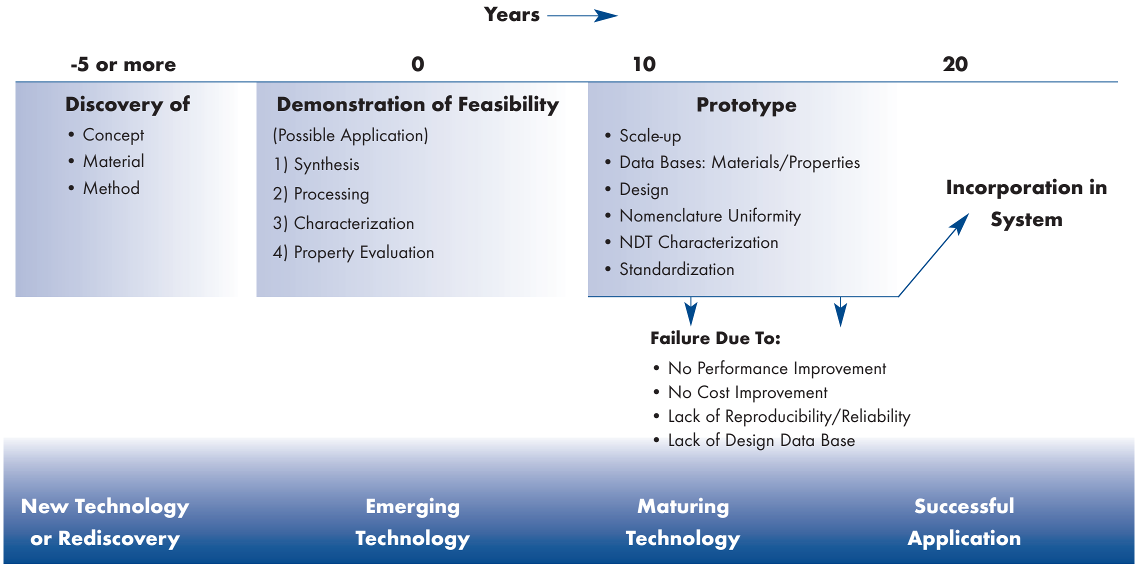

Figure 3. **Materials Technology Evolution[6].**

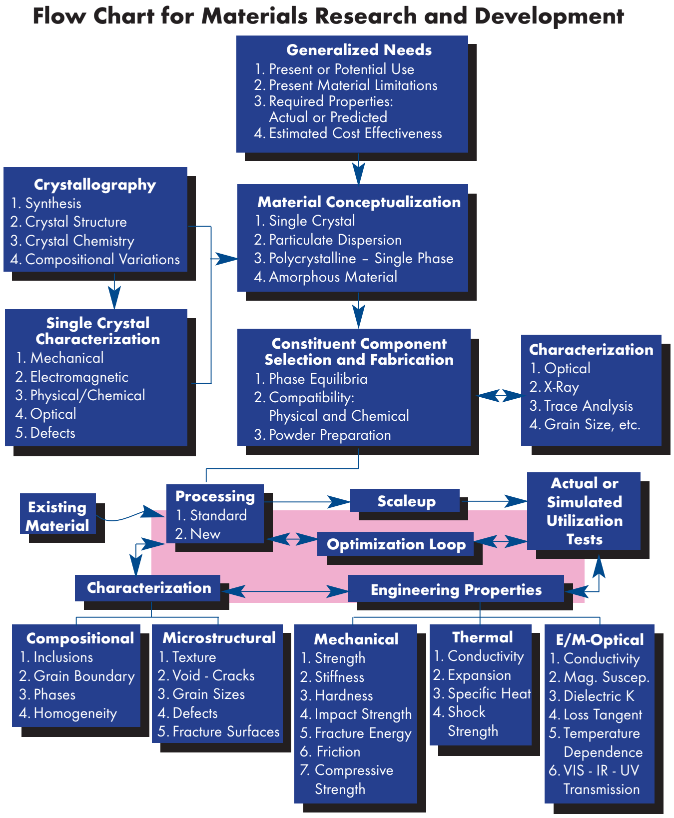

Figure 4. Conventional Materials Research and Development Flowchart[7].

non-destructive or destructive means and materials testing/evaluation of the desired electrical, mechanical or durability requirements, including property design allowables used by design engineers. (See for example, MIL-Handbook-17, a composites materials handbook for organic matrix, metal matrix and ceramic matrix composites.) Of course, there are always the underlying competing goals of performance, cost, production capacity and strategic availability, as modified by environmental and safety issues, which may have to be traded off to achieve the desired performance within budgetary constraints. All of these issues should be taken into account during the research, development, design and acquisition cycle.

New materials technology emerges from a systematic research and development strategy. Basic (6.1) and applied research (6.2) agendas typically can be determined in two ways:

- Strategic (technical) opportunities – knowledge driven
- Strategic objectives – application pulled

Armor Materials by Design is an example of a basic research Strategic Research Objective (SRO) that the Army uses to help guide the basic research agenda; it is an application pull, strategically focused process. This Armor Materials by Design SRO is not how to design components (systems) with existing materials, but rather how to select and design materials for very demanding passive armor applications. Conventional materials research and development typically follows a more sequential process as illustrated in Figure 4.

Passing the Torch: Materials Engineers Turn Young Americans on to Science

Scientists, engineers, and technologists form a very small segment of our national workforce – only about five percent. The National Science Foundation (NSF) reports in "Science and Engineering Indicators 2004" that while Americans express strong support for science and technology (S&T), they are not very well informed about these subjects.[1] For instance, in the US and Europe, most adults pick up information about S&T primarily from watching television; the print media are a distant second. In addition, most Americans (two-thirds in the 2001 NSF survey) do not clearly understand the scientific process. Knowing how ideas are investigated and analyzed – a sure sign of scientific literacy – is important.

A recent Building Engineering and Science Talent (BEST) publication entitled "The Quiet Crisis: Falling Short in Producing American Scientific and Technical Talent" reports that a quarter of the current science and engineering workforce, whose research and innovation generated the economic boom in the 1990s, is more than 50 years old and will retire by the end of this decade.[2]Because it is essential to keep a minimum number of scientists & engineers in the workforce and to have a reasonably educated and interested population with regard to scientific issues, the US Army has been engaged in a number of programs designed to encourage young students to consider science as a possibility for their future.

Most Army S&T labs have outreach programs at the local level. These programs range from judging at science fairs to participating in career day at schools to going out to classrooms to work with kids in hands-on science activities. Two of the local programs at Aberdeen Proving Ground (APG) are the Kids & Chemistry Program and the Science-in-the-Library program. These programs involve materials scientists and engineers from the Army Research Laboratory and Edgewood Chemical Biological Center. In the Kids & Chemistry Program, Army volunteers go into local schools and perform hands-on science experiments (e.g. Jiggle Jelly, What's In a Color? and The Cool Blue Light). In Science/Chemistry-in-the-Library Program, Army volunteers go into libraries and schools in Baltimore City, Howard, Cecil and Harford County, Maryland, and New Castle County Delaware and work with kids doing hands-on experiments ranging from "Monster Snot!" (the Science of Slime – Polymers) to "It's Gross and We Ate It!" (Food Chemistry)

DEMANDS AND REQUIREMENTS OF MATERIALS FOR THE CURRENT AND FUTURE FORCE

The revolutionary demands of the Future Force will require tailor-made materials (materials by design), multifunctional materials, biomimetic and biologically-inspired materials, nanostructured materials, hybrid materials, coatings and ultra light structures. When compared to existing materials, these new materials should show major performance improvements at the same or significantly reduced weight, and must also meet safety and environmental requirements. Research to describe and characterize the fundamental physics and mechanics of damage and failure, especially in dynamic environments unique to the Army will also be critical. In addition, requirements for cost reduction and reliability

to "Chemistry of Crime" (Forensic Science), along with a variety of other experiments. The kids always get a hand-out that includes take-home experiments. None of the chemicals involved require ventilation (therefore making them safe to work with at libraries and schools). Both programs have National Chemistry Week activities and work with approximately a thousand kids annually.

In the Fall of 2002, the US Army initiated a nationwide "electronic science fair" called eCybermission. eCybermission is an on-line competition for students in 6th through 9th grades. Students form teams of 3-4 students and have a team advisor. The team members pick a real-life problem that applies to one of the four science, math, and technology challenge areas: Sports and Recreation, Arts and Entertainment, Environment, or Health and Safety. Then the challenge is for the students to develop a solution to the problem using science, math, and technology while having a positive impact on the community. All projects are submitted and judged on-line. There are regional and national awards given out. For the 2003-2004 competition, there were over 1,600 projects submitted for evaluation, involving almost 6,000 students nationwide!

A new initiative that has started within the last two years at a few Army S&T labs is regional outreach directly at schools through the Materials World Modules (MWM) Program. MWM is an inquiry-based science and technology program developed at Northwestern University with funding from the National Science Foundation. The MWM program was designed to serve as a resource for teachers to help them to excite their students about materials science and the world we live in. Rollout of the program by the Army was begun in 2003 by a team at Picatinny Arsenal. The Army Research Lab joined the effort in 2004, and currently several dozen schools are involved. The Army program offers schools one free MWM kit per year (kits include supplies for various experiments, as well as teacher and student manuals), along with support from the Army S&T staff. Schools may choose to have a researcher come to their school and work with students as they perform exploratory experiments and/or the design phase of the module, or they may prefer to have a researcher support the schools in the role as guest lecturers on specific topics. The MWM kits focus on topics in materials science, and include biodegradable materials, biosensors, composites, ceramics, concrete, food packaging, polymers, smart sensors, and sports materials. The modules emphasize active, hands-on learning and provide students of all ability levels with opportunities to apply what they learn in the classroom to real-world problems.

The challenge of engaging adults in science is a daunting task. The key is to engage students before they decide that science, math and technology are either too hard for them to master or not relevant to their lives. The sciences typically involve a significant amount of non-trivial in-class and laboratory work. If the interest of students can be piqued at a young age, they will be more excited about learning necessary basics of science and math and more motivated about moving on to advanced levels of learning and discovery. In order for this to happen, it is essential that young students be exposed to real-world applications of materials science (versus just facts in textbooks). It is important for them to realize that science is all around them, and essential for them to have role models and mentors in their lives that will open up the world of science and technology to them. The Army is striving to help schools fulfill these needs and thereby foster the development of the S&T's of tomorrow.

FOR MORE INFORMATION PLEASE SEE:

Kids & Chemistry Program – http://www.ecbc.army.mil/about/kids&chemistry/index.htm

Science-in-the-Library program – http://mdchem.org/citl/citl_main

eCybermission – http://eCybermission.com

Materials World Modules – http://www.materialsworldmodules.org

ACKNOWLEDGMENT

The MWM Program was made possible through the leadership of the late Dr. John H. Hopps, Jr., Deputy Undersecretary of Defense for Laboratories and Basic Sciences.

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Table 1. Performance Requirements for Future Force Systems and Functions.

FUTURE FORCE SYSTEMS/FUNCTIONS	PERFORMANCE REQUIREMENTS
INDIVIDUAL PROTECTION	Ultra-lightweight and Conformable Multiple Threat Protection Target: 3.5 lbs/ft^2 Signature Management and Control
ARMORED FUTURE LAND SYSTEMS	Lightweight/Mobile Threat Designable/Repairability Target: Med. Threat at 30% of Present Tech. Multifunctional: Ballistic/Structural/Stealth
TRANSPARENT ARMOR (EM WINDOWS)	Designable for Personnel and Vehicles Multifunctional: Microwaves, IR, Visible
ADVANCED AIRCRAFT	Lightweight/Mobile Repairability/Multifunctional Signature Management and Control

enhancements will continue to push the limits of manufacturing science and technology.

In order to expedite the incorporation of new materials technology into the Army's Current or Future Force, the existing paradigm of a culturally comfortable sequential R&D process must be modified. The adapted process would accelerate the progression of critical research needs by concurrent experimental validation coupled with modeling and simulation and rapid bracketing of 6.1 and 6.2 R&D for strategically focused efforts. For example, in the *Armor Materials by Design* SRO three underpinning science and engineering goals have been established:

- Full Length Scale Modeling/Simulation
- Ballistic Energy Absorption Mechanisms
- Hybrid Multifunctional Integration

Figure 5 schematically illustrates the concurrent approach envisioned for the *Armor Materials by Design* SRO.

One of the key elements in the *Armor Materials by Design* SRO is determining the various performance requirements (capabilities) and then the related technical metrics as shown in Table 1. These metrics can then guide the research program and allow for evaluation of progress toward the goals.

FUTURE OF ADVANCED MATERIALS DEVELOPMENT FOR THE ARMY

Most systems are critically dependent on materials technology and there is no reason to believe that the properties of materials will not continue to advance either in a predictive, linear way (evolutionary – Figure 6), as illustrated below for the thermal conductivity improvement of certain ceramics.[8] Likewise, properties can experience exponential growth, as for the case of high temperature superconductors[9] (revolutionary – Figure 7), as they have over the past 30 years. Other examples of phenomena that have experienced revolutionary advances include transistor densities (Moore's Law), specific strength and stiffness of composites, flux magnetization product of permanent magnets, optical transparency of glass fibers, critical temperature of superconductors, sonar

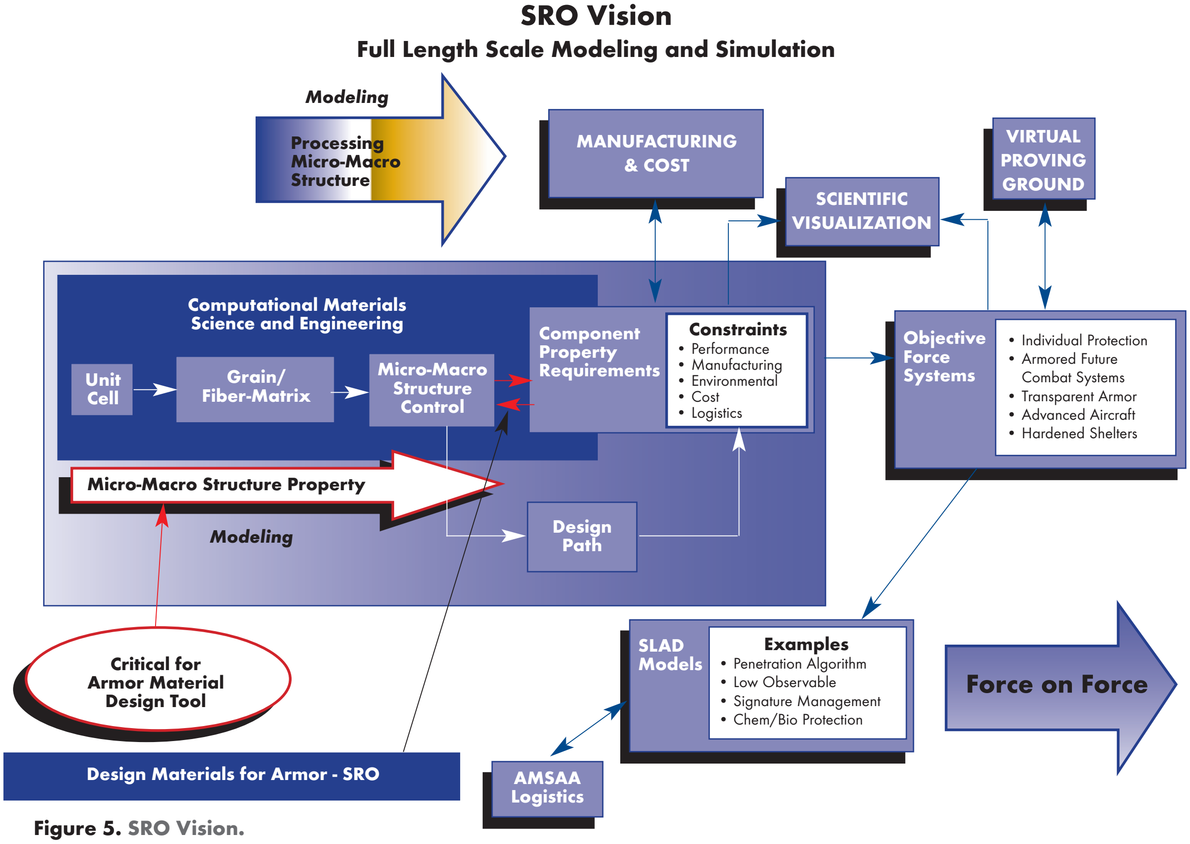

Figure 5. SRO Vision.

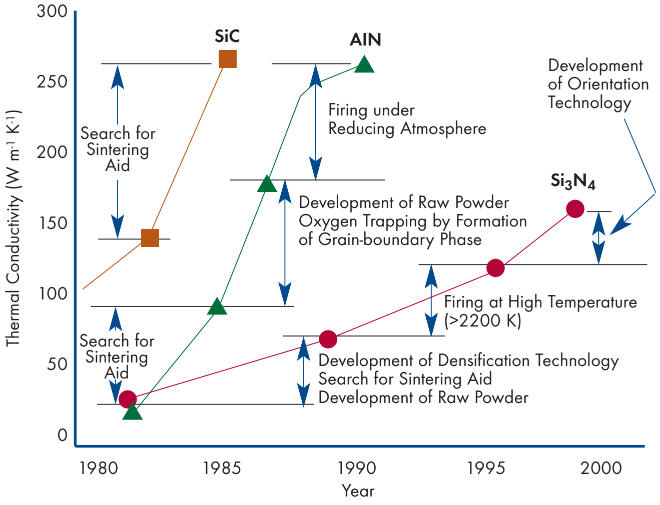

Figure 6. **Trends in the Enhancement of Thermal Conductivity of Ceramics[8].**

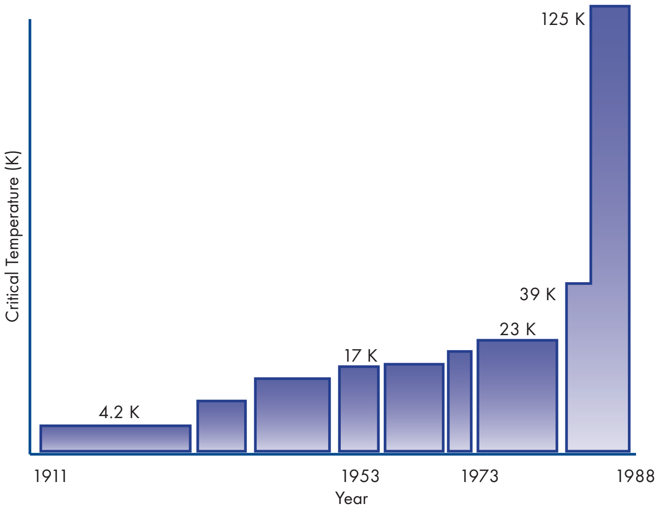

Figure 7. **Progress of Critical Temperature of the Best Superconducting Materials as a Function of Time[9].**

sensitivity, and size of manufactured detail (chips).

The development of armor materials has shown a similar revolutionary trend (Figure 8). Armor materials have progressed from heavy (high areal density) metallic systems to advanced, lightweight (low areal density) composite and hybrid materials that can provide structural support to a weapon system as well as threat protection. The figure shows that the development of armor materials has led to a decrease in areal density which corresponds to an increase in mobility for weapon systems.

Examples of revolutionary engineering systems using advanced designs and materials include the Hindenburg Zeppelin, the Rutan Voyager aircraft, and a more recent example is the bicycle used by Lance Armstrong in the Tour de France. All of these depended on visionary people who employed leap-ahead design and advanced materials. Over the next 30 years there exists a very high probability for unprecedented developments in materials, computers, miniaturization and sensor technology, as well as the blurring of the clear distinction between synthetic and biological materials. Energy will be supplied from miniature fuel cells, batteries or micro machinery/engines. For the first time in our history, materials can be designed and synthesized atom by atom for specific applications. Computer modeling and simulation technology will be advanced to the point of being able to design armor and systems and to simulate their performance on the battlefield.

The revolutionary advancement of materials has already had an impact on the performance of weapons systems, and it will continue directly to enable higher mobility systems for the Future Force. Figure 9 shows the progression of weapons systems over the past 25 years toward the higher mobility systems of the near future.

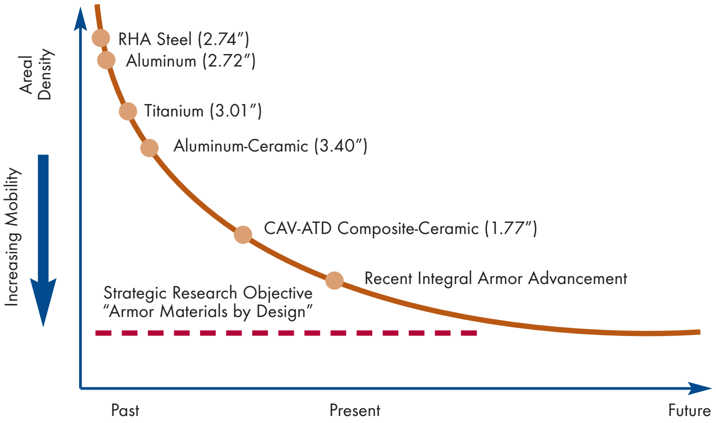

Figure 8. **Revolutionary Composite Armor Improvements.**

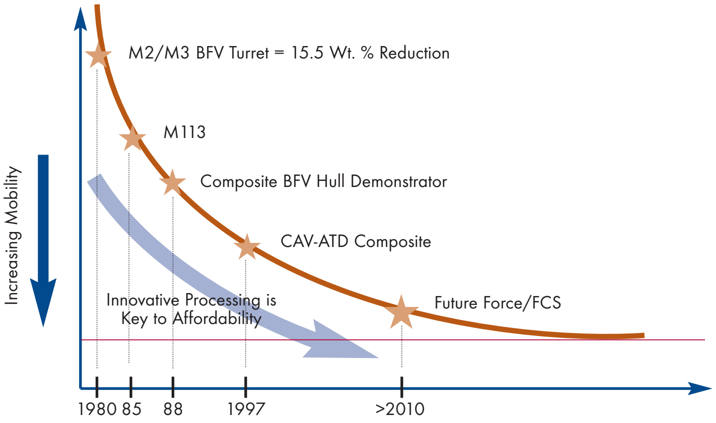

Figure 9. **Revolutionary Impact of Advanced Materials on the Mobility of Weapons Systems.**

ADVANCED MATERIALS GOALS FOR THE FUTURE FORCE

Advanced materials will play a crucial role in the Army's Transformation to meet current and future threats faced by the United States. Several key factors will contribute to the development of these materials and their implementation in the Army's forces. The bottom line for the Future Force is to reduce weight while maintaining or enhancing performance. In order to accomplish this goal, the following materials science and engineering research and development priorities need to be addressed:

- Performance based strategic focus with the appropriate technical metrics based on property Figures of Merit for the specific applications
- Development and exploitation of advanced, hybrid and multifunctional materials
- Novel designs/structures that exploit materials properties
- Integration of computational modeling for materials design, processing and performance prediction and appropriate testing for validation

The following articles present a variety of functionally oriented materials programs being carried out in the Army Research Laboratory. We believe the technologies developed under these programs will have profound impact on the development and capabilities of the Army's Future Force while simultaneously allowing the improvement of Current Force capabilities.

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Advanced Materials Aid the Army's Transformation

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Turning Young Americans on to Science

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Protecting the Future Force:

A New Generation of Metallic Armors Leads the Way

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INTRODUCTION

Metallic armor is the most mature class of armor materials and is still widely used for ballistic protection today. Although the materials for metallic armor are highly developed, new and innovative metallic armor systems are being used to improve the ballistic protection (while reducing the weight) of various weapons systems. Historically, most metallic armor evolved from designing materials to meet structural or other requirements rather than from designing specifically for ballistic protection. This design paradigm is changing; partly to meet the requirements for the Army's Transformation to a lighter, more survivable force. Metallic armor systems are now being designed to optimize mass, space, and cost efficiency. This article briefly reviews the history, testing, and types of modern passive metallic armor materials, and also highlights the emerging hybrid metallic technologies designed to meet future armor requirements. Current design approaches for modern metallic armor materials systems are also discussed.

Figure 1. RHA and CHA Has Been Used in Tanks for Decades, such as in the M60 Patton Tank.

HISTORY AND MATERIALS

The use of metals for armor dates back to the discovery of bronze in 3000-2000 B.C. The advantage of metallic armor over softer materials, such as leather and wood, was obvious. However, the trade-off between mobility and protection for survivability was recorded as early as the battle between David and Goliath where agility, accuracy, and mobility defeated heavy armor. This very delicate balance is still a challenge in implementing armor for system survivability today. This section covers some of the traditional and current monolithic metallic armor materials, and also discusses metallic composite and hybrid armor systems.

MONOLITHIC METALLIC ARMOR

Development of Steel Armor

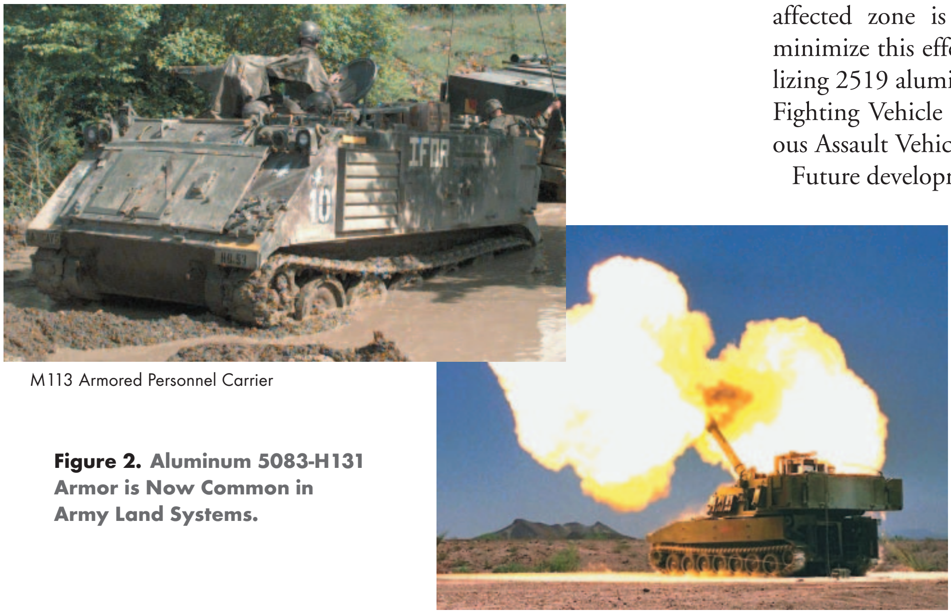
Steel armor comprises the bulk of past, present, and likely, future armor materials. This is because it possesses a number of desirable attributes that should not be overlooked. Steel is inherently inexpensive due to the low raw material and fabrication costs, as well as the enormous commercial steel production capacity. It provides good ballistic protection from a wide spectrum of threats with excellent multi-hit capability. It can be easily cut, machined, formed, and welded, is easily field repairable, and has good degradation resistance against the ambient environment.[1]

In the latter part of World War II and in the decade following, there was an intense period of investigation into the physical metallurgy and mechanical properties of high strength steels at the Army's Watertown Arsenal Laboratories. It was found that steel at maximum hardness, but with enough toughness to resist cracking in all situations, provided the best ballistic performance.[2,3] The optimum combination of strength and toughness was obtained with a medium-low carbon, low alloy steel with a Stage III* tempered martensite microstructure. At present, the two major types of steel armors are Rolled Homogeneous Armor (RHA, MIL-DTL-12560) and Cast Homogeneous Armor (CHA, MIL-DTL-11356). The specifications for these steels have changed substantially since their inception between the World Wars (Figure 1).[4] As commercial steels' production capability improved, both in terms of quality and output, the armor steel specifications were modified to reflect these changes. Inclusions, sulfur, phosphorus and tramp element levels have been drastically reduced, while strength and, particularly, toughness have increased. The Charpy V-Notch test for toughness was popularized by Watertown Arsenal specifically for the quality control of armor steel. Resistance to adiabatic shear has been increased with improved steel cleanliness and microstructural refinement.[5]

High hardness steel armor (HHA, MIL-DTL-46100) was developed during the Vietnam War era for use against ball ammunition. The composition is similar to RHA, but it has a maximum of 0.32 wt. % carbon and it is tempered to Stage I.* This steel is extremely mass efficient against ball ammunition, particularly at highly oblique angles of impact. It was initially developed as appliqué (i.e., nonstructural) armor, but welding techniques have been refined to the point that vehicles can be manufactured using this alloy as the structural material without cracking in service. The Light Armored Vehicle (LAV) is made of this steel above the beltline, while RHA is used below the beltline.

Development of Aluminum Armor

Aluminum alloy 5083-H131 (MIL-DTL-46027) is a non-heat-treatable, strain-hardened aluminum-magnesium alloy. It is very resistant to cracking and stress-corrosion cracking. It is readily weldable and corrosion resistant. It has excellent resistance to fragmentation threats. The M113 Armored Personnel Carrier, M109 Paladin Self Propelled Howitzer (Figure 2), and the lower half of the Bradley Fighting Vehicle (Figure 3) are made from 5083.


M113 Armored Personnel Carrier

M109 Paladin Self Propelled Howitzer

Figure 2. **Aluminum 5083-H131 Armor is Now Common in Army Land Systems.**


Figure 3. **The Bradley Fighting Vehicle Makes Use of Both 7039-T64 (Upper Half) and 5083-H131 (Lower Half).**

Aluminum alloy 7039-T64 (MIL-DTL-46063) is an aluminum-magnesium-zinc alloy that is heat-treatable to a hardness higher than that of 5083. It exhibits better performance against ball and armor piercing (AP) threats than 5083 with some loss in performance against fragmentation threats. It is susceptible to stress corrosion cracking, particularly in the short-transverse longitudinal (S-L) direction, and thus it is not recommended for future vehicles. The upper half of the Bradley Fighting Vehicle is made from 7039 (Figure 3).

Aluminum alloy 2519-T87 (MIL-DTL-46192) is an aluminum-copper-manganese alloy that is heat treatable to hardnesses between those exhibited by 5083 and 7039. It exhibits better performance against fragmentation threats than 5083, and has almost the same performance against ball and AP threats as 7039. It has good resistance to stress corrosion cracking, but poor resistance to general corrosion. There is a dramatic loss of ballistic properties near welds (metal in the heat-affected zone is much weaker), so joints are designed to minimize this effect. The first production armored vehicle utilizing 2519 aluminum will be the Marine Corps Expeditionary Fighting Vehicle (formerly known as the Advanced Amphibious Assault Vehicle, or AAAV, Figure 4).

Future development in aluminum armor focuses on attaining higher strength without sacrificing dynamic ductility, while maintaining all the corrosion and weldability characteristics of 5083. The 5059 alloy, much like 5083 but at a higher strength level, is currently being evaluated as an aluminum armor candidate.

Development of Titanium Armor

The high cost of weight-efficient titanium relative to steel has previously limited its application to aircraft armor where weight is a premium. However, recent investment in low cost titanium has enabled its application

Figure 4. **The Marine Corps Expeditionary Fighting Vehicle (EFV) Will Be the First to Utilize 2519-T87 Armor.**

in advanced lightweight armored ground vehicles. The armor composition of 6 wt. % aluminum, 4 wt. % vanadium (Ti-6Al-4V) was developed by Watertown Arsenal for armor applications (MIL-DTL-46077). This material is used in the annealed condition, rather than the much harder solution-treated and aged (STA) condition, as employed by other metallic armors. The best performance is normally obtained when this alloy is as soft as possible.

METALLIC HYBRID LAMINATES

Metallic Laminates

Dual hardness armor steel (DHA, MIL-DTL-46099) was developed to achieve improved performance over HHA. Armor piercing threats are typically defeated by fracturing them using a hard face plate, and then catching the debris with a softer back plate. DHA steel has a 59-63 Rockwell C hardness (HRC) steel for the face plate, normally S-7 tool steel, roll-bonded to a 50-53 HRC low alloy steel back plate. The steel compositions are carefully chosen to match the martensite start temperatures to avoid plate warping during quenching. This is the best performing steel armor against small arms ammunition, both ball and AP, but it is also the most expensive. It is difficult to form and weld, and large plates often have areas that are not completely bonded.

Very hard steel in the vicinity of 55 HRC backed by 2519 aluminum armor has been shown to have favorable mass, space and cost efficiencies against certain AP threats. Conversely, 5083 aluminum armor backed by HHA has been used for protection from ball and fragmentation threats. Having the aluminum alloy on the front face changes the penetration mode of the HHA backing from plugging to ductile tearing, thereby improving its mass efficiency.

Metal-Composite Hybrids

Monolithic metallic armor is now routinely backed by a polymer matrix composite in armor systems. The composite serves as a spall shield that minimizes the trauma to the interior of the vehicle if the metallic armor is penetrated. Typically, the fibers that are used to reinforce the polymer matrix are ballistic nylon, Doron, S-2 glass, or Kevlar™ aramid. (See our article on composite armor for more information on these and other composite materials.) Nearly all modern systems employ spall liners.

The costly ceramic-faced armor used in pilot and copilot seats aboard the UH-60 Blackhawk helicopter were replaced with AISI 4350 steel at 60 HRC. Both the ceramic and the steel are backed with Kevlar™ to contain spalled fragments of the armor that may result from a ballistic hit. While the steel armor is heavier than the ceramic, no weight penalty was incurred because some existing nose counterweight material was eliminated. The replacement of steel for ceramic saved the Army millions of dollars over the production run.

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a) Vest View

b) Scale View

Figure 5. **Dragon Skin® Flexible Body Armor Vest Completely Repels Eleven Rounds of 7.62mm Ammunition. a) Vest View – Strike Points Highlighted by Red Circles, b) View of Individual Scales.**

Table 1. Armor Design Rules of Thumb.

Monolithic Systems	Multi-Material (Hybrid) Systems
Harder is better, "adequate" hardness to break up the projectile	Harder may not be better, but a hard face usually is
Tougher is better, "adequate" toughness to resist cracking	Tougher may not be better, but a tough backing usually is
Thicker is better	Thicker may not be better
Heavier is better	Heavier may not be better
One thick plate is better than two thin laminated plates	Two thin laminated plates may be better than one thick plate
More obliquity(angle of impact) is better	More obliquity may not be better

High hardness steel or titanium armor that has been tightly wrapped with a thin layer of Kevlar™ has been shown to have improved ballistic performance. This effect has been exploited in the Dragon Skin® flexible body armor manufactured by Pinnacle Armor, Inc. (Figure 5). Individual "scales" of titanium composite are assembled into flexible, breathable body armor which successfully repels rifle fire through Level III ballistic protection, and into Level IV[§].

Metal-Ceramic Hybrids

Typical metal-ceramic armor consists of a hard ceramic face supported by a metallic backing. As a concept proven with DHA, a hard strike face is very effective in breaking up the threat. Ceramics can have a higher hardness than the hardest steels, and thus they are an efficient material to break-up, shatter, erode, dwell or condition the projectile before it hits the back plate. The metal back plate catches the fragments of both the ceramic and the projectile.

Recent research at ARL has led to the development of metal-encapsulated ceramic armor. In this concept, the armor ceramic is strongly confined to enhance dwell[†]. Metal-ceramic bonding with increased shear strength and reduced impedance mismatch at the interface have shown to have a significant affect on promoting dwell, and delaying ceramic failure for improved ballistic performance. Currently, there are efforts to design titanium and aluminum alloys with enhanced bonding to the encapsulated ceramic and also improved performance as a structural backing material. In addition, stiffening the metallic backing can further enhance the ceramic's performance by resisting bending during a ballistic event. Therefore, continuous ceramic fiber and particulate-reinforced metal matrix composites are being exploited as a stiffening layer between the armor ceramic and metal backing.

Metal-Ceramic-Composite Hybrids

There are several metal-ceramic-composite hybrid armors in development, while others have already been fielded. These systems utilize hard ceramic as the strike face to break up the threat and a metal to provide structure and catch fragments from the ceramic and the projectile. A polymer matrix compos-

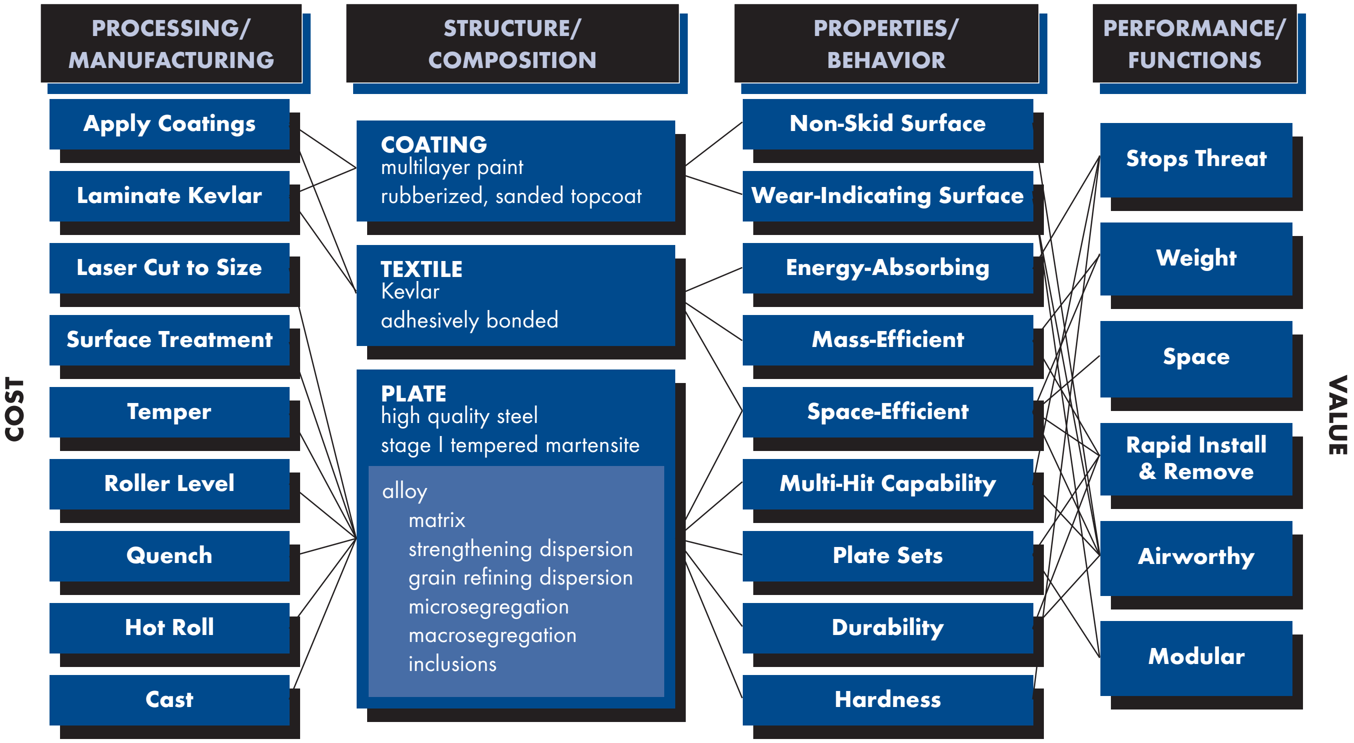

Figure 6. System Flowblock Diagram for Helicopter Armor.

MH-47 Chinook

UH-60 Blackhawk

Figure 7. Emerging Armor Systems are Being Employed to Improve Survivability of Helicopter Cargoes and Crews.

ite is also used to catch any spall off the back of the metal. The Stryker-Interim Armored Vehicle and the EFV utilize this type of metal-ceramic-composite armor system to provide superior ballistic protection.

CURRENT DESIGN APPROACHES FOR METALLIC ARMOR MATERIALS SYSTEMS

The historical approach to metallic armor development has been based on the trial-and-error, "heat and beat, shoot and see" philosophy. In the past, armor designers relied on empirical data and engineering judgment aided by analytical models to design candidate systems. The candidate armor materials were then tested, and the design was refined or discarded. Today, however, metallic armors are designed with knowledge-based alloy development (both in chemistry and thermomechanical processing), coupled with a phenomenological understanding of the penetrator-target interaction.

Present metallic armor research is directed at the metallic component in a hybrid materials design. Within a hybrid system, the properties that are desired are often not the same as those desired in a monolithic system (Table 1).

Present Research

The Ballistic Protection System (BPS) was developed by the Protective Materials Company with assistance from ARL in response to a request for helicopter armor from the Technology Applications Program Office (TAPO) of Special Operations Command (SOCOM) in 2000. The system design approach can be represented by the flowblock diagram of Figure 6.[6] The helicopters of interest were the UH-60 Blackhawk and the MH-47 Chinook, and the areas of protection were both the crew and cargo areas. (Figure 7)

The designed armor uses a high quality, high hardness steel, and is wrapped by a thin layer of Kevlar. A multilayer paint is applied to give the top surface non-skid and wear-sensing properties, as well as environmental resistance. The overall thickness of the system is less than 3/8 inch, giving excellent space efficiency, and allowing easier installation. Because the steel can be laser cut to high precision without further machining, significant cost savings are achieved.

The armor system consists of a set of plates for an individual aircraft (Figure 8), which enables the system to be tailored to specific missions in a modular fashion. It can be rapidly installed and removed. Since the predominant material is steel, it has excellent multi-hit capability, durability, and cost efficiency. For all these reasons, it has received an airworthiness readiness (AWR) certificate. This armor system has also recently been deployed on the US Marine Corps CH-53E Super Stallion.

"Cybersteel 2020: Naval Materials by Design," [6] is an ongoing research program by Northwestern University's Materials Technology Laboratory under funding by the Office of Naval Research to develop improved blast-resistant alloys. With computational thermodynamic and strength design methods, this particular project investigates models for new secondary hardening martensitic steels that may reach previously unattainable levels of extreme dynamic fracture toughness and ultrahigh strength. Secondary hardening steels rely on alloying elements, such as Cr, W, Mo, and V, to precipitate fine dispersions of alloy carbides during tempering heat treatments. The

Figure 8. BPS Installation in an MH-47 Chinook Helicopter.

nucleation of this stable phase replaces coarser cementite (Fe_3C) particles, resulting in a microstructure that imparts improved strength and fracture resistance. By optimizing other compositional and processing components that meet requirements for weldability and cost, these new concepts for achieving enhanced blast-resistance will also provide the basis for the next generation of naval hull steels.

CONCLUSION

Advanced metallic armor materials continue to exhibit properties that cannot be matched by other materials. Among them are cost, fabricability, durability, multi-hit capability, and a broad threat spectrum resistance. Metallic armor is evolving into the role of a structural armor backing that motivates the development of metal-matrix composites, micro-intermetallic laminates, and hybrid periodic core materials. On the horizon is the reality of multi-functional metallic armor by design.

NOTES

* *Stage* refers to the fracture mechanism of the steel. *Stage I* tempered alloys are composed primarily of austenitic structures, which are very strong, hard, and extremely crack-resistant, but are brittle. *Stage II* tempered materials feature some combination of austenitic (hard) and martensitic (soft) morphologies, thus representing a compromise of strength and toughness. Most structural steels are *Stage II*. In *Stage III* tempers, martensitic effects dominate over residual austenite fractions. These materials are much more ductile than their more austenitic counterparts, and thus are far better at absorbing and mitigating kinetic energy from shock and blast – these are desirable qualities in armor materials.

§ Ballistic Level of Protection pertains to the total kinetic energy of a single representative round of ammunition that an armor system can mitigate. Established by the National Institute of Justice (NIJ) standard, Level III is defined as full protection against high-powered rifle rounds at representative muzzle velocities (e.g. 7.62mm full metal jacket at 2750 ft/s or less). Similarly, Level IV is defined as protection against armor-piercing rounds (e.g. 0.30 cal APM2 at 2850 ft/s).

† *Dwell* occurs when a projectile erodes and flattens on the armor surface with no significant penetration into the armor.

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Protecting the Future Force:

Ceramics Research Leads to Improved Armor Performance

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INTRODUCTION

Ceramics have been used in armor systems for the last half-century, mainly for personnel and light vehicle protection against small arms and machine gun threats. The widespread use of two-layer, ceramic-based body armor by US Soldiers in Afghanistan and Iraq is helping to save lives (Figure 1). Other currently fielded ceramic armor technologies include helicopter seats (Figure 2) and the US Army's armored mobile gun system as shown in Figure 3. Future applications include the US Marine Corps Expeditionary Fighting Vehicle (formerly known as the Advanced Amphibious Assault Vehicle, or AAAV) and the US Army's Future Combat System.

Ceramics are attractive as armor materials because they are more weight-efficient than traditional monolithic armors, such as "rolled homogeneous armor" (RHA), against a variety of threats. Properties that make ceramics efficient include low density, high hardness, high compressive strength, and high elastic modulus. However, the low tensile strength typical of ceramics severely limits their performance, and thus stand-alone ceramic armors can be inferior to traditional steel armors. To exploit an armor ceramic's high compressive strength, it must be properly integrated into a ceramic armor system. It is important to make the following distinction between ceramic armors and armor ceramics: "Armor ceramics refer to the actual ceramic materials themselves. Ceramic armor refers to an armor system designed to defeat specific ballistic threats and which contains ceramic components." [1]

Ceramic properties important for armor applications are understood, but their exact correlation with armor performance remains elusive, partly due to numerous defeat mechanisms invoked by a wide variety of threats. A particular ceramic that is optimal in one application may perform poorly in another. Other reasons are the complexity of the impact process: spatial and temporal stress state variation, damage generation and propagation, and stress wave interactions. This article presents an overview of the fundamental defeat mechanisms of ceramic armors (the application) and provides interpretations of the impact and shock response of ceramics so that the role of advanced armor ceramic materials within armor systems can be better understood. Ceramic armor designers know that performance is strongly system- as well as threat-dependent. Therefore, it is essential to discuss these aspects to bridge ceramic armor and armor ceramic development.*

a) Boron Carbide Small Arms Protective Inserts (SAPI) Interceptor Plates, Cercom Inc.;
b) Ceradyne Body Armor and Inserts; c) Interceptor Body Armor, Simula Inc.;
d) M-Cubed Reaction-Bonded Silicon Carbide SAPI Interceptor Plates, Simula Inc.

Figure 1. **Examples of Ceramic Body Armor Plates and Inserts[i].**

FUNDAMENTALS OF CERAMIC ARMOR

The purpose of armor is to enhance personnel and vehicle survivability by defeating projectiles and fragments, that is, to prevent target perforation and structural failure, which can occur with or without penetration. For example, a cannon ball may cause massive deformation and structural failure without

Figure 2. **Helicopter Seats[i]: European Tiger Helicopter Seat, Cercom Inc. (Left); AH64 Apache Helicopter Seat Using Hot-Pressed Boron Carbide, Simula Inc. (Middle); and MH-60 Blackhawk Seat, Ceradyne Inc. (Right).**

Figure 3. **Stryker Combat Vehicle Mounts a Licensed Version of the MEXAS™ System[†] and is Based on the Light Armored Vehicle 3rd Generation (LAV III) Chassis and Hull. General Dynamics Land Systems – Canada[ii].**

penetration, or shock waves may result in spall or behind armor debris due to tensile wave reflections. Consequently, the armor must absorb the ballistic impulse without failure (by structural deformation and attenuation of elastic waves), while dissipating the projectile's kinetic energy (KE). The primary role of the armor ceramic is to convert the projectile's KE into elastic stored energy or plastic work on the projectile. For brittle projectiles, the elastic stored energy can result in projectile fragmentation. As a result of either plastic work or fragmentation, the "failed" projectile remnants may also disperse, which distributes the projectile's KE over a greater target area. The high elastic wave speeds in armor ceramics also increases the amount of material involved in the defeat process. Finally, ceramics absorb the ballistic impulse by spreading the load onto the backing armor components, and in effect increasing the amount of backing material involved with the impact. The deformation of the backing material absorbs the momentum of the projectile and target debris, in essence, catching them.

The armor response to ballistic impact consists of: impact, pre-penetration, material failure, penetration, and momentum absorption. Impact is studied using shock physics to understand dynamic material properties and stress states within both the penetrator and the target. Pre-penetration refers to penetrator shatter, fracture or erosion prior to penetration. These impact loadings typically result in damage accumulation and target material failure, such as ductile material plasticity or brittle material fracture, studied using fracture mechanics, and materials science, such as indentation testing.

The penetration process may be categorized by the penetrator response. The penetrator may just make a hole in the target, slowing down until stopped or until target perforation occurs. During this process, the penetrator may remain rigid, or it may deform plastically (if it is fashioned from a ductile material like lead, steel, or copper), or it may shatter and penetrate as a concentrated debris cloud, or it may erode. Finally, the impactor momentum is absorbed by target deformation or elastic wave dissipation. The backing material catches the remaining projectile and fractured ceramic, termed the capture phase. Composites and fabrics are often used for this role, and are discussed in other articles.

Basic components of a two-component ceramic armor are a hard face (ceramic) bonded to either a soft backing (composite or fabric) or a hard backing (metal). Fielded ceramic armors, (Figures 1-3), have more elaborate designs, due to the need to satisfy a multitude of performance and environmental requirements. These include multiple impacts and impacts at edges and joints, which significantly affect the ceramic armor designs. In some designs, for example, ceramic tile edges are raised to equalize protection across the ceramic tile. However, simple two-component systems are adequate to understand how ceramic armors work.

Threat Classes

Threats are delineated by type, kinetic energy (KE) or chemical energy (CE) and by penetrator caliber, length to diameter aspect ratio (L/D) and impact velocity. Fragments from fragmenting munitions (grenades) and from improvised explosive devices (IED's) are threat classes not discussed in this article.

Small-Caliber KE Projectiles

Small-caliber projectiles typically include bullets and fragments with sizes up to 7.62 mm (0.30 cal.) and velocities below 1 km/s (3281 ft/s). L/D ratios vary from 1 to about 5. They may be composed of steel, lead, tungsten carbide, or tungsten alloy. For armor piercing projectiles, core nose shapes may be blunt or sharp. Projectile energies are typically on the order of several kilojoules (kJ).

The interaction between a 7.62 mm APM2 steel core and a boron carbide based target is shown in Figure 4 using a sequence of 1 MeV flash X-ray radiographs taken at various times during the ballistic event. After the initial impact phase at 6 µs, the nose of the core has eroded without penetration into the ceramic. During this initial time period or pre-penetration phase the high ceramic hardness overmatches the impact load, causing the penetrator to dwell on its surface. However, ceramic damage is accumulating, and by 16 to 25 µs, the core has entered the penetration phase, having begun to penetrate while shortening (eroding) the penetrator. Even though the ceramic has failed, it continues to offer sufficient resistance to continue to erode the projectile and even contribute to its fracture. The reason why dwell ends in this particular case is simply because the backing material fails and cannot properly support the ceramic. The loss of support allows the back of the ceramic to experience large tensile stress, which combines with the compressive stress to induce damage and cause a loss of load-bearing capacity. Thus, the back of the ceramic can no longer support the top of the ceramic, and dwell ends. The opening of a Hertzian cone[§] crack and bulging of the back of the ceramic is also evident.

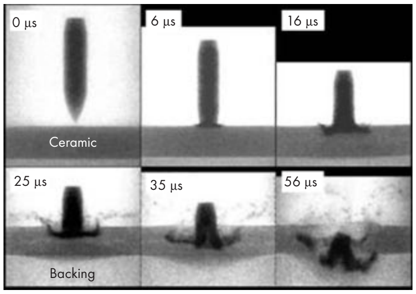

Figure 4. **X-Radiographs Showing Time History of a 7.62 mm APM2 Bullet Core Impacting Boron Carbide Illustrating Dwell, Penetration by Erosion, Bullet Fragmentation and Capture.**

At 35 µs, the bulging is much more severe and fracture of the core is evident. At 56 µs, the core has completely penetrated the ceramic and continued into the backing material. The residual core was fractured into at least two pieces that were stopped within the backing material (capture phase). If it completely penetrated through the backing material, this would be termed break-out or perforation. The impact velocity at which this break-out just occurs (velocity at which 50% of projectiles are stopped and 50% completely perforate the armor) is referred to as the ballistic limit velocity of the armor.

In summary, the role of the ceramic is to erode the projectile nose and spread the resulting ballistic load onto the backing material (e.g. the bulge diameter is larger than the bullet diameter). In this case (but not always) the projectile fractures. For small-caliber KE threats, the important ceramic properties are low density and high hardness. A lower density enables the use of a thicker ceramic for a given weight, which would be more effective in spreading the load.

Medium- and Large-Caliber KE Projectiles

Medium and large-caliber threats, 20-140 mm, intended to defeat heavy armor applications, typically have an intermediate velocity, 1.3 - >1.6 km/s, and are composed of a high density metal (~ 18 g/cm^3) that is resistant to shattering. These high L/D ratio penetrators (currently fielded threats exceed 30:1) impact with megajoules (10^6 J) of KE[‡] The primary mechanism to defeat these threats is erosion. In order to erode the projectiles, high ceramic compressive strengths are required to generate several GPa of pressure on the penetrator tip for an extended period of time (tens to hundreds of microseconds) causing the penetrator to yield and flow laterally. The damaged, failed and comminuted (pulverized into small particles) ceramic properties dominate the erosive behavior and the damaged ceramic must be confined, either inertially or geometrically, to maintain adequate pressure on the penetrator to continue this process, while consuming the KE penetrator. In these systems, the confining backing and lateral materials are chosen to provide stiff supporting structural elements.

The penetration and erosion process are often approximated by analytical models based on hydrodynamic principles (such as Bernoulli's laws) modified to account for target and penetrator strengths (~3 times the dynamic ceramic yield strength). These lumped strength parameters make direct correlations of ballistic performance with basic armor ceramic properties challenging. [2]

Shaped-Charge Jets

For high velocity impacts of shaped-charge jets, the ceramic strength is overwhelmed by the high impact pressures as the process is more purely hydrodynamic. These jets (typically copper) are formed using high-explosives upon impact and produce a long metallic stream or a plasma jet with a variable diameter and velocity along its length, which stretches during the penetration process. Hence the rod, or jet, stretches during the penetration process. The tip velocity is between 6 and 10 or more km/s, and the tail velocity is typically ~2 km/s producing impact pressures on the order of 100 GPa. The ceramic's low density makes it efficient on a mass basis (but not on a space basis) relative to armor steels. The ability of the ceramic to bulk (increase volume) upon failure within a confined armor impinges debris on the jet helping to misalign a jet that is inherently weak in the lateral direction.

The effectiveness of ceramic armor against shaped-charged jets is important, as these threats become more common in the battlefield, which is evident with the Rocket Propelled Grenades (RPGs) being used in Iraq. Defeat of shaped-charge jets is a much more complicated process than for KE threats, and thus will not be addressed in this article.

Recent Ideas: Interface Defeat[**]

Ceramic armor enhancements continue as penetrator threats evolve. Increased ceramic efficiency is possible by delaying penetration and/or by increasing the comminuted ceramics' erosion efficiency; for example by using modest lateral confinement to constrain broken ceramic pieces. A most historic and significant observation was made in 1987 during ballistic experiments where a tungsten-alloy, long-rod penetrator impacting a highly confined ceramic target at 1.6 km/s, was completely consumed, without penetration (Figure 5) [3]. It was also observed that with less confinement, partial penetrator dwell occurred on the surface prior to penetration. This work led to a better understanding of the importance of delaying, mitigating, and confining the damaged ceramic. The practicality of these laboratory targets as armors is limited. However, much of what was learned is now being explored and incorporated into practical ceramic armor designs which promise substantial improvements in weight efficiencies.

This experiment was significant as it demonstrated that brittle ceramics are impenetrable by most common threats if the ceramic is prevented from failing (although it may be highly damaged). Systematic laboratory experiments determined a critical velocity (impact load) that armor ceramics (of a given thickness) can withstand before penetration occurs [4]. This critical velocity was approximately 1.5 km/s for tungsten-alloy penetrators (and greater than 2 km/s for lower density penetrators), providing total interface defeat of very long rods. Another demonstration of ceramic impenetrability is shown in Figure 6 for a 25.4 mm thick aluminum oxide tile with a steel backing [5].

CERAMIC DAMAGE

Ceramic armor performance is system- and threat-dependent as these affect the type and distribution of damage within the ceramic. This damage results from activation of pre-existing defects caused by hydrostatic, shear, and tensile stresses. During a ballistic event, these stresses interact with pre-existing defects

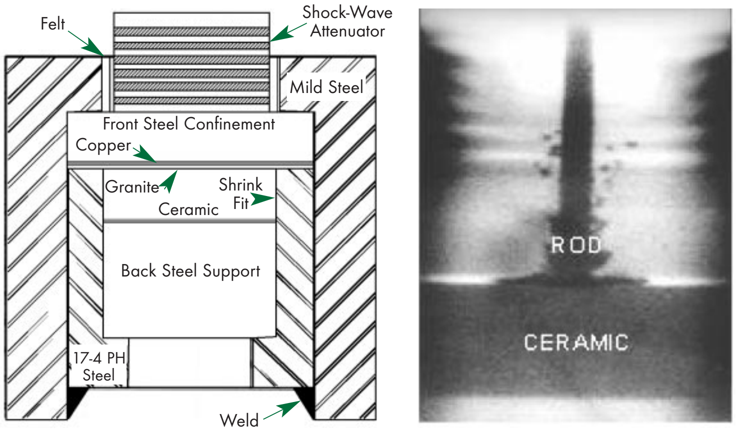

Figure 5. Schematic Illustration of Highly Confined Ceramic Target (Left). X-Ray Radiograph of a Long-Rod Penetrator Dwelling on a Ceramic (Right) [3].

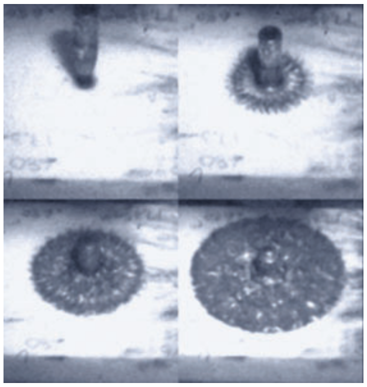

Figure 6. **Dwell of a Hard-Steel Core APM2 Bullet on a Steel-Backed Alumina Tile.**

Photos Courtesy of Southwest Research Institute (SwRI), San Antonio, TX [5]

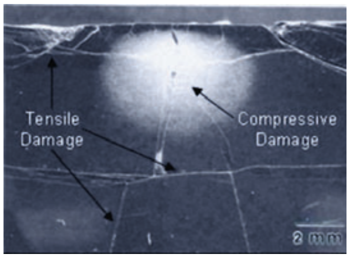

Photo Courtesy of Dr. J. Shih

Figure 7. **Tensile and Compressive Damage in a Post-Impact Silicon Carbide Ceramic Recovered from an Interface Defeat Experiment.**

generating tensile and compressive damage regions within the armor ceramic. The silicon carbide shown in Figure 7 was recovered from an interface defeat experiment where impact occurred at the top-middle surface. Both damaged and undamaged regions can be seen. Tensile damage consists of relatively large macrocracks that may actually split the ceramic tile into several large pieces, while compressive damage consists of a high density of microcracks. A ceramic's resistance to penetration is the result of the integrated mechanical response of these damaged and undamaged regions coupled with the mechanical response of the entire system. This is why a ceramic's performance is system- and threat-dependent, and also why understanding the mechanisms responsible for damage is so important.

Pre-Existing Microstructural Defects

Ceramics are inherently brittle when subjected to tensile stresses because of their atomic bonding, and also because they lack an adequate number of independent dislocation slip systems or adequate dislocation mobility to support bulk plasticity, in contrast to most metals. Lack of metal-like ductility makes the mechanical response of ceramics very sensitive to intrinsic and extrinsic material defects. These defects range in size from subnanometers to hundreds of micrometers. They are detrimental because they act as stress risers, which can result in crack formation and cause failure when the ceramic is subjected to an applied stress. Microstructural defects such as pores, inclusions, large grains, and microcracks are the most detrimental because of their relatively large size (micrometers).

Armor ceramics are available as pressureless sintered (lower cost) or hot-pressed (higher cost). Table 1 lists a sampling of ceramic producers used for current armor applications. The origin of microstructural defects is intimately connected to the methods by which ceramic bodies are fabricated and finished. Armor ceramics are normally produced via powder processing routes, that is, micron-sized ceramic powders are pressed into "green bodies" that are less than 60% dense (i.e., porous) and then are densified (sintering process) at high temperatures (2000°C) with or without an applied pressure (0-200 MPa) to achieve a 98-100% theoretical density. Sintering additives are typically used to decrease the densification temperature, and as a result cost.

An exception to the sintering process is reaction-bonding where the porous powder body is infiltrated by a liquid, such as aluminum or silicon, in a vacuum or reactive atmosphere. This liquid may react with powder additives or atmospheric gases to minimize the residual solidified liquid. For these processes, the nature, size, and frequency of microstructural defects is very dependent on the quality (e.g., size distribution, level of impurities), preparation (e.g., mixing and milling), and processing (e.g., densification) of the powders. Incomplete sintering or trapping of volatile impurities or contaminants results in residual porosity (faceted or irregularly-shaped pores), as shown in Figure 8, for a commercially-available pressureless sintered silicon carbide.

Inclusions (metallic, carbon, and possibly brittle second phases), can be present in the densified ceramic because they often exist in the starting powders as impurities, introduced inadvertently during powder preparation, or created as a result of high temperature reactions (Figure 9). Large grains can result from a broad particle size distribution in the starting powder, incomplete powder milling operation (used to reduce the size of the largest particles), or abnormal grain growth (poor distribution of sintering additive).

Microcracks can form from pores and inclusions because of differences in elastic and thermal expansion properties between them and the parent phase. They can also form within the grains and along grain boundaries of the parent phase because of the crystallographic orientation dependence of the elastic and thermal expansion properties. During the cool-down period from exposure to high temperatures, each individual grain or phase wants to contract, but this contraction is resisted by neighboring grains or material. This results in residual stresses due to the

Table 1. **Current Ceramic Armor Producers.**

Ceramic Type	Ceramics	Producer
Sintered	99.5% Alumina	CoorsTek
	Alumina	Morgan Matroc (UK)
	Alumina	ETEC
	Sintered SiC	Ceradyne
	Pure Carbon SiC	
Reaction-Bonded	SiC	M-Cubed (Simula)
	SiC	MC^2 (Australia)
	B_4C	
Hot Pressed	B_4C	Cercom
	TiB_2	
	WC	
	SiC	
	B_4C	Ceradyne
	TiB_2	
	SiC	
	B_4C	Saint-Gobain
	SiC	

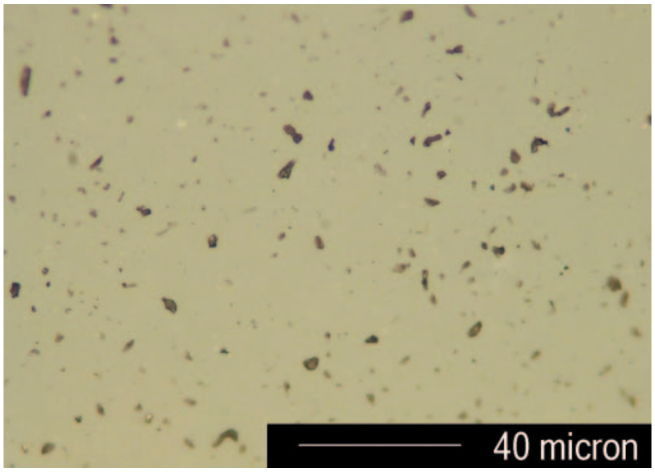

Figure 8. **Pores (Dark Spots) in a Commercially-Available Pressureless Sintered Silicon Carbide [5].**

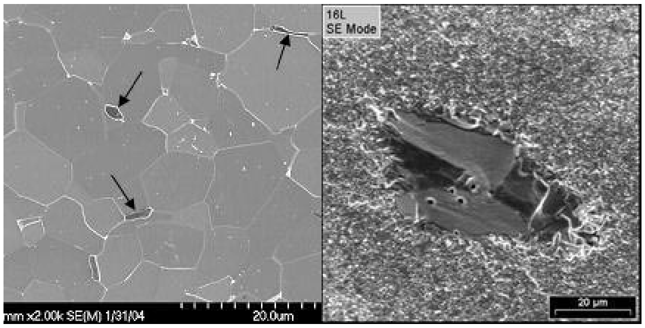

Figure 9. **Graphite Inclusions (Arrows) in Hot-Pressed Boron Carbide (Left) and Vanadium Carbide Inclusion in Hot-Pressed Tungsten Carbide (Right) Ceramics [5].**

build-up of tensile stresses at some grain boundaries, but more importantly, at junctions of multiple intersecting grains. The magnitude of this residual stress increases with increasing grain or inclusion size. Thus, for sufficiently large grain or inclusion size, spontaneous microcracking occurs, which relieves the residual stresses. Lastly, microcracks can also be introduced into surface regions of ceramics during final machining and surface finishing operations (e.g., cutting or surface grinding). These operations essentially involve the oblique impact of hard particles, such as diamond, on the ceramic. This impact creates a region of localized surface damage, which may include relatively long microcracks that penetrate into the ceramic. If subsequent surface finishing operations are poor in terms of quality, they will fail to eliminate these microcracks.

Tensile and Compressive Failure

For penetration to occur, ceramic material must be displaced, either pushed aside or through the back of the target (i.e., plugging), by the projectile. Both tensile and compressive damage, initiated from pre-existing defects, if sufficient in severity, may allow displacement of the fractured ceramic to occur.

In a ballistic event, tensile cracking normally leads to both a loss of mechanical confinement of compressively damaged regions and concentration of the impact load on the target material directly underneath the projectile. This further leads to an increased likelihood of compressive damage (pulverization) of the ceramic or plugging of the target. Understanding of this pulverization (failure) process in brittle solids like ceramics is not as complete as that for tensile failure. Part of the reason is that there are a number of micromechanisms for compressive damage and these can be Mode I (also called tensile crack initiation or opening cracks), Mode II (shear), or mixed-mode in nature depending on the magnitude of the shear and hydrostatic stresses. Another reason is that unlike tensile failure, where a single flaw can cause failure, compressive failure occurs as a result of complex interactions between billions of microflaws, dislocations, and crystallographic twins under multiaxial, high pressure, high strain rate loading conditions. Note that in the compressive damage region, the ability to resist shear deformation is based upon the interlocking of and frictional resistance between micron-sized fragments. From the very fact that penetration did not occur in regions as shown in Figure 7, it is safe to say that the amount and distribution of compressive damage was below the critical value.

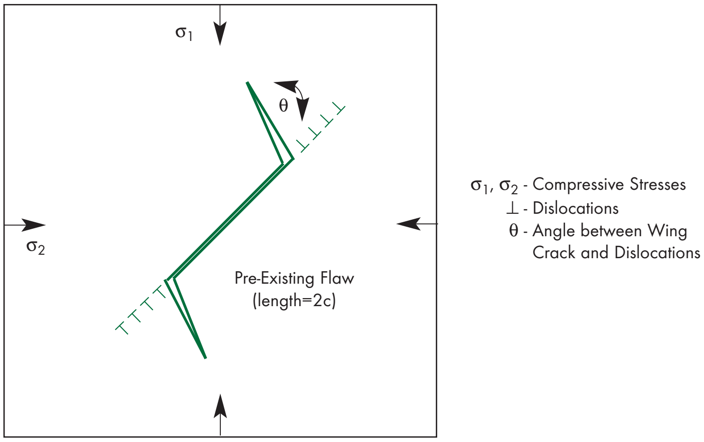

Figure 10. **Possible Micromechanism for Compressive Damage in Ceramics [6].**

Some factors that govern compressive damage can be found in the geological literature [6] and also within the compressive damage region itself (as shown in Figure 7). Consider the micromechanism illustrated in Figure 10, which shows a pre-existing microcrack of length 2c subjected to compressive stresses σ_1 and σ_2. The stresses are such that shear or sliding failure (Mode II) of the pre-existing microcrack occurs. Frictional resistance (but m=μ is the coefficient of sliding friction) must be overcome for the cracks to grow. As a result of sliding failure, dislocations and wing-cracks[††] (at an angle θ) can be initiated at the tips of the pre-existing microcrack. For the sake of simplicity, we designate a ductile response if dislocation emission dominates and brittle response if wing-crack formation dominates. The formation of the wing-cracks is actually a crack opening or Mode I event even though the process is shear driven. Therefore, intuitively, for an increasing σ_2 confining stress, wing-crack formation would be suppressed and a ductile response encouraged. Consequently, any process that decreases the σ_2 confining stress (e.g. tensile cracking) encourages a brittle ceramic response. The critical applied stress σ_1 (i.e. caused by ballistic impact) needed to initiate and grow the wing-cracks is dependent upon a number of factors including pre-existing flaw size (frequently assumed as proportional to grain size), coefficient of sliding friction, wing-crack length, fracture

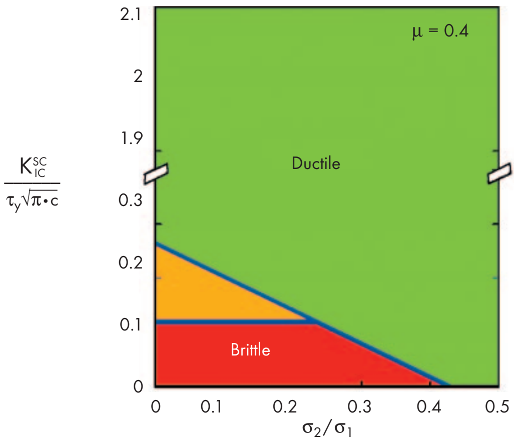

Figure 11. **Ductility Map [6].**

toughness (short-crack), and confining hydrostatic stress.

A convenient way to illustrate this dependence is by the "ductility map" shown in Figure 11. This map displays the regions where dominantly brittle and ductile responses would be expected depending upon short-crack fracture toughness (K_{IC}^{SC}), pre-existing flaw size (2c), and relative confining stress (σ_2/σ_1). The coefficient of sliding friction is 0.4 for this map. Decreasing coefficients of sliding friction expand the brittle region. Consideration of this map shows that increasing short-crack fracture toughness, sliding friction coefficient, and confinement stress while decreasing pre-existing defect size suppresses compressive damage. This has implications for ceramic improvement.

MODELING CERAMIC IMPACTS

As illustrated in Figure 10, the micromechanisms associated with compressive strength degradation of ceramics from impact began from damage accumulation under time-dependent, high-amplitude loads which are extremely complex. Understanding and modeling of the fracture process in ceramics began with a detailed study on quasi-static fractures induced by indentation loading. The indentation modeling effort mostly focused on the contact-load induced micro/macro cracking that occurs due to contact loading [7]. Since then, numerous studies have clearly established the presence of dislocations and twinning in the brittle ceramics due to high pressures and high strain rate loading conditions [8-9].

Resistance to projectile penetration is greatly influenced by the boundary conditions and intrinsic dynamic properties of the ceramic. The initially intact ceramic uses its full, pressure-dependent, compressive strength to prevent projectile penetration until a damage threshold condition is reached. While the stress state at the penetrator tip remains in compression (shear), the ceramic accumulates damage through shear (Mode II) until a threshold condition is reached. However, the inertially confined cracked-up ceramic continued to resist projectile penetration, suggesting that damage threshold doesn't degrade ceramic performance. However, the compressive failure due to axial splitting and faulting can occur through creation of wing-cracks at pre-existing defects as illustrated in Figure 10. Eventually, tensile stresses generated by complex wave interactions with lateral boundaries degrade ceramic properties further and enable projectile penetration.

In thin ceramic tiles, a complex pattern of ring, radial, cone, and lateral cracks are formed prior to projectile penetration. In thick, confined tiles, as shown in Figure 7, the ceramic material directly beneath the nose of the eroding projectile can form a region of finely comminuted, pulverized ceramic, referred to as the "Mescal Zone," but that even though severely damaged the ceramic continues to resist projectile penetration [10].

Prior to 1988, very few material models that could describe the inelastic behavior of brittle ceramics under shock and high strain rate loading conditions were implemented in hydrocodes (shock-wave propagation based finite element/difference numerical codes). Several ceramic damage models have now been successfully implemented in design hydrocodes during the late 1990's, and model parameters for several armor ceramics have been determined. These models predicted the unconfined thin tile response to APM2 projectile impacts as well as the confined thick tile response to a KE projectile extremely well.

THE FUTURE OF CERAMIC ARMOR TECHNOLOGY

The applications of ceramics for armor are growing rapidly as the need for lighter and more agile combat vehicles increases. Ceramic armor technology offers the best potential for meeting future protection requirements, particularly for the US Army's Future Combat System. Armor ceramic performance strongly depends upon the threat conditions and the ceramic armor design or configuration.

Improvements in armor ceramic performance requires, as a first-step, elimination, or reduction of, the size of pre-existing microstructural defects. It is also possible to reduce the armor ceramics' sensitivity to these types of defects. Understanding the micromechanisms responsible for tensile cracking and compressive damage helps to identify directions for both material and computational modeling improvements. While these areas have been the focus of numerous research efforts for many years, it is only now that with a renewed emphasis on understanding damage and its implications, as well as better experimental and computational tools, that the science to advance ceramic armor and armor ceramic development exists.

NOTES & REFERENCES

[i] Images reprinted with permission of Cercom Inc., Ceradyne Inc., and Simula Inc.

[ii] Images reprinted with permission of General Dynamics Land Systems – Canada.

* Interested readers are encouraged to contact the authors for recommended review articles, textbooks and journal publications, in which numerous additional technical publications are referenced.

† Manufactured by IBD Corporation (Germany).

§ A conical-shaped crack that forms in a brittle material (typically ceramic) when struck by a projectile on its surface.

‡ 1 Megajoule (10^6 J) of kinetic energy (KE) is roughly equivalent to a 16-lb bowling ball traveling at 147 miles per hour.

** Upon impact, the projectile material (typically metal) is forced to flow radially outwards on the surface of the ceramic without penetrating it significantly.

†† Wing-cracks are cracks that extend out of the plane of the original crack in the direction of maximum principal stress.

The catalysis for the extension of wing-cracks is shear failure of the initial crack.

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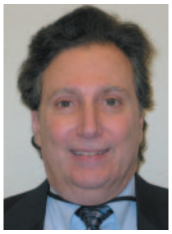

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Protecting the Future Force:

Transparent Materials Safeguard the Army's Vision

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Back in the fall of 2000, AMPTIAC printed an article on transparent armor in our quarterly journal (known then as the AMPTIAC Newsletter*). It was written by four gentlemen from ARL – Parimal Patel, Gary Gilde, Peter Dehmer, and James McCauley. Note that two of these men, Dr. Patel and Mr. Dehmer, have returned to help prepare this update (please also note that Dr. McCauley has written the leadoff article in this issue). From the time of its publication to the present day, it has been, by an overwhelming margin, the single most popular article in our history (as measured by reprint requests and downloads off our website). There was some initial hesitation to write this piece, as we tend to shy away from revisiting old ground unless some significant advance in the state of the art has taken place since initial publication. However, we pressed ahead for two very important reasons: First, we could not dedicate a section of the Quarterly to Survivability Materials* without *covering Transparent Armor. Second, we were (and are) confident that our readers, both new and old, will find this a fascinating treatment of the subject. Readers familiar with our earlier article will find some familiar portions in this piece, but will also be gratified to learn of the great advances made in the past four years. It will quickly become apparent to all that the "torch" that is transparent armor has been successfully passed from one team to the next. Enjoy!* - Editor

INTRODUCTION

While many of the hazards faced by our soldiers in the field are apparent, a more thorough assessment of a typical soldier's "theater of risk" reveals some suprising findings. A significant portion of a soldier's duties involve protection of facilities and personnel in confined environments. These tasks are akin to providing guard duty at military posts and check-points in strategic locations. The soldiers posted at these positions become the front lines of defense against impending attack; however, they are often also the target of terrorist-based actions because of their relatively exposed position. One manner of reducing the risk to the soldier is to provide enhanced protection in equipment that allows the soldier to perform the assigned duties efficiently, while offering some ballistic safety. Current system ballistic safety is limited by the mass efficiency of existing materials designs. One of the key protection capabilities for successful improvements in mission safety is transparent ballistic glass that enables soldiers to observe the potentially hostile environment through a protective shield. Therefore, transparent armoring technologies are a significant component of military effectiveness.

Figure 1. Face Shield and Body Shield.

Transparent materials are a subsection of materials that are transparent to certain wavelengths of energy. Window glass, for example, is transparent in the visible frequencies, while a radome material, such as fused silica, is transparent to radar frequencies. The Army Research Laboratory (ARL) has invested consistently to bring the best technical advancements in polymers, glasses, ceramics and adhesives to transparent system designs. These materials have application not only in ballistic glass but also in infrared (IR) domes, radomes, sensor protection, and personnel protection. This paper will provide an overview of the technology and applications, give specific examples of materials of interest, and relate the challenges that have been overcome during the past decade while also discussing those that remain.

Ballistic glass is a material or system of materials designed to be optically transparent, yet protect against ballistic impacts, and resist fragmentation. This class of materials is used in such diverse applications as protective visors for non-combat usage, including riot control (Figure 1) or explosive ordinance disposal (EOD) (Figure 2) actions, to protect sensors from debris, and to protect vehicle occupants from terrorist actions or other hostile conflicts. Each of these systems is designed to defeat specific threats; however, there are general requirements common to most. The primary requirement for a transparent armor system is to provide a multi-hit defeat capability while retaining visibility in the surrounding areas. Land and air platforms of the future have several parameters that must be optimized, such as weight, volume, and cost. Often, these ballistic protection materials must be compatible with night vision equipment to allow the soldiers to be effective in all environments. One potential solution to increase the ballistic performance of a window material is to increase the thickness. However, this solution is impractical in most applications, as it will increase the weight and impose space limitations or impact other systems in the fielded environment. In addition, thick sections of transparent materials often experience greater optical distortion than thinner sections, which reduces the transparency.

The development of modern armor systems is driven by the doctrine of fire and maneuver. The demand is for lightweight solutions that enable soldiers and vehicles to be highly mobile, destroy their targets, and return home safely. The armor must provide protection from a wide variety of bullets and fragments, and must not hinder the soldier's ability to do their job. The modern battlefield has evolved to the point that there are no defined battle fronts, and therefore everyone is at risk and must be protected. Each of these issues must be considered when designing any armor system. As opposed to conventional armor, transparent armor has an additional requirement in that the material must be transparent to visible light, which dramatically limits the material choices for an armor system.


Figure 2. EOD Helmet.

Among the transparent materials available, new material systems being explored to meet the requirements for ballistic applications include crystalline ceramics, new polymer materials, new interlayer technologies, and new laminate designs. The fundamentals of transparent ballistic materials are discussed here, along with insights for future designs and potential approaches to advanced technologies.

APPLICATIONS AND REQUIREMENTS

Common military applications for transparent armor include ground vehicle protection, air vehicle protection, personnel protection, and protection of equipment such as sensors. Commercial applications requiring transparent armor include items such as riot gear, face shields, security glass, armored cars, and armored vehicles.

Visors

With the onset of many new peacekeeping roles within the military, it is necessary to provide a greater degree of protection to the individual soldier. Facial protection via the use of transparent armor is one area of interest within the Army, marked by a recent program within the Army Research Laboratory to improve the current visor design.[1] Two types of visors were marked for improvement, the riot visor, and an explosive ordnance disposal (EOD) visor.

Riot visors are typically made from injection-molded polycarbonate that has an areal density of 1.55 lb/ft^2 (0.25" thick). The riot visor is a piece of equipment that is designed to defeat threats from large, low-velocity projectiles, such as rocks and bottles, and small, high velocity fragments. Recent research and development has focused on replacing the baseline polycarbonate designs with improved polymer materials. Among the candidate materials for riot visor improvements are advanced polyurethane polymers. Polyurethanes possess a wide range of properties that can be exploited to improve performance or reduce weight. However, due to the limited size of the window element in the riot visor configuration, the decision was made to keep the existing platform design weight and improve the ballistic performance. A target performance enhancement of 30% improved fragment protection was selected. In addition, the improved ballistics element means that riot visors achieve new standards for 9 mm handgun protection.

A second application for lightweight armors is in the EOD visor. Because the EOD visor covers a significant facial area, the contribution of the transparent laminate to the overall system mass is significant. Therefore, ballistic programs to improve performance in EOD designs sought to reduce the weight of the overall application. For an equivalent protection baseline, a 30% reduction in total mass was desired as a success metric.

Unlike the monolithic riot visors discussed previously, the EOD visors are composed of laminated plastics. ARL attempted to reduce the weight of EOD visors by varying both laminate construction and material selection. Laminate designs investigated included plastic/plastic, glass/plastic, and glass-ceramic/plastic.[1] Ballistic testing of these material systems particularly encompassing polyurethane showed a marked reduction in areal density from the current laminated design. Among the laminates tested, those possessing hardened designs, e.g., those with Vycor™ fused silica and TransArm™, provided the best ballistic performance.

Electromagnetic Windows

Many ceramic materials of interest for transparent armor solutions are also used for electromagnetic (EM) windows. These applications include radomes, IR domes, sensor protection, and multi-spectral windows. Optical properties of the materials used for these applications are very important, as the transmission window and related cut-offs (UV, IR) control the electromagnetic regime over which the window is operational. Not only must these materials possess abrasion resistance and strength properties common of most armor applications, but because of the unique high-temperature flight environment of aircraft and missiles, they must also possess excellent thermal stability.

Artillery Projectiles

EM window materials are also currently being investigated by the Army for use in artillery projectiles. While the optical trans-

Figure 3. Army Ground Vehicles.

parency is not important for this application, material properties such as low dielectric constant and low loss tangent are imperative.[2] Future artillery projectiles will be subjected to much higher muzzle velocities (Mach 3), where aerodynamic heating becomes a concern. New window materials must be capable of withstanding 15,000 g's of inertial setback loads with 15,000 rad/s^2 of angular acceleration. Additionally, as communication requirements change, the transmission and reception frequencies are changing to accommodate the more rapid exchange of data. Available plastic window materials are incapable of surviving in these environments. The new operational demands require new polymeric and complex laminate constructions for the radome and EM window designs. Prototypes for new systems utilize a glass-ceramic material known as Macor® for the nose tip*, which was chosen for electrical properties, high temperature capability, and ease of machining. However, replacement ceramics with a reduced dielectric constant and higher operating temperature capabilities are still sought.

Ground Vehicles

Ground vehicles represent one of the largest application needs for transparent armor, including high mobility multi-wheeled vehicles (HMMWVs), tankers, trucks, and resupply vehicles (Figure 3). There are several general requirements for the application of transparent armor to windshields and side windows on these vehicles.[3] The first is that the armor must be able to withstand multiple hits since most threat weapons are typically automatic or semiautomatic. The windows must also be full-size so that the vehicle can be operated without reducing the driver's field of view. One of the requirements for future transparent armor systems intended for vehicle use[3] is a reduction in weight. The added transparent armor weight can be significant, often requiring enhancement of the suspension and drive train to maintain the vehicle performance capability and payload capacity. Thinner armor systems are also required, as thinner windows can increase the cabin volume of the vehicle. Future systems must also be compatible with night vision goggle equipment and offer laser protection.

Due to their size and shape, the majority of armor windows are constructed of glass and plastic, but reductions in weight and improvements in ballistic protection are needed. Based on the number of vehicles in service, the window dimensions, and the associated costs, improved glasses, glass ceramics and polymers appear to be the new materials of choice. Compositional variations, chemical strengthening, and controlled crystallization are capable of improving the ballistic properties of glass. Glasses can also be produced in large sizes with curved geometries, and can be produced to provide incremental ballistic performance at incremental cost. The use of a transparent ceramic as a front-ply has been shown to improve the ballistic performance further while reducing the system weight.

An excellent example of the current need for transparent materials is represented by the recent fielding of add-on armor kits for the military line of HMMWVs. In an effort to improve the protection of soldiers in theater operations, the Army designed an add-on armor capability that was developed and fielded in a very short suspense. More than 4000 of these armor survivability kits (ASKs) have been produced in less than one year. However, the kits add significant weight to the transport platforms, and therefore, impact mission loads for the vehicles. The transparent armor in these kits is a significant burden, contributing as much as 30% to the overall weight but only covering 15% of the total area. Developing lighter weight solutions with improved protection will allow transition of these armor upgrade kits to vehicles without dramatically impacting mission capability.

Air Vehicles

Air vehicles include helicopters, anti-tank aircraft, fixed wing aircraft, and other aircraft that are used in combat and support roles. Transparent armor applications in these vehicles include windshields, blast shields, lookdown windows, and sensor protection. Requirements for aircraft systems are similar to those for ground vehicles, and systems are designed for use against 7.62 mm, 12.7 mm projectiles, and 23 mm High Explosive Incendiary (HEI) threats.

The Army Aviation Applied Technology Directorate has an Advanced Lightweight Transparent Armor Program (JTCC/AS) to develop advanced transparent armor with an areal density no greater than 5.5 lb/ft^2†. The goal of this program is to defeat a 7.62 mm PS Ball M 1953 threat. This constitutes a 35% reduction in weight over currently fielded systems. Optical requirements include a minimum 90% light transmission with a maximum haze of 4%. A second goal of the program is to defeat the blast and fragments from a 23 mm HEI projectile detonated 14 inches from the barrier, without exceeding a 6 lb/ft^2 areal density limit.[4] Many of these transparent armor systems utilized for military applications would also have use in commercial systems, such as law enforcement protection visors, riot gear, and windows in cars, trucks, and buses, as well as structural hardening in buildings. The cost/performance trade-off is not as critical in the commercial arena since VIP protection systems can use more exotic and expensive materials to protect against significant threats.

DESIGNING A TRANSPARENT ARMOR SYSTEM

Polymeric Materials

Amorphous glassy polymers are used in a wide variety of applications in which transparency is critical; these include lenses, goggles, and face shields for soldier, law enforcement, and medical personnel; ballistic shields for explosive ordnance disposal personnel; windows and windshields for vehicles; and canopies for aircraft and helicopters. The vital consideration for materials selection is the behavior of the material in response to mechanical deformation, chemical exposure, ultraviolet irradiation, heat, humid environments, and other potential in-service hazards.

Two distinct groups of glassy polymers are classified in relation to their physical and thermo-mechanical properties as thermoplastics and thermosets. Thermoplastics are linear or branched polymers that become soft and deformable upon heating, while thermosets, on the other hand, are rigid and possess an interconnected three-dimensional network that limits flow under elevated temperatures. Both types of polymers have a subset of materials that are visibly transparent.

Transparent polymers can be fabricated with sufficiently high strength and stiffness and developed as lightweight, low-cost alternatives to traditional glass components. Unlike glass, the physical properties of amorphous polymers vary significantly with temperature and rate of deformation. In general, material characteristics of a polymer change from being a rigid glass to an entangled rubbery-like structure once heated above a critical temperature known as the glass transition temperature. This critical temperature is indicative of an upper limit for the service temperature applicable to these amorphous polymeric materials.

Thermoplastics

As a thermoplastic material, poly (methyl methacrylate) (PMMA) has better impact resistance than most types of glass and is commonly used as a substitute for glass housings or enclosures, where hardness, optical clarity, and ultraviolet (UV) stability requirements are essential. The use of PMMA for military applications dates back to World War II. PMMA was the material of choice (really the only material available) for lightweight domes and canopies on aircraft of that era.

PMMA is manufactured in sheet form via casting or extrusion, and the product sheets can then be thermally formed into complex shapes. Casting is used to produce the thicker sheets usually used in transparent armor applications. As casting technology has improved, PMMA has found wide use as bullet resistant glazing for protecting against handgun threats. Monolithic PMMA is nevertheless brittle, and polycarbonate (PC) has been used as a substitute in applications where impact performance is most critical. PC has outstanding impact toughness (almost 300-times stronger than single-strength glass), and it has a higher glass transition temperature and better flame and fire resistance than PMMA. However, one of the drawbacks of PC is its susceptibility to degradation upon exposure to organic solvents, UV-irradiation, scratches, and abrasion. To be used in outdoor applications, PC requires UV-stabilizers and surface modification with hard coatings to ensure long-term durability. Despite these limitations however, polycarbonate (PC) has been the material of choice for both military and commercial eye protection since its introduction nearly 40 years ago.

For thermoplastics including PC and PMMA, extrusion molding and injection molding are the predominant processes for making an end product. The choice of proper molecular weight of polymers is critical in these processes to ensure desired rheological characteristics at elevated temperatures. Alternatively, some commercially available PMMA are fabricated by casting the material between two glass plates to achieve a cast sheet with excellent optical clarity at a desired thickness. An advantage of this casting process is the ability to produce a PMMA sheet with a significantly higher molecular weight and enhanced mechanical properties, which are not attainable in thermo-molding processes due to the practical limits and degradation of polymers.

Polycarbonate is the most common plastic used for transparent armor applications. It is an inexpensive thermoplastic material that is easily formed or molded, and offers excellent ballistic protection against small fragments. PC has been used by the US Army for aircrew visors and sun, wind, and dust (SWD) goggles since the early 1970's and spectacles since the mid 1980's. This equipment provides protection from small (1 gram or less), slow moving (650 ft/sec) fragments, but does not provide full-face coverage. It is currently used in applications such as goggles, spectacles, visors, face shields, laser protection goggles, and is also used as a backing material for enhanced protection from more advanced threats. It has been found to be more effective in the thinner dimensions required for individual protection than in the thicker sections required for vehicle protection.

Several investigations have been undertaken to develop new thermoplastic polymers for improved ballistic protection. The efforts uncovered several candidate materials, including transparent nylons. However, many of these promising materials are not available in commercial quantities which limits their use for future designs.

Thermosets

In the ophthalmic industry, CR-39® allyl diglycol carbonate monomer is sometimes used for casting plastic lenses for prescription eyewear that require high quality optical properties. During World War II, CR-39® resin was used to produce transparent tubes that were embedded in fuel lines to function as a visible gage that indicated fuel flow to each engine. These new plastic tubes replaced glass tubes, which often shattered during combat, spraying gasoline throughout the cockpit. Plastics made from CR-39® exhibit excellent chemical resistance and thermal properties, yet are thermosets in nature and do not possess high impact strength. A new series of thermoset polyurethane-based polymers are currently commercially available, which offer excellent chemical resistance and impact strength and can be formulated to meet the desired physical and mechanical properties. Lenses or other forms of plastics fabricated from castings of either CR-39® or polyurethane-based thermoset polymers are commercially available.

Polyurethanes (PU) have a unique morphology, possessing a combination of hard and soft domains. The properties of a PU can be tailored to specific applications by adjusting the size and ordering of these domains, yielding materials that range from being rigid and brittle, like a glass, to flexible and ductile, like an elastomer. It is becoming increasingly common to use a number of specially formulated urethanes in transparent armor designs. Thermoset PU's can be processed via casting or liquid injection molding. They are clear with a very light tint and demonstrate very good impact resistance, even when fabricated in thick sections.

Table 1. Typical Polymer Properties for Materials Found in Military Ballistic Systems.

		Lexan Polycarbonate	Simula Polyurethane	Plexi Glass G PMMA
Density,	g/cm^3	1.2	1.104	1.19
Areal Density at 1″ thick	lb/ft^2	6.2	5.7	6.2
Tensile Strength	MPa	66	62	72
Tensile Modulus	MPa	2208	689	3102
Shear Strength	MPa	45	–	62
Shear Modulus	MPa	1000	–	1151
Compressive Strength	MPa	83	72	124
Compressive Modulus	MPa	1660	1241	3030
Flexural Strength	MPa	104	89	104
Flexural Modulus	MPa	2586	2020	3280
Max Operating Temperature	°C	121	149	95
Glass Transition Temperature	°C	145	-75	100

The result of ballistic testing an all-polyurethane visor showed that it performed better than both polycarbonate and PMMA, on an equal weight basis. Because of its physical properties, this PU shows promise as a replacement for PC for monolithic eye protection and as the backing plies in all-plastic and glass/plastic laminated armor systems. Thermoset polyurethanes have also demonstrated promise in mechanical and ballistic screening and are an example of a research area with a broad horizon for future applications. The specific character of urethanes can be specifically tailored by selecting the concentration of backbone monomers, resulting in a very diverse set of material parameters. A wide range of transparent urethanes have demonstrated improved fracture performance compared to polycarbonate but with improved durability and improved scratch resistance. Some basic properties of these polymeric materials are shown in Table 1.

Material Characteristics and Design of Transparent Polymeric Materials

As pointed out, monolithic PC has outstanding impact toughness particularly at low temperatures, while PMMA has better hardness and environmental durability. The ductility of PC is reported to be associated with the molecular motion of main chain molecules at low temperatures[5]. The molecular motion is presumably present even upon exposure to high-rate impact, and can therefore provide efficient dissipation of impact energy. This molecular mechanism is not prevalent in PMMA; and in fact, monolithic PMMA has significantly lower impact energy absorption capability than PC, particularly in the thickness range of interest for eye/face protection applications. As a consequence, the potential of monolithic PMMA has not been historically realized in the ophthalmic industry due to the concern of spall upon impact, and thus PC is the predominant choice of material for eye protection.

Recent experimental results revealed that monolithic PMMA exhibits a greater increase in energy absorption when the plate thickness is increased compared to PC.[6] Furthermore, PMMA and PC plates with an equivalent thickness of about 12 mm have displayed similar impact performance against 0.22-caliber fragment-simulating projectiles, albeit absorbing the energy by different deformation and failure mechanisms. The challenge is to choose an adequate transparent armor from the numerous commercially available products that are claimed to be capable of withstanding a level of ballistic impact according to the National Institute of Justice (NIJ) specifications and standards.

In general, the material characteristics of most concern to system engineers include the overall weight (or areal density), optical clarity, and cost. However, from a material scientist's perspective, a better understanding of molecular mechanisms on high-rate mechanical deformation is important to facilitate the synthesis and design of next generation transparent polymeric materials with desired strength and toughness.[7]

Recently, Dr. Boyce's team at the Massachusetts Institute of Technology's Institute for Soldier Nanotechnologies has demonstrated a new approach to design novel hierarchical assembly materials with significantly improved ballistic impact resistance against a fragment simulating projectile[8,9]. The new macro-composite material assembly, shown in Figure 4, encompasses a distribution of discrete lightweight components, such as platelets, discs, tablets, etc., dispersed in a continuous matrix of another lightweight material possessing contrasting and complementary mechanical behavior (e.g., hardness, stiffness, ductility, and strain-hardening). In this macro-scale demonstration, the dimensions (thickness, t_2 and diameter, d) of the discrete components are small (but still macro-scale) in comparison to the overall sample thickness (t_1). In addition, the geometrical parameters such as the size and distribution of discrete discs can be tailored.

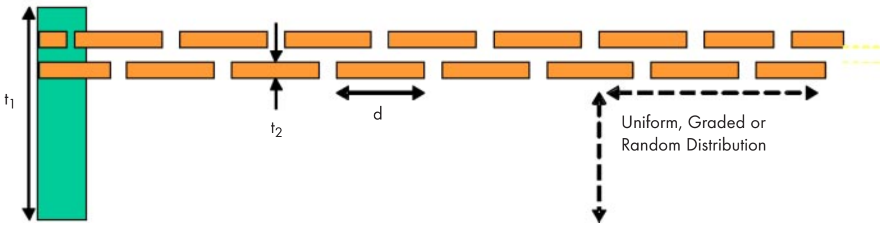

Figure 4. Hierarchical Material Assembly for Macro-Scale Demonstration.

Preliminary findings, obtained for a simplified materials assembly design

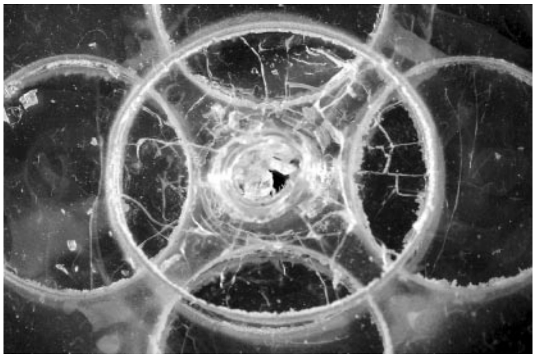

Figure 5. Cracks Arrested at the Interface of PC Matrix and PMMA Disc (~1″ Dia.).

consisting of PMMA discs distributed in a PC sample, demonstrate that the overlapping of discs increases the interaction zone between the projectile and the target by forming a network of interacting energy absorbing components. Experiments and computational simulations indicate that this magnification in the interaction zone results in a greater energy absorption and increased penetration resistance. This new design also demonstrates an enhanced multi-hit defeat capability. Figure 5 shows the impact zone of a recovered hierarchical assembly sample. The brittle failure of PMMA discs facilitates the impact energy dissipation, yet it is confined locally and the cracks are arrested at the matrix-platelet interface, thus inhibiting catastrophic failure.

The above configuration is an example of how engineering composite designs can improve energy absorption by inducing desired failure criteria into the polymer matrix. Future efforts seek to extend this knowledge of polymer failure during ballistic defeat into designing nanostructured polymer matrix materials. The proposed outcome from such research is to increase the multi hit performance of polymer matrix transparent armor solutions by reducing the probability of catastrophic failure for each impact.

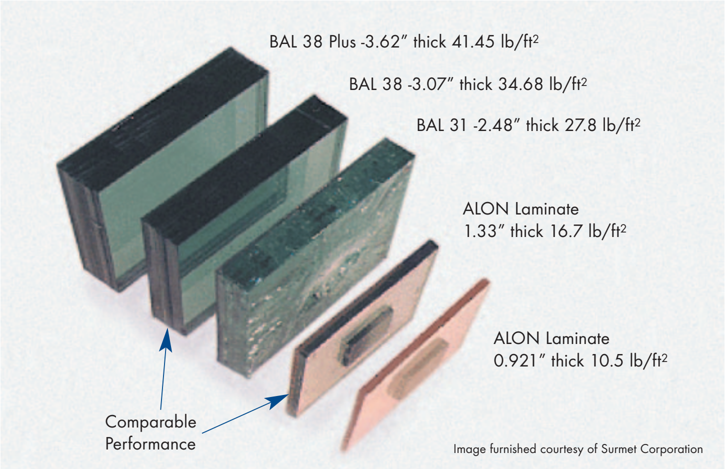

Image furnished courtesy of Surmet Corporation

Figure 6. Comparison of ALON™ to Standard Armor Systems**.

Regardless, the performance parameters of both thermoplastic and thermosetting polymer materials are being advanced, and can be exploited to improve ballistic protection limits in military and commercial applications. There is significant work to be performed, however, to transform ideas into fieldable and reliable designs.

Glasses and Glass-Ceramics

Greater requirements for optical properties and ballistic performance have generated the need for new armor materials. The major challenges for these materials are cost, available sizes, and the ability to produce curved products at reasonable delivery costs. Chemical or thermal treatments can increase the strength of glasses, as can the controlled crystallization of certain glass systems to produce transparent glass-ceramics. AREVA, Ltd.§ currently produces a recrystallized lithium silicate-based glass-ceramic known as TransArm™, for use in transparent armor systems. It has all the workability of an amophorous glass, but it demonstrates properties similar to a ceramic after it has been crystallized. Vycor™ is a 96% fused silica glass, which is water-clear, high-strength, and shows promise as an armor material, especially because of its low specific gravity.

There are several inherent advantages of glasses and glass-ceramics. First, compared to more traditional ceramics, the cost of glass-ceramics is lower. Glass-ceramics can be processed to produce curved shapes that are often achieved only by costly machining for traditional ceramics. Finally, the fabrication methods of glass-ceramics allow large material shapes to be achieved, since much of the processing is akin to glass manufacturing. All of these advantages lead to an improved readiness level for inclusion in window designs.

Transparent Crystalline Ceramics

Transparent crystalline ceramics are used to defeat advanced threats. Three major transparent candidates currently exist: aluminum oxynitride ($Al_{23}O_{27}N_5$) (ALON™‡), magnesium aluminate spinel ($MgAl_2O_4$) commonly referred to as just spinel, and single crystal aluminum oxide (sapphire). ALON™, one of the leading candidates for transparent armor, is patented by the US Army and its production and development was advanced by the Raytheon Corporation. Figure 6 provides a comparison between representative sections of ALON™ and some glass-based ballistic standards (BAL 31 and BAL 38). Thicknesses of comparable ballistic performance are highlighted.

The incorporation of nitrogen into aluminum oxide stabilizes the matrix, and results in a cubic crystal structure that is isotropic and can be produced as a transparent polycrystalline material. Polycrystalline materials can be produced in complex geometries using conventional ceramic forming techniques such as pressing and slip casting. Table 2 lists some properties of ALON™ compared with other ceramics and glass-ceramics. Although becoming commercially viable, ALON™ still is available only in limited sizes and at relatively high costs, owing in large part to the post manufacturing polishing costs, particularly for armor based needs where optics are important.

The Surmet Corporation has acquired Raytheon's ALON™ business and is currently building a market for the technology in the areas of point of sale scanner windows and as alternatives to quartz and sapphire in the semiconductor market. The

Table 2. Selected Mechanical Properties of Transparent Glasses and Ceramics.

		ALON™	Fused Silica	Sapphire	Spinel	Zinc Sulfide
Density	g/cm^3	3.69	2.21	3.97	3.59	4.08
Area Density (at 1″ thickness)	lb/ft^2	19.23	11.44	20.68	18.61	21.20
Young's Elastic Modulus	GPa	334	70	344	260	10.7
Mean Flexure Strength	MPa	380	48	742	184	103
Fracture Toughness	$MPa\sqrt{m}$	2.4	-	-	1.7	-
Knoop Hardness (HK$_2$)	GPa	17.7	4.5	19.6	14.9	2.45

high hardness of ALON™ provides a scratch resistance that exceeds even the most durable coatings for glass scanner windows, such as those used in supermarkets, thus leading to enhanced life cycles. Leveraging ALON™ into new applications is a mechanism to increase ALON™ production and capabilities, which will facilitate the fielding of armor designs for military applications.

Surmet has successfully produced a 15″ x 18″ curved ALON™ window and is currently attempting to scale-up the technology and reduce the cost. Through government small business innovative research (SBIR) and other investment funding, the US Army and US Air Force are pushing the envelope of development into next generation applications, including domes for advanced missile targeting systems and armor for commercial and military vehicles.

Ceramic magnesium aluminate spinel (spinel) is transparent in its polycrystalline form and possesses a cubic crystal structure. Transparent spinel has been produced by sinter/hot isostatic pressing (HIP), hot pressing, and hot-press/HIP operations. The use of a HIP can improve optical and physical properties of spinel by increasing density and reducing voids resulting from powder consolidation and binder volume. Some typical properties of spinel are listed in Table 2.

Spinel offers some processing advantages compared to ALON™, especially since spinel powder is available from commercial powder manufacturers in bulk quantities, while ALON™ powders are proprietary. Spinel is also capable of being processed at much lower temperatures than ALON™ and has been shown to possess superior optical properties within the IR region.[10] The improved optical characteristics make spinel attractive in sensor applications where effective communication is impacted by the protective dome's absorption characteristics. Opening the transparent frequency range implies that spinel-based sensor protection may offer enhanced performance capability. The spinel products business is being pursued by two key manufacturers in the United States, Technology Assessment and Transfer (TA&T) and the Surmet Corporation. Despite significant investments in the technology, spinel products are still available only in research applications at this time.

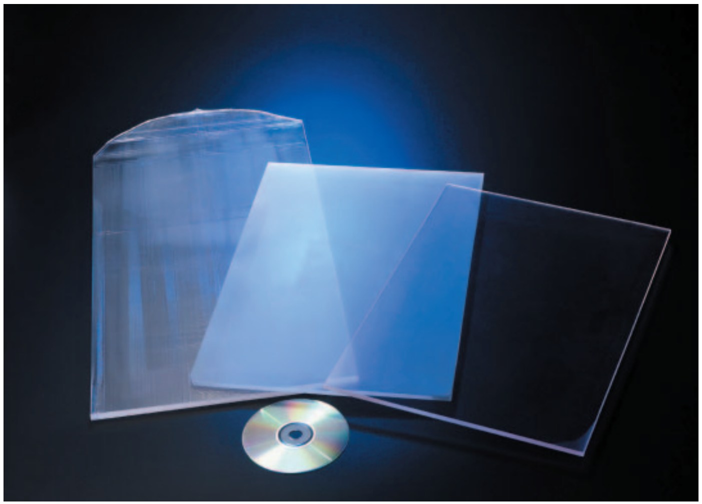
Image Furnished Courtesy of Rob Nash Studios, LLC

Figure 7. Three Product Stages of a Saphikon® EFG™ Sapphire Window; Including As-Grown, Rough Cut and Optically Polished.

Polishing the finished ceramic products is an essential process to achieve optical clarity and low haze. Whether for scanner or armor applications, windows require a high degree of mechanical polishing with diamond pastes to achieve an optical finish. The number of processing stages and length of processing time drives up final production costs and limits the supply rates for many of the advanced polished ceramic designs. Additionally, as curvature is introduced into the formulation of new armor platforms, more complex and automated polishing equipment becomes essential to keeping distortions low, allowing parallel surface machining in curved structures. New approaches intended to reduce finishing costs are underway and may lead to improved capability for fielding large-dimensional transparent ceramics. Clearly opportunities to produce optically transparent ceramics with minimal polishing would reduce overall product costs significantly.

Sapphire is a transparent ceramic possessing a rhombohedral crystal structure. From a production and application perspective, sapphire remains the most mature transparent ceramic and is available from several manufacturers, but the cost is high due to the necessary high processing temperatures and machining and polishing steps. Sapphire has a very high strength, but clarity and transparency are still highly dependent on the surface finish. Limitations to larger area sapphires are often business related, in that larger induction furnaces and costly tooling dies are necessary to increase beyond current fabrication limits. However, as an industry, sapphire manufacturers have endured significant competition from coating hardened glass and new ceramic alternatives, such as ALON™ and spinel, and still managed to offer advanced capabilities and expand business markets.

The high level of maturity in sapphire can be attributed to two business areas, EM windows and electronic/semiconductor industries. One producer, Saint Gobain Group, produces transparent sapphire using an edge-defined growth technique (Saphikon® EFG™ Sapphire) that offers unique potential. Sapphire grown by this technique produces an optically inferior material to single crystal sapphire, but is much less expensive and retains much of the hardness, transmission, and scratch resistant characteristics. With optical polishing, large area windows can be fabricated to meet commercial demands. Saint Gobain is currently capable of producing 0.43″ thick (as grown), by 12″ x 18.5″ sheets (Figure 7), as well as thick, singly-curved sheets. They have commercialized the capability to meet requirements for flight on the F-35 Joint Strike Fighter and F-22 Raptor next generation fighter aircraft. Saint Gobain, however, has not expanded production to make sapphire plates larger than 12″ x 18″. ARL has investigated edge defined growth sapphires for ballistic window applications and determined that sapphire is a competitor to ALON™ and spinel if product demand can drive production. In a free market, sapphire producers are limited in production volume because of the growth methods and product demand, and business needs and commercial value drive production decisions.

There are some challenges that must be overcome for these materials to be viable for window applications. The major challenge is in manufacturing large plates (curved and uncurved) that can be made reproducibly with high yields. Another challenge is in finishing the final part. This encompasses the grinding steps to get the correct geometry and more importantly, the final polishing. As the size of the plates get larger, the equipment available to polish these windows is scarce and is currently, a limiting step in the production of windows. Novel techniques need to be developed to grind and polish windows in a timely, cost efficient manner. Still, the future of these technologies offers great promise in dramatically improving soldier protection and in reducing system weight for future fighting platforms.

CONCLUSIONS

Protection of all vehicles in the combat theater has become a realized need over the past couple of years. The realization that future business of the United States military will involve regular combat actions in hostile environments, where single vehicles and supply convoys are as great a target as organized troop formations, brings with it the realization that all military personnel are at great risk. Coupled with the need to reduce the logistic burden in theater environments, the military leadership continues to strive for weapons and transportation systems that possess reduced weight and operational costs, and increased maneuverability and transportability.

The approach discussed here involves reducing the weight of transparent armor systems by incorporating the most advanced technical capabilities available from a wide range of materials types, specifically polymers and ceramics. Transparent ceramics were shown to offer significant ballistic protection at reduced weights over conventional glass/plastic systems. Although significant advances in production capability for advanced ceramics has been realized over the past five years, several major issues remain, such as availability, the shapes and sizes available, and cost. Although they are now capable of meeting size demands for flat plate ceramics, with transparent areas greater than 12 inches by 18 inches, low demand and high production costs have prevented businesses from investing in putting larger dimensions into production. Furthermore, producing transparent ceramics that possess compound curvatures remains predominately a research and development program for all of the ceramics industry.

Costs also remain high for ceramic armors due to the high purity powder requirements, the high processing temperatures, long processing times, complex processing steps, and high machining and polishing costs. Several programs continue to reduce these costs. However, expectations to reach current glass/plastic systems costs are unrealistic.

Polymeric material advancements, such as the improvement of the optical properties of polyurethane, have led to a renewed interest in these materials to reduce the overall weight of armor systems. It has been shown that polyurethanes offer superior ballistic performance at a reduced weight, as compared to current polycarbonate backing materials.

Numerous polyurethane materials are currently being explored as direct replacements for polycarbonate. In addition, there are significant research and development activities on design, synthesis and processing of advanced, high performance hierarchical assembly or nano-engineered polymeric matrix materials among government laboratories, industry, and academia. With successful insertion of these new materials into transparent armor systems, a significant weight reduction could be realized, along with an increase in ballistic performance and ability to defeat future threats. Still, the road ahead has danger lurking in the unseen byways and beyond the next ridge. Therefore, transparent materials for armor applications must continue to improve and increase the protection at the individual, vehicle, convoy, and battalion levels.

NOTES & REFERENCES

* Corning Inc., One Riverfront Plaza, Corning, NY 14831

† *Areal density*, in units of weight/area, is the typical method of normalizing ballistic performance of materials of varied construction. In general, this can be converted to a traditional density by summation of component densities; however, this is not usually reported. For a monocoque design, areal density divided by thickness is the density

§ AREVA T&D UK Ltd., Registered Office. St. Leonards Avenue, Stafford ST17 4 LX

‡ Raytheon Electronic Systems, Lexington Laboratory, 131 Spring Street, Lexington MA 02421. Registered trademark No. 2554362. March 2002

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Dr. James M. Sands is currently the Leader of the Transparent Materials Technology Team in the Survivability Materials Branch of the Weapons and Materials Research Directorate at Aberdeen Proving Grounds, MD. Dr. Sands began his research career at the US Army Research Laboratory in 1998, working as a contractor, until joining as a civil servant in 2000. He earned his doctorate in Materials Science and Engineering from the Pennsylvania State University; and a BA degree in Chemistry and Mathematics from Augustana College (SD). Dr. Sands has more than 20 combined refereed publications, conference proceedings, and Army technical reports to his credit.

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Dr. Parimal J. Patel has fourteen years of experience in processing of ceramics including high modulus oxynitride glasses and fibers, Si-N-O dome materials, and aluminum oxynitride (AlON). He is currently investigating the processing of AlON as well as testing and evaluation of ceramics and glasses for transparent armor applications. He received his BS in Ceramic Engineering from Rutgers University in 1990, with a focus on processing of oxide and non-oxide glass optical waveguides. He received his PhD in 2000 from Johns Hopkins University. His dissertation topic was "Processing and Properties of Aluminum Oxynitride Ceramics."

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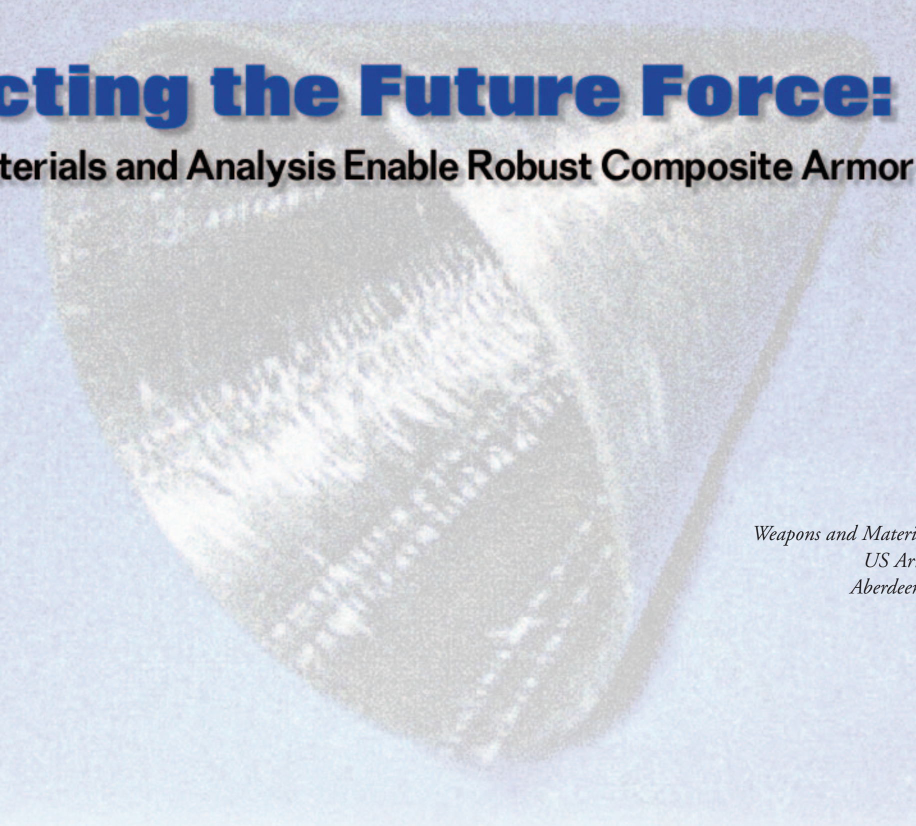
Professor Mary C. Boyce is the Kendall Family Professor of Mechanical Engineering at the Massachusetts Institute of Technology. Her research areas focus primarily on the mechanics of elastomers, polymers, and polymeric-based micro- and nano-composite materials, with emphasis on identifying connections among microstructure, deformation mechanisms, and mechanical properties. She has published over 100 technical papers in the field of mechanics and materials. Professor Boyce has received numerous awards and honors recognizing her research and teaching efforts; among them are the NSF Presidential Young Investigator Award, Fellow of the American Academy of Mechanics, Fellow of the ASME, and Fellow of the American Academy of Arts and Sciences.

Protecting the Future Force:

Advanced Materials and Analysis Enable Robust Composite Armor



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INTRODUCTION

The US Army is undergoing a paradigm shift toward highly mobile, rapidly deployable, readily sustained units of action having unprecedented lethality and survivability. While current ground fighting vehicles have evolved to their 70+ ton status, in part to defend against the ever-increasing lethality of ballistic threats, their sheer mass and support requirements do not make them easily transportable or readily sustainable. Therefore, as the US Army transforms, future combat systems (FCS) will employ lightweight, highly mobile, transportable, and lethal armored vehicles that maintain the highest level of survivability.

To achieve armor performance exceeding that of the current combat vehicles for new vehicular systems weighing less than 20 tons, significant advances in survivability technology are required. Advanced materials and their multifunctional integration are critical to the successful design of new light armors. One such light armor solution being developed is an advanced composite armor that combines ceramics, metals, and polymeric composites to provide unmatched mass efficient protection. Such rapid advancements are only possible with similar developments in individual materials and modeling technology. As ceramics and metals are the focus of other articles in this issue, this paper will first highlight the evolution of 'the plastic tank' and then detail the recent advancements in organic materials technology and advanced simulation capability for application of composites in vehicle armor.

THE 'PLASTIC TANK' - A HISTORY OF COMPOSITE STRUCTURAL ARMOR

Composite armor systems are not new. During the pioneering light armor experiments against small arms threats conducted in the late 1960's, Wilkins and co-workers [1-3] determined that hard ceramics coupled with a thin ductile backing form effective, mass efficient armor systems. These researchers recognized that ceramics possess characteristics such as low density, high hardness, and high compressive strength; all of which were well-suited for light armor systems. When coupled with composite materials having superior strength-to-weight and stiffness-to-weight properties, ceramic/composite armor provides mass efficient ballistic protection against a number of threats. Integrating these materials as a mass efficient armor system on armored vehicles has been reported in the open literature since the 1980's [4], and the US Army's efforts in the development and application of composite armor during this time are detailed below.

Through several key R&D programs during the 1980's and 1990's, the Army established a confidence-building baseline for the application of polymer matrix composites (PMCs) to lighten heavy forces while also improving survivability for light forces. The first application of thick-section PMCs to armored vehicles was in a demonstration program in the late 1980's under which a polyester/glass composite hull was developed to replace the aluminum hull on the Bradley Infantry Fighting Vehicle (BIFV). The resulting vehicle, with a thick-section composite hull and appliqué ceramic armor tiles, became known as the Composite Infantry Fighting Vehicle (CIFV) and demonstrated the ability of PMCs to perform well structurally in an armored vehicle [5]. This vehicle was followed by the Composite Armored Vehicle (CAV) program; established to assess the application of PMCs in the ground-up design of an armored vehicle [6]. To meet the stringent weight and ballistic performance requirements of the CAV, which is shown in Figure 1, the concept of a multifunctional PMC-based armor was developed. The resulting composite integral armor (CIA) performed exceptionally well and was subsequently adapted for

Figure 1. **Composite Armored Vehicle (CAV).**

incorporation into designs for the Army's Crusader Self-Propelled Howitzer (SPH) and its Resupply Vehicle (RSV) [7].

An example of the armor designed for the CAV is shown in Figure 2. Each layer serves a specific purpose, yet combinations of layers provide role-sharing multifunctionality. A thin, protective PMC facesheet on the outside of the vehicle serves to protect the ceramic ballistic tiles from incidental damage, while the ceramic tiles are utilized to break up and/or erode the projectile upon impact. The subsequent rubber (EPDM) layer is utilized to improve multi-hit ballistic performance. The thick-section composite plate serves as the structural support for the vehicle, a structural backing for the ballistic tiles and also catches the remnants of the projectile and fractured ceramic, while absorbing the residual kinetic energy. Finally, a fire-protective "spall" layer of phenolic is incorporated on the inner surface of the vehicle. Other layers can be incorporated to provide additional functionality, such as electromagnetic ground planes, signature control, etc.

While composite integral armor developed under the CAV and Crusader programs engendered confidence in the ability of PMCs to simultaneously meet ballistic and structural properties in combat vehicles, the mass efficiency (ballistic performance per unit areal density) falls significantly short of the current requirements. Advancements in materials technology and numerical simulation capabilities were identified as enabling technologies to aid in future developments of advanced composite armor, and some of these recent efforts are detailed in the following sections.

FIBER COATINGS: SIZING MATTERS

Composites used for structural armor are different from those used in appliqué or body armor applications. Typically, body-armor grade composites are resin starved, consisting of approximately 80 weight percent fiber, and are engineered to readily delaminate, which enables the high strength, high modulus fibers to elongate and absorb the impact energy. These non-structural armor textiles are highly mass efficient, and there are a number of composite vehicle armor appliqués that incorporate them. However, they serve only to increase ballistic protection, not support load. Composites being considered for FCS vehicle applications are being designed to be multifunctional, and as in the CAV detailed above, the FCS composite armor will be an integral part of the vehicle, carrying typical vehicle kinematic loads. These composites under development are comparable to traditional structural composites having approximately 50 volume percent fiber.

While efficient for carrying load, composites used for structural armor are not as mass efficient ballistically as their armor grade counterparts. However, if these composites were to possess strong fiber-matrix interfacial adhesion at structural loading rates, and weak interfacial strength at ballistic loading rates, they would behave structurally under vehicle loads, yet absorb energy like an armor grade composite under ballistic impact. The result would be an optimized multi-functional armor composite. Recent research has indicated that this may be possible through innovative manipulation of the chemical and physical interactions between the matrix and fibers.

Woven and non-woven fabrics constructed using continuous glass-fiber reinforcements are commonly used in PMCs. During industrial glass-fiber manufacturing a multicomponent thin coating, known as a sizing, is applied to the fibers for protection against damage during processing and to control their performance in composite articles. Conventional glass-fiber sizings incorporate organofunctional molecules, known as silane coupling agents, to enhance the adhesion between the glass-fiber reinforcement and the polymeric matrix and to increase the durability of the composite. The complex chemical and physical interactions due to the silane coupling agent result in the formation of a nanometer sized interphase region between the glass-fiber surface and the polymeric matrix.

The interphase region that surrounds glass-fibers in a composite is essential to its performance, yet is poorly understood. For example, existing traditional fiber sizings are not optimized to tailor simultaneously a composite's static and dynamic response. Yet, it has been recognized that these sizings affect structural durability, impact resistance, and damage tolerance.

Published research indicates that the impact response of a PMC can be tailored for high-energy absorption by designing

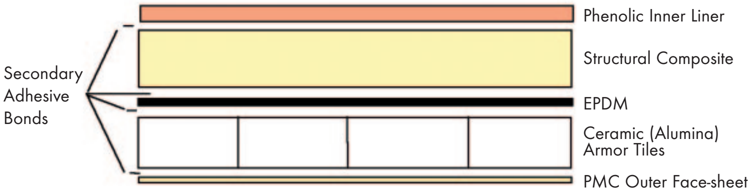

Figure 2. **Example of the Composite Integral Armor Developed under the CAV Program.**

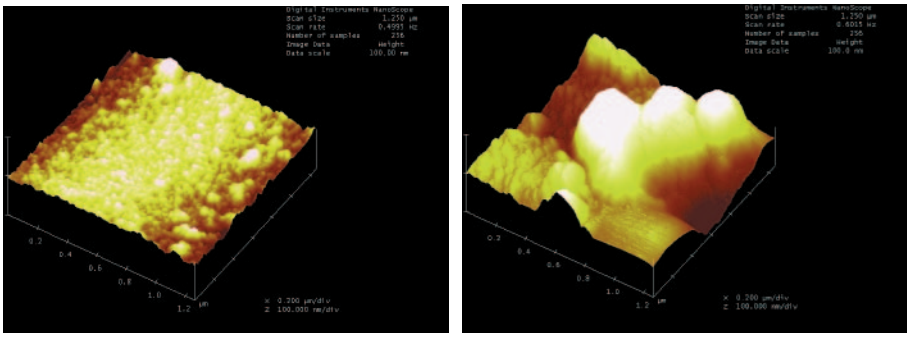

Figure 3. Surface AFM Images of Standard Commercial Fiber (Left) in Comparison to ARL Nano-Roughened Commercially Produced Fiber (Right).

weak fiber-matrix interfacial interactions. Conversely, structural performance (strength) is achieved by strong fiber-matrix interfacial interactions. Hence, the aforementioned trade-offs exist. Although the achievement of simultaneous high strength and energy absorption levels is desirable, the technology has not been available. New approaches are now available to overcome these traditional materials shortcomings.

The glass-fiber sizing research being performed at ARL has systematically examined the nature of the glass-fiber/thermosetting polymer interphase region to develop the fundamental understanding necessary to propose and validate an entirely new class of sizing materials. Specifically, mixed organofunctional silane coupling agents are being employed to vary the chemical reactivity toward the polymeric matrix phase to produce bond strengths that are dependent on the viscoelastic properties of the matrix and fiber-coating. This results in an inherent "viscoelastic switch" at the fiber-matrix interphase that yields strong fiber-matrix interactions (high structural strength) at low strain rates and weak fiber-matrix interactions (ballistic performance) at high strain rates. This triggered response is coupled with the application of inorganic-organic sol-gel processes to develop silane-based, glass-fiber sizings that increase the surface roughness of commercially produced glass fibers. The result is an increased coefficient of friction between the fiber and matrix during the fiber pullout stages of composite failure, further resulting in enhanced energy absorption in the composite during ballistic events. These results were first documented mechanically on micro-scale model composite specimens. Subsequently, the experimental inorganic-organic hybrid fiber sizings were scaled-up and applied using commercial manufacturing equipment to demonstrate their behavior in macroscale composite materials.

Figure 3 shows the successful nano-texturing of the fiber surfaces produced on a commercial scale using atomic force microscopy (AFM). Glass reinforced composite materials were manufactured using these specialized fabrics, and the structural and impact energy responses were measured. Figure 4 captures the impact energy absorption and structural performance of composites produced using state-of-the-art commercial sizings and the ARL inorganic-organic hybrid sizings. These results show the traditional trade-offs found when using commercially available fibers that have been coated with either a structural or ballistic sizing. In comparison, these trade-offs do not exist for the ARL inorganic-organic hybrid sizing, and the impact and structural performance of this optimized sizing are both excellent. A 40% increase in the energy absorption of composites fabricated with no loss in structural properties will enable the use of PMCs in ballistic applications where they have not been used previously, perhaps with reduced cost.

ADVANCES IN MODELING: ROBUST COMPOSITE MATERIAL MODEL FOR IMPACT AND BLAST

Less than ten years ago, a review paper on the state-of-the-art in numerical modeling of high-velocity impact stated that there was no definitive computational model for ceramics and that high velocity impact calculations of fiber-reinforced composites were a research task [8]. These limitations in numerical techniques and robust material models resulted in much of the design of composite armor systems being guided by experimental efforts. However, since then the advances in numerical techniques and development of robust material models have allowed modelers to simulate accurately what is observed experimentally, and this has allowed greater insight into how the components of the composite armor work together during the impact event. These recent developments have allowed experiments and simulations to be utilized together to improve the performance of composite armor for FCS.

MODELING COMPOSITE ARMOR

Accuracy in modeling of ceramics has been aided by the use of LaGrangian particle techniques, either smooth particle hydrodynamics (SPH) or general particle algorithms (GPA), which, when coupled with a validated material model, have given very good correlation with experimental observations of impact into

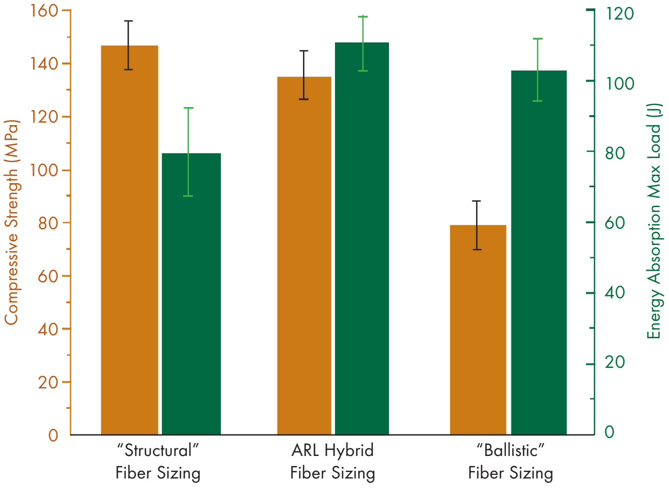

Figure 4. Mechanical Performance of Composites with Various Sizings. The ARL Sizing Shows Exceptional Performance in both Energy Absorption (Shown in Green) and Compressive Strength (Shown in Orange).

ceramics. One such material model, the Johnson-Holmquist ceramic model, has been able to accurately simulate the full gamut of ceramic response: everything from the phenomenon of interface defeat, where a projectile is stopped on the surface of the ceramic, to the dwell-penetration transition and direct penetration [9]. Thus, as the issue of ceramic modeling may have evolved toward a (somewhat accepted) phenomenological material model (though an accepted micromechanical model is still being sought), composite material modeling for dynamic events has also seen significant advances. Detailed below are some of the extensive efforts to develop, characterize and validate a robust material model, specifically for the analysis of a composite undergoing highly transient and damage-inducing (blast or ballistic impact) loading.

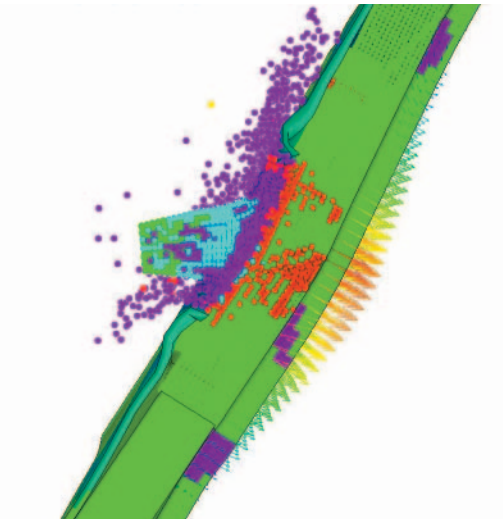

Figure 5. **Modeling Ballistic Impacts into Composite Armor Has Evolved Significantly in Recent Years.**

The modeling of ballistic impacts into composite materials has evolved from two different analysis methodologies. One set of models has been developed from the analysis of high velocity impacts into metallic materials, where the response of the material is governed by wave propagation. The second set has been developed from the quasi-static damage mechanics analysis of composite materials. In the former case, the behavior of a material is modeled by analyzing the hydrostatic and deviatoric components of stress. However, due to its inherent orthotropy, decoupling of the stress tensor of a composite material proves to be problematic: there are terms related to the deviatoric stress that affect the hydrostatic components and vice versa. Nonetheless, with suitable assumptions and corrections, Anderson and co-workers [10, 11] overcame this issue, and several models have evolved using this formulation. These models have proven unique in that they allow a polynomial equation of state to be utilized, which has proven important in the analysis of armor grade composites and for hypervelocity impact simulations (Figure 5) [12].

The present model, developed by the Materials Sciences Corporation (MSC) and the US Army Research Laboratory, has been generalized from the quasi-static damage mechanics analysis of composite materials [13, 14]. Further improvements of this model have recently been made at ARL and the University of Delaware [15] under the Army's Materials Center of Excellence. Composite materials mitigate impact energy through a number of different material damage mechanisms. This is unlike many metallic components, where localized impact energy is typically mitigated by localized plastic deformation. Shown in Figure 6 are a number of these mechanisms, such as fiber shear fracture, fiber tensile rupture, matrix cracking, delamination and fiber crushing, that are observed experimentally and must all be taken into account.

Table 1. **Input Parameters Required for the Composite Material Model.**

Material Properties Required in the MSC Composite Material Model

Mass density
Young's modulus – longitudinal direction
Young's modulus – transverse direction
Young's modulus – through thickness direction
Poisson's ratio ba direction
Poisson's ratio ca direction
Poisson's ratio cb direction
Shear modulus ab direction
Shear modulus bc direction
Shear modulus ca direction
Material axes option
BETA Layer in-plane rotational angle in degrees
Longitudinal tensile strength
Longitudinal compressive strength
Transverse tensile strength
Transverse compressive strength
Through thickness tensile strength
Crush strength
Fiber mode shear strength
Shear strength, ab plane
Shear strength, bc plane
Shear strength, ca plane
Scale factor for residual compressive strength
AMODEL Material models:
EQ. 1: Unidirectional layer model
EQ. 2: Fabric layer model
Coulomb friction angle for matrix and delamination failure
Element eroding axial strain
Scale factor for delamination criterion
Limit damage parameter for elastic modulus reduction
Limit compressive relative volume for element eroding
Limit expansive relative volume for element eroding
Coefficient for strain rate dependent strength properties
Coefficient for strain rate softening property for fiber damage A direction
Coefficient for strain rate softening property for fiber damage B direction
Coefficient for strain rate softening property for fiber crush + punch shear damage
Coefficient for strain rate softening property for matrix and delamination damage
Coefficient for strain rate dependent axial moduli
Coefficient for strain rate dependent shear moduli
Coefficient for strain rate dependent transverse moduli

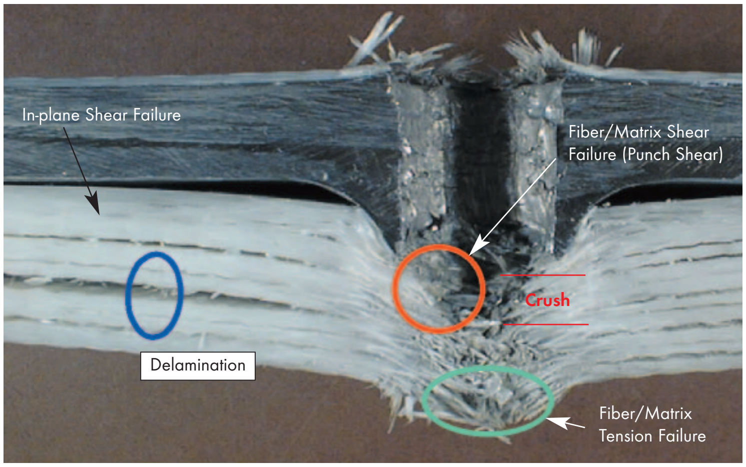

Figure 6. **Damage Mechanisms Observed During the Impact and Penetration of a Composite.**

Generally, in composite damage mechanics models, material damage and failure are accounted for only by a resultant decrease in the material stiffness in the corresponding material directions. The current model utilizes this concept, but also accounts for the inter-relations of the different failure modes through quadratic failure criteria and a novel damage tensor that relates the specific failure modes to the extensional and shear moduli that are compromised. The formulation is based on the continuum damage model for composite failure developed by Matzenmiller et al. [16] and has been extended to incorporate strain rate sensitivity of both stiffness and strength and post failed material softening.

While the details of this elegant and complex material model are beyond the scope of the current article (for further details, refer to [13]), it is not surprising that there are a number of material constants that must be determined in order to generate accurate simulations. Table 1 shows a list of the constants required by the composite damage model, which has been incorporated into the commercial dynamic finite element analysis software LS-DYNA, where it is known as MAT 161/162. Obviously, in order to perform accurate simulations of a composite material using the current model, a substantial material characterization program is required. As part of the Composite Material Technology (CMT) program, the Center for Composite Materials (CCM) at the University of Delaware has been working with ARL and MSC to fully characterize materials of interest and validate these values by performing simulations of the experiments using LS-DYNA and the current material model.

Figure 7 depicts the effort of determining the material behavior associated with the punch shear of S2-glass/epoxy composites. Punch shear experiments were conducted for a number of punch-die diameters at a variety of rates from quasistatic, to drop tower, to split Hopkinson pressure bar. Simulations were then performed, and the quantitative values were compared with those obtained from the experiments. Materials that have been characterized include S2-glass/SC15 epoxy, S2-glass/SC79 epoxy and IM7 carbon/SC79 epoxy.

COMPOSITE ARMOR SIMULATION

To illustrate the insights that can be gained from simulations of composite armor, consider the following problem shown in Figure 8. The simulation, conducted using the nonlinear analysis software Autodyn, consists of a half-symmetric model of a ceramic tile with a thin composite cover plate on top and supported by a thin PMC, all of which is backed by a glass-fiber

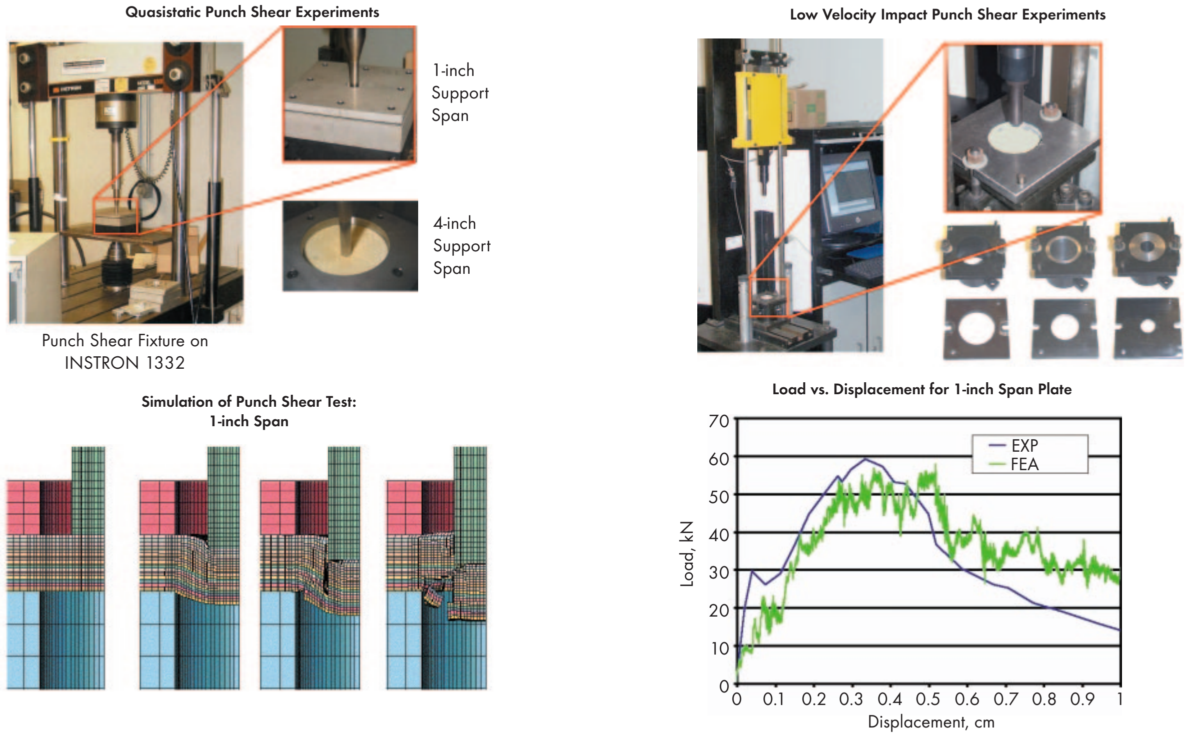

Figure 7. **Experimental Set-ups for Quasistatic and Drop Tower Punch Shear Experiments, Simulation of the Punch Shear Experiment and a Comparison of the Load vs. Displacement Curves from the Experiment and the Finite Element Analysis.**

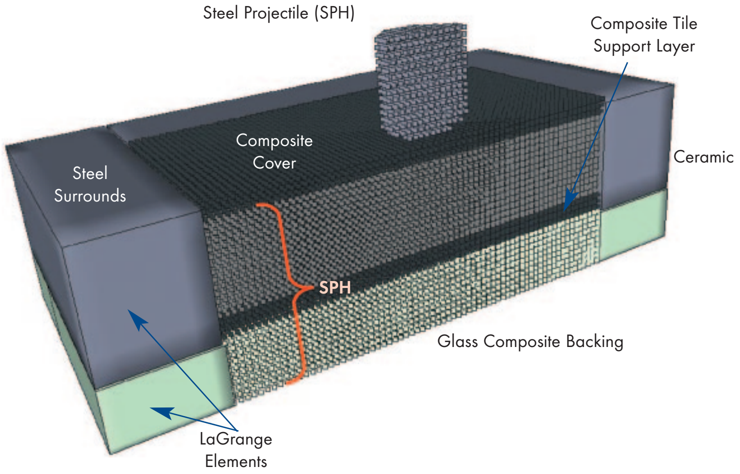

Figure 8. **Model Used for the Numerical Simulation of a Composite Armor System.**

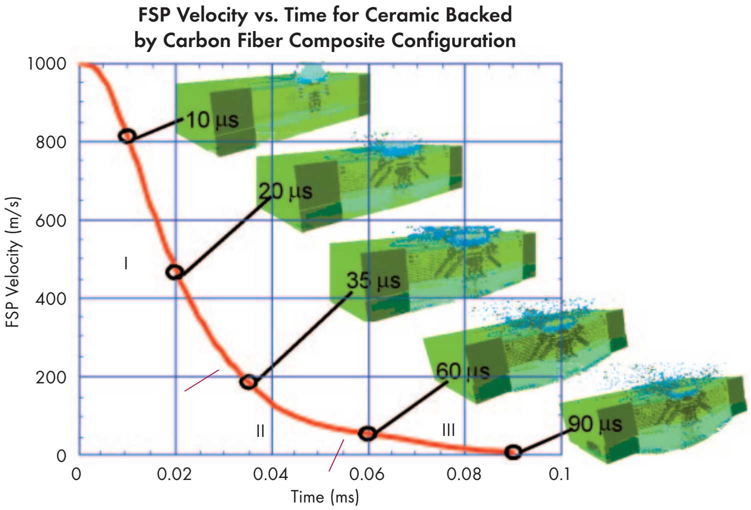

Figure 9. **Projectile Velocity as a Function of Time for the Baseline Configuration.**

PMC. In the impact region, all of the materials are modeled using smooth particle hydrodynamics (SPH). The tile itself is surrounded and confined by steel brackets modeled using LaGrangian elements.

As a measure of how the composite armor reacts upon impact, the deceleration of a target point on the rear surface of the fragment-simulating projectile (FSP) is tracked during the impact event. The deceleration of the FSP for this baseline case is given in Figure 9. From this figure, it can be seen that the deceleration curve of the FSP has three distinct portions: an initial steep deceleration up to approximately 35 µs, a transition region from roughly 35-45 µs, and a final, more moderate deceleration curve from 45-90 µs.

By observing the plots of the material damage through time, an understanding of the mechanisms behind these regions becomes discernible. The initial rapid deceleration is caused by the hard ceramic deforming the FSP. During this time, the ceramic itself fails, its failure starting on the surface opposite the impact surface due to the tensile reflections from the initial compressive stress wave. In Figure 9, green regions indicate undamaged material, and colored regions indicate material that is either plastically deformed or damaged. The cyan color of the projectile indicates that it is plastically deforming. For the composite, the cyan and orange coloring indicates transverse shear damage, the purple indicates in-plane tensile failure and for all materials, red indicates bulk failure. The cracking of the ceramic leads to the formation of a conoid (a cone of ceramic material under the impactor) which loads the backing plates.

Extensive transverse shear damage mechanisms appear in all of the composites by 20 µs. The initial deceleration of the projectile transitions to a more moderate deceleration of the projectile at approximately 30 µs, and it is at this time that the damaged composites have displaced enough locally to allow the failed ceramic in the conoid to start moving, both in the direction of the projectile and laterally, out of the way of the projectile. The effectiveness of the ceramic diminishes greatly from 30 µs to 45 µs. After 45 µs, the damaged glass/epoxy composite catches both the ceramic rubble and the plastically deformed projectile.

SUMMARY

The application of polymer-matrix composite materials to armor systems has principally been driven by the need to increase performance (survivability) in very lightweight fighting vehicles. The stringent weight requirements for these types of applications have provided the motivation for the development of multi-functional armor systems. Ceramic-composite armor systems have been developed to provide ballistic protection from a range of battlefield threats and also serve as the vehicle structure.

Substantial progress has been made in the development of materials technology for lightweight fighting vehicles, including advances in fiber sizings that have been formulated to provide strain-rate sensitive response (strong fiber-matrix interfacial adhesion at structural loading rates, and weak interfacial strength at ballistic loading rates). Additionally, the development, characterization and validation of improved material constitutive models have allowed ballistic experiments to be studied using numerical simulations, which have provided new insight into how the materials behave and interact during impact. Further advances in materials technology and their incorporation into lightweight armor will focus on the increased integration of multifunctionality, such as the incorporation of power storage, communication, sensing, and health monitoring, which are described elsewhere in this issue of the *AMPTIAC Quarterly*. Numerical simulations will allow engineers to examine the influence of multifunctional materials on improving the performance of ceramic composite armor that will be utilized in future combat systems.

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Manufacturing a More Affordable Army through Low Cost Composite Processing

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INTRODUCTION

The United States Army is currently undergoing one of the largest and most significant transformations in its history. The ultimate goal is to ensure the overwhelming superiority and effectiveness of both its defensive and offensive systems in the face of constantly evolving threats and technological advances. To do so, the Army will have to become lighter and more lethal; and will have to gather and synthesize information in new ways to optimize its performance. A key component of this transformation is the transition from “legacy” systems to next-generation systems that are lighter, rapidly deployable, and highly networked. A second and equally important element is the exploitation of new materials and technologies to deliver the weight reduction, mobility, survivability, and lethality performance required by the Army Transformation.

There will be a period of transition wherein both current and future Army systems will constitute the overall arsenal of Army weaponry and equipment. This provides a unique opportunity to compare historical system production levels with anticipated production levels of entirely new systems. In addition, it emphasizes both the scale and scope of systems the Army requires to execute its mission. Figure 1 highlights the challenges associated with manufacturing an array of Army systems, and specifically, the broad and unique applications of polymer-based composites across systems of varying complexity and production levels.

ENABLING MATERIAL AND PROCESS TECHNOLOGIES

The Army’s goal is not simply to “keep pace” with technology but rather anticipate the trajectory and evolution of strategic technologies, and thereby develop new and effective means to defeat emerging threats and preserve a superior tactical advantage. Exploiting materials technology is central to this basic goal, and polymer-based, fiber-reinforced composite materials have and will continue to play a critical role in this area. Advances in composite systems are basically two-fold: the first is the development of fundamentally new fibers, resins, and other “constituent” materials. The second is the integration of available materials into new composite and multifunctional material solutions that give significantly improved sets of properties (for example, mass-efficient structural armor). Advances in constituent materials, such as low viscosity, high performance epoxy resin systems, have enabled a shift from capital-intensive equipment such as large pressurized autoclaves to lower cost vacuum driven processes based on liquid injection molding technology.

Process Models, Sensors, and Control

The Army has made substantial and sustained investments in high performance computing (HPC), having established several centers to develop and apply computing excellence. These computing resources have been leveraged by both government and university researchers through the Army’s Major Shared Resource Centers (MSRC) to develop increasingly complex models of various materials and processes of interest to the Army. However, a trend is underway to develop more computationally efficient codes that can operate on platforms that are likely to be found on manufacturing shop floors – such as personal computers. Process simulation, together with sensor and control technologies, constitutes a research area known as “intelligent processing.” Traditional processing relies largely on historical information gathered by trial and error; by contrast,

Figure 1. **The Diverse Array of Current and Future Army Systems.**

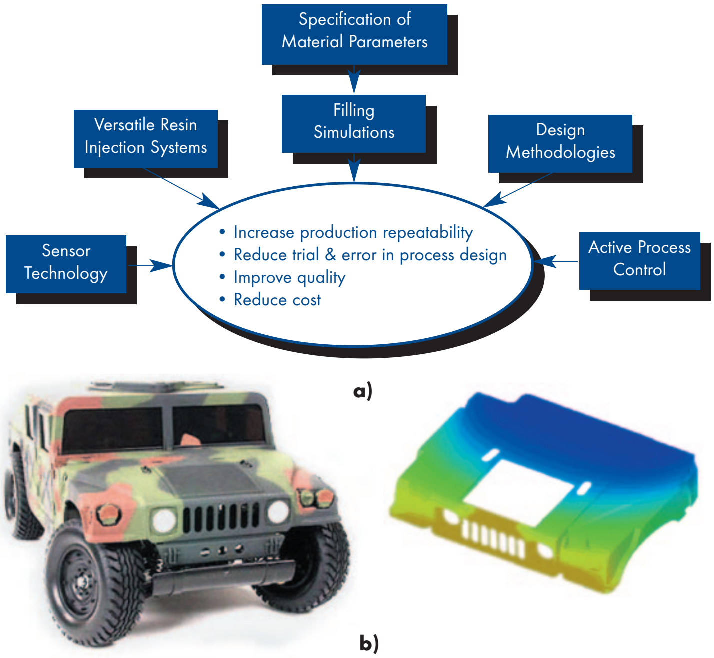


Figure 2. **The Application of Intelligent Processing Tools to a HMMWV Hood Structure [1].**

intelligent processing uses both predictive and diagnostic tools to optimize the composite manufacturing process. Unforeseen disturbances during processing can be actively compensated for and minimized. In addition, the introduction of automation reduces labor, improves repeatability, and increases yield. Figure 2a demonstrates the various tools that must be developed and integrated to obtain this goal.

Simulation tools such as LIMS (Liquid Injection Molding Simulation) and SLIC (Simulation-based Liquid Injection Control) developed at the University of Delaware were used to demonstrate and experimentally validate the intelligent processing approach [1, 2]. Figure 2b shows how one can model resin flow in the hood of a HMMWV using modeling and simulation tools. Placement of sensors in the mold will allow one to detect flow disturbances and re-direct flow through pre-selected auxiliary gates to ensure successful manufacturing despite unforeseen variations. The strategic control environment could be developed off-line using the simulations to create all the different possible scenarios. The control strategy can then be implemented on the manufacturing floor using a computer to interface with the sensors in the mold and the auxiliary gates. This concept has been integrated in a Resin Transfer Molding (RTM) workstation. The workstation can accept the data created by the simulation environment for detecting the disturbance and for triggering the control action for that particular scenario.

In order to meet the requirements of the Army Transformation, selected materials must be able to solve a host of system issues while remaining weight efficient and cost effective. The tailorability of composites allows designers to maximize performance at a minimal weight. In addition, the ability of composites to perform multiple functions as a material system offers the flexibility to maximize the efficiency of designs.

In the past, the Army has segregated ballistic and structural requirements; composite systems now combine these two requirements in certain applications. Current efforts are focused on combining power, sensor suites, communication, and health monitoring with structural composite elements. The only way to accomplish these tasks is to take a holistic approach to developing systems for the Army. The total requirements for the system have to be considered while the designer is selecting materials. In addition, the tooling schemes and manufacturing processes should be considered to ensure that the most cost-effective material solution is chosen.

As these multi-functional composite materials are being designed into future platforms, new test methods are being developed to ensure that the systems will perform as required. While developing manufacturing technologies, the Army considers repair concepts to reduce the life-cycle costs and logistics footprint of future platforms. Innovative approaches towards composite manufacturing are essential to prepare for these and other requirements.

Novel Fabrication Technologies

Process innovations have led to the development of more flexible manufacturing technologies for both prototype and production operations. For example, the Army has co-sponsored the development of a new, highly flexible process that provides

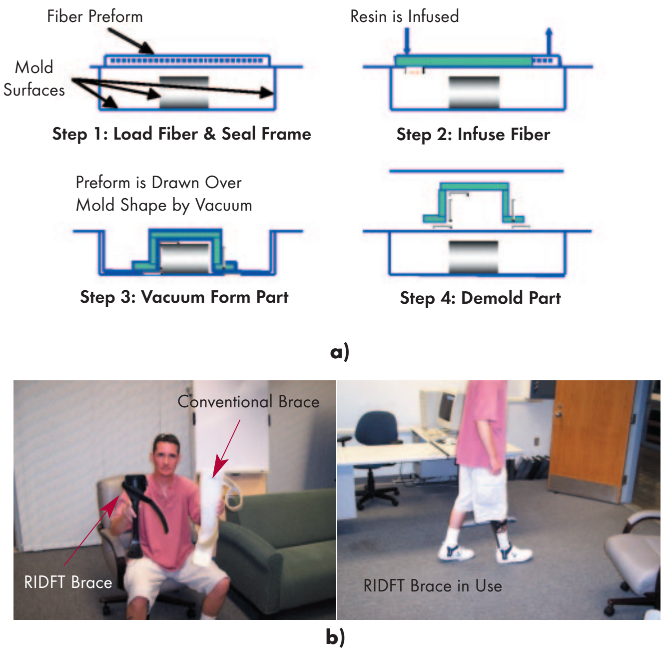


Figure 3. **a) The RIDFT Process and b) a Custom Fabricated Leg Brace.**

a rapid, low cost means of fabricating components with various geometric, material, and design complexities. The process, invented at Florida State University and known as Resin Infusion between Double Flexible Tooling (RIDFT), uses vacuum-based infusion to wet-out a fibrous preform and then draw it down to fully conform to the desired tool shape (Figure 3a). A particularly novel feature is the ability to use inexpensive, rapidly prototyped tooling; this permits one to move seamlessly from concept to design to near-net fabricated component [3]. The process enables the cost-effective ability to fabricate customized components or replacements parts, and is capable of low to intermediate production runs. RIDFT is a particularly conformal process that allows for "deep draw" of fibrous preforms. For example, the process was used to fabricate curved components for Army unmanned aerial vehicles (UAVs), as well as prototype Army helmet shells for human factors testing. More recently, the RIDFT process was demonstrated as an effective method for producing a leg brace for an individual impaired by a leg injury while serving in Iraq.

Anthony P. Muller, HMC (Chief Hospital Corpsman), NMCB (Naval Mobile Construction Battalion) 14 based in Jacksonville, Florida was injured in a mortar attack in Iraq in May 2004. He is undergoing therapy and rehabilitation and as part of the process he is required to wear a supporting leg brace. This presented an opportunity to demonstrate RIDFT's rapid, flexible, and low cost means of developing a lightweight brace for an individual. Compared to the conventional brace, the finished RIDFT brace was 22% lighter, covered 40% less of the sailor's skin, and had an integrated carbon fiber/epoxy structural spring to assist with impaired ankle/foot functioning. More importantly, the brace was both customized to the sailor's leg to ensure optimal performance (Figure 3b) and delivered to him within hours of the initial design requirements assessment. This is a technology that could not only benefit Army, Navy, and other members of the military community, but a host of individuals who could use customized, lightweight braces.

Integrated Composite Manufacturing Approaches

There are three emerging areas that could significantly shape the future of manufacturing Army systems. The first is the development of multifunctional material solutions to address weight and volume constraints of future Army system designs. The essential challenge is to provide the same functionality at reduced weight. This functionality could, for example, simultaneously require armor, structural support, EMI shielding, lightening strike protection, and communication hardware. Advances in materials, design, and integration techniques offer the potential to produce a truly "multifunctional" composite system. Figure 4 displays a notional section of structural armor wherein an electromagnetic radiating element serves as an antenna. This system has four distinct types of materials: a polymer resin, a fibrous glass reinforcement, a metallic film, and an array of ceramic tiles. The processing challenges are obvious: each material potentially introduces an additional processing step (and hence, labor, time, and expense). There is relatively little processing science associated with manufacturing of this kind, and the Army has initiated several programs to explore these issues.


Fabrication of "Smart" Perform with Conductive Back-plane Elements

Co-processing of Preform, Ceramic Tiles, and Antenna Element

Integration into Notional Vehicle Structure

Figure 4. **A Notional Multifunctional Structural Armor and Antenna Concept.**

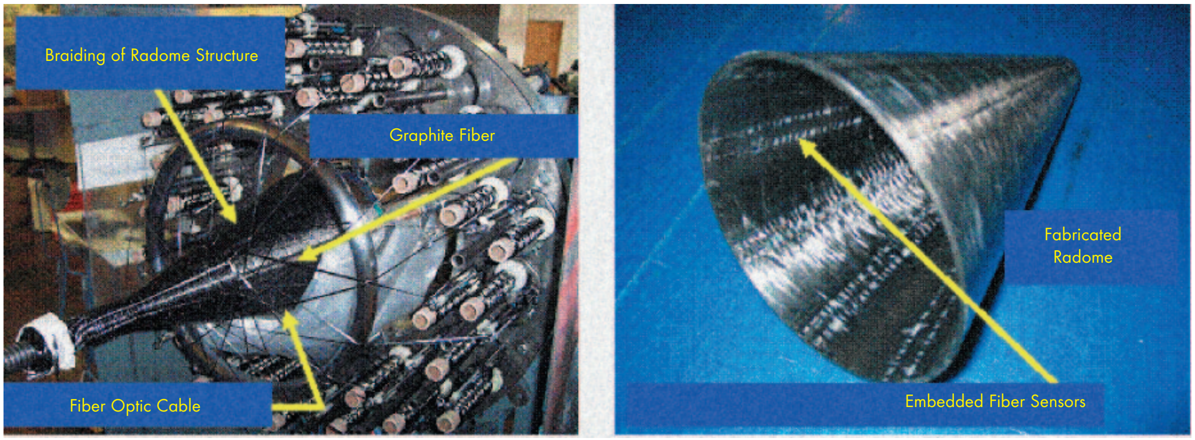


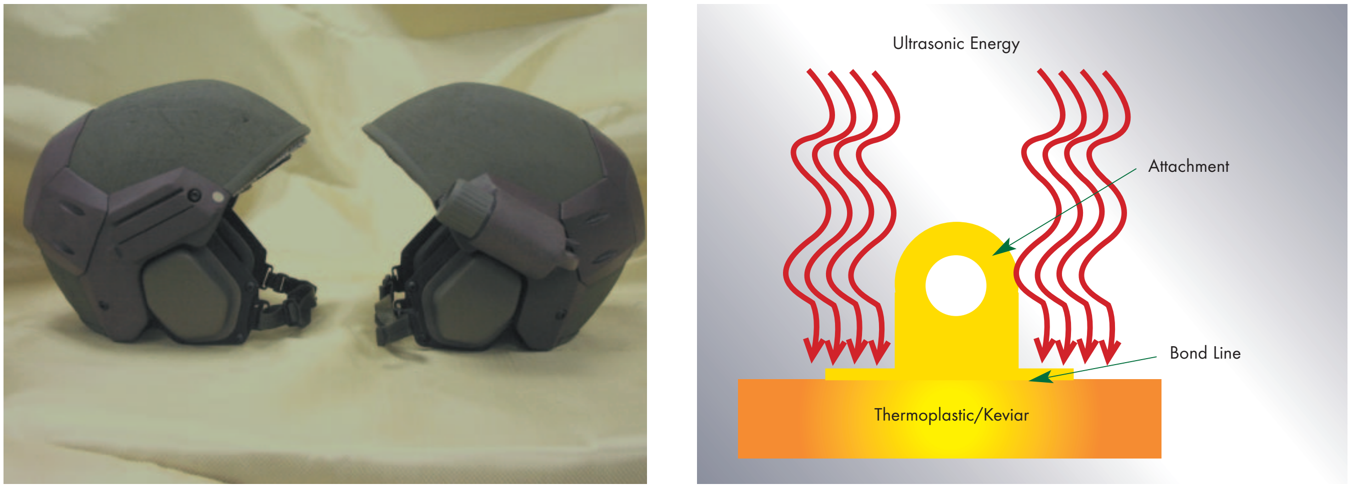
Figure 5. A Braiding Process for Embedding Structural Health Monitoring Sensors.

The second area influencing composite manufacturing is that of structural health monitoring (SHM). SHM is an enabling technology for condition-based maintenance and it has the potential to reduce significantly the overall "cost of ownership" of fielded systems. The Army has leveraged both academic and industrial sectors to begin identifying the type of process technologies that will be appropriate for embedding and connecting the type of promising SHM sensor hardware that is currently being developed. Fiber optics, for example, have proven successful as temperature, pressure, and strain measurement devices. Fiber optics are also attractive in that they closely resemble the fibers used in many continuously reinforced composites, though their diameter and flexibility may vary greatly from the reinforcing fiber.

Mentis Sciences Inc. has been developing a highly novel fiber feed system which they have integrated with their missile radome fabrication technology (Figure 5). Essentially, this technique uses braiding to both form the structural radome component and simultaneously co-locate with a high degree of accuracy a series of fiber optic sensors. The use of such structural health monitoring sensors in missile structures has the potential to assess damage of a missile component during transport, use, and storage.

A third area is that of intelligent component integration. Previous studies and programs have indicated that 10-20% weight reductions and 30-50% fabrication cost reductions are possible if new technologies could be developed to minimize or eliminate the number of fasteners and mechanical attachment systems currently used with composite materials. Drilling bolt holes into a composite not only reduces the load bearing capacity of the structure, it also greatly increases overall manufacturing costs due to machining, cleansing, fastener installation, and assembly steps. The remedy to this problem is two-fold: (1) better designs that minimize or eliminate the need for traditional mechanical fasteners; (2) new process and fastening technologies that are compatible with composite materials.

For example, the Army is developing the "soldier as system" concept and as such will require not only more mass-efficient ballistic protection materials but also an array of hardware to be both permanently and temporarily attached to the helmet shell (Figure 6a). This has stimulated the exploration of thermoplastic-based composites. Traditional helmets have been made with



a) Bonded Helmet Shells

b) Ultrasonic Bonding Process

Figure 6. Thermoplastic Bonding Technology Applied to Prototype Helmet System.

a thermoset phenolic resin. In addition to improved ballistic performance, thermoplastic materials (unlike thermosets) can be remelted and reformed several times. Ultrasonic, infrared, and induction processes can be used to bond one type of polymer system to another. This opens up significant possibilities not only for the design of attachment systems (Figure 6b) but also for low cost manufacturing techniques that can reduce or eliminate the need for drilling, clamping or other purely mechanical fastening techniques.

SUMMARY

The Army, with a few notable exceptions such as personnel protection, sabots, and rotorcraft, currently makes relatively low use of polymer composites. Collaborations between government, academia, and industry have been vital in reducing the risk and expanding the role of composites in both current and notional systems. As the Army transforms its heavy forces will become lighter and more lethal.

The future of Army process and manufacturing technology will be guided primarily by the new and evolving requirements that will be developed to provide the United States with superior land combat systems and technologies. Both current and emerging materials will be examined for their strategic benefits, and the appropriate manufacturing technologies will be developed to implement them into Army systems. It is increasingly likely that combinations of materials will become the standard, rather than the exception: lethality, survivability, and multifunctionality all demand "more for less." Future developments will provide innovative solutions to co-processing dissimilar materials so as to minimize overall cycle times, touch labor, and manufacturing costs. Manufacturing in the future is likely to be as much about processing *information*, such as model, sensor, and control data, as it is about processing the material itself.

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Army Targets Age Old Problems with New Gun Barrel Materials

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INTRODUCTION

For centuries, gun barrel designers have focused their efforts on the development and use of steels that possess higher strength and toughness. Good mechanical properties are required to withstand the high interior ballistic (explosive) loads to which these pressure vessels are subjected. In addition to high internal pressure, the cannon bore (internal surface of the cannon cylinder) is exposed to very high temperatures, as the propellant ignites and begins the evolution of hot gases to provide the propulsive force for the projectile. With the advent of ever more robust propellants, bore surface erosion has become increasingly problematic. This has forced barrel designers to implement various means that include coatings and alternate material liners to combat the phenomena. The desire for longer lasting tubes has been a major motivator for research of new and more robust materials for cannon design. Likewise, gun barrel manufacturers have committed significant effort to developing processes that result in high quality cannons capable of withstanding these erosive environments.

The Army's desire to reduce the weight of its fighting force to improve mobility on the battlefield (thus making it easier to deploy assets to wherever they are needed around the globe) has further challenged gun designers and manufacturers. This article provides some insight into the various materials and processing approaches being investigated to provide extended life and/or reduced weight of gun barrels.

HISTORICAL PERSPECTIVE

One of the first major advances made to iron cannons was the development of a technique in the 1850's by Captain Thomas Jefferson Rodman to cast a cannon over a water cooled core in a heated flask. In addition to a number of processing advances, the technique resulted in a significant improvement in tensile fracture strength of the metal as it left the bore in a state of residual compression [1]. The slow cooling of the iron resulted in a material having a tensile strength of approximately 30,000 psi. Through a series of tests, Rodman was able to demonstrate clearly the superiority of his gun steel and casting methods; however, he did not fully understand the importance that the pre-stress condition played in the improved performance of the cannon.

By 1880, Army engineers at the US Ordnance Department had a full understanding of the presence of the compressive residual stress within the bore of guns cast by the Rodman technique (Figure 1). A full description of this method of casting and finishing an iron cannon, as well as the testing procedure used to verify the residual stresses, is documented [2].

In the 20th century, variations in the chemistries of Chromium-Molybdenum-Vanadium (Cr-Mo-V) steels have been introduced that allowed for moderate increases in strength, toughness and fatigue properties. Most of these improvements come from superior processing and techniques that produce higher-quality steels (less contaminants and defects). The last major advancement in armament steels occurred in the 1970's with the introduction of ASTM A723 steel, which has yield strength more than five times that of the steel produced by Rodman more than a century earlier. It replaced the 4335-V modified steel that had been in use since before World War II. The A723 steel is processed through either vacuum arc re-melt (VAR) or electro-slag re-melt (ESR). Both processes significantly reduce the amount of sulfur and phosphorus and, combined with an increase in the nickel content, make A723 steel an excellent candidate for "modern" armament applications. More recently, the armament community has pushed for materials with even higher strength and toughness due to more aggressive environments and higher cannon firing pressures.

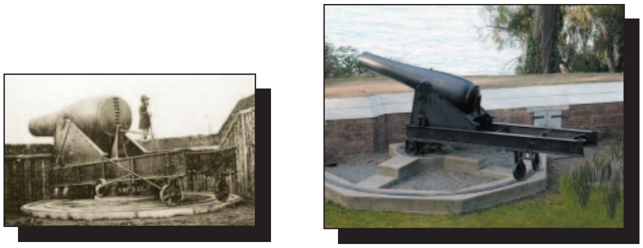

Figure 1. The Rodman Cannon (ca. 1860 to 1900) was a Staple of Coastal Defense (Model 1861 15-inch Columbiad in the 1860's [Left]; and Today [Right] at Fort Mason's Point, San Jose, CA.)

SYSTEM IMPLICATIONS

As research of advanced gun barrels moves to materials other than steel, it is important to point out the implications associated with barrels having a hybrid material construction, and quite possibly, reduced mass. The introduction of multiple materials into the construction of cannons is likely to result in mismatches of thermal expansion, and consequently, stresses that must be accounted for in the design. In addition, these materials often have different thermal conductivities that can result in insulative behavior through the thickness of the barrel wall. Finally, many of the lightweight reinforcing materials that have been considered have melting points well below that of steel resulting in the need for more careful monitoring of cannon thermal stresses and the impact of relatively high rates of fire on barrel temperature.

It is also important to understand the significance that gun barrel mass plays in the overall system design. Weapon recoil force, F_r, can be expressed as

$$F_r = \left(\frac{1}{2}\right)\left(\frac{I^2}{m_r L_r}\right),$$

Where I is the impulse imparted by the cannon to the system, m_r is the mass of the recoiling parts, and L_r is the length of the recoil stroke. From this equation, it is clear that reducing the mass of the recoiling parts adversely increases the total force and imposes additional system burdens on the recoil mechanism. Because of this deleterious effect of reducing barrel mass on the management of the recoil force, weight reduction of cannons has not been heavily pursued. However, several techniques to manage the recoil more effectively have resulted in renewed interest and emphasis on lightweight barrels utilizing advanced materials.

The fire-out-of battery concept invokes the release of the recoiling parts from the latch position prior to firing, and allows for the forward motion of these components. This forward momentum must then be countered and overcome upon firing and results in a net reduction in the total recoil force. Such an approach can be used to reduce the total force that must be mitigated by the recoil system and has been demonstrated in both 105mm direct fire [3] and 155mm howitzer test beds [4].

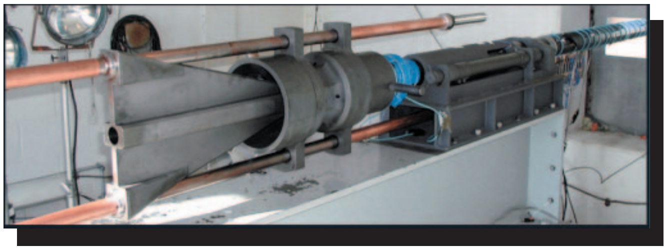

Figure 2. Rarefaction Wave Gun or RAVEN[1].

A more recent advanced gun system is the Rarefaction Wave Gun (RAVEN), shown in Figure 2. This concept utilizes a sliding breech block that is timed to open such that the venting of combustion gases takes place without degrading the performance of the propellant [5]. The early venting significantly reduces the total recoil force imparted and minimizes the accumulation of heat in the barrel, thus enabling the consideration of advanced lightweight materials.

STRESSES IN GUN TUBES

Autofrettage is a process unique to large caliber gun fabrication, where beneficial residual stresses are developed at the bore surface. Autofrettage induces compressive residual stresses that can result in thinner walled gun tubes. As such, these stresses provide added fatigue resistance and lower overall barrel weight. The compressive residual stresses are largest at the bore surface and act to resist crack initiation as well as subsequent crack propagation. Historically, these residual stresses were approximated utilizing approaches such as that presented by Hill [6]. Hill's approach accounted only for closed-ended pressure vessels, and does not consider the Bauschinger effect [7]. Recent work published by Parker has taken the classical approach further to include the Bauschinger effect for a typical open-ended steel pressure vessel. Parker and Underwood [8] further improved this work to include the Bauschinger effect on several different candidate pressure vessel steels.

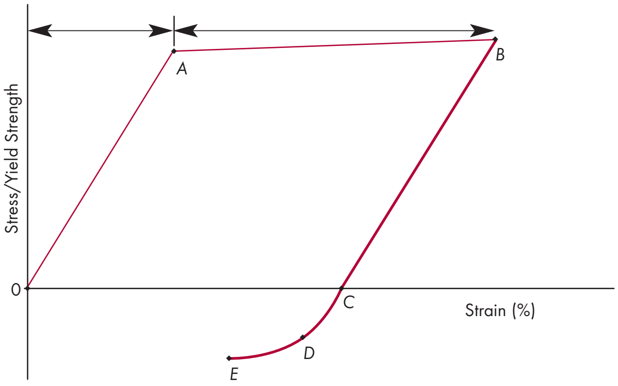

Figure 3. Uniaxial Stress – Strain Behavior during Initial Cycle.

Referring to Figure 3, when a gun tube undergoes autofrettage the stress within the gun tube follows path *O-A-B* during the initial loading and path *B-C-D-E* during the removal of this loading. Hence, a family of uniaxial cycles, *O-A-B-C-D-E*, each a function of initial plastic strain and radial location, defines the equivalent stress for the gun steel during the autofrettage process. This, along with appropriate equilibrium, compatibility and boundary conditions, is sufficient to calculate numerically the residual stress locked into the tube by autofrettage. Results of such calculations are well documented for the current range of gun steels [7] and conform extremely well to the ASME Pressure Vessel and Piping code [9].

Accurate numerical analyses of stress, strain and the Bauschinger effect in gun tubes require high quality uniaxial stress-strain data and an accurate numerical fit to such data [10]. These data provide the equivalent stress input to yield criteria such as Von Mises and Tresca [7] for the solution of complex 2D and 3D problems. It has been shown numerically that the loss of compressive residual hoop stress at the bore of an autofrettaged pressure vessel can be accurately predicted when accounting for the loss of stresses due to the Bauschinger effect and open-ended pressure vessel conditions.

Composite Overwraps for Improved Gun Barrel Performance

Another method for developing pre-stress in the cannon is to use an external sheath. With external sheathing, it is possible to induce the beneficial pre-compression in gun bores through elastic material deformations rather than the plastic deformations imposed via autofrettage. For brittle bore materials (such as ceramics that lack any plastic deformation capability), a sheathing layer is the only avenue for achieving pre-stress in the bore. External sheaths may be metallic cylinders that are shrink-fit or press-fit over the bore liner, but another attractive technique is to overwrap the bore with a polymer-matrix, fibrous-composite sheath. Sheathing with composites offers the advantages of relatively simplified manufacturing and lighter weight. In the fiber direction, glass/polymer composites are nominally as strong as steel, but are one-third as dense. Carbon/polymer composites are nominally three to four times stronger in the fiber direction than steel, but one-fifth as dense.

Composite-overwrapped gun barrels are typically fabricated using the filament winding process. The most efficient technique for fabricating an overwrapped gun barrel is to simply filament wind directly onto the outer diameter of the bore liner. Additionally, the fibers must be deposited in layers at prescribed angles in order to achieve the strength and stiffness requirements for a given design. For maximum pre-compression and ballistic strength (resistance to firing loads), the layers comprising the overwrap require a fiber architecture with fibers oriented predominantly in the hoop-direction. To achieve a stiff barrel (i.e., a barrel that resists "whip" deformations), it is necessary to orient fibers in the axial direction. Typically, overwraps are designed with a balanced fiber architecture that varies along the length of the barrel. A gun barrel design tool has been developed by the University of Delaware to facilitate designing composite overwrap cannons. The tool has been used by Benet Laboratories, part of the US Army Armaments Research, Development, and Engineering Center (ARDEC), to design the 105 and 120mm cannons (Figure 4) that have been fabricated and tested.

To achieve the pre-compression, significant levels of tension must be developed and maintained in the fiber overwrap during the filament winding process. The US Army Research Laboratory (ARL) has undertaken efforts to increase the level of tension (of the fibers) that can be developed via overwrapping in order to achieve significant increases in pre-compression of the barrel liners. Compared to the levels of tension available using conventional equipment and techniques, the ARL technique has been shown to realize a four-fold increase. Extensive experimental testing has been performed to validate modeling of the high-tension overwrap process, and it is currently being applied to ceramic tubes to enable structural integrity under ballistic firing conditions.

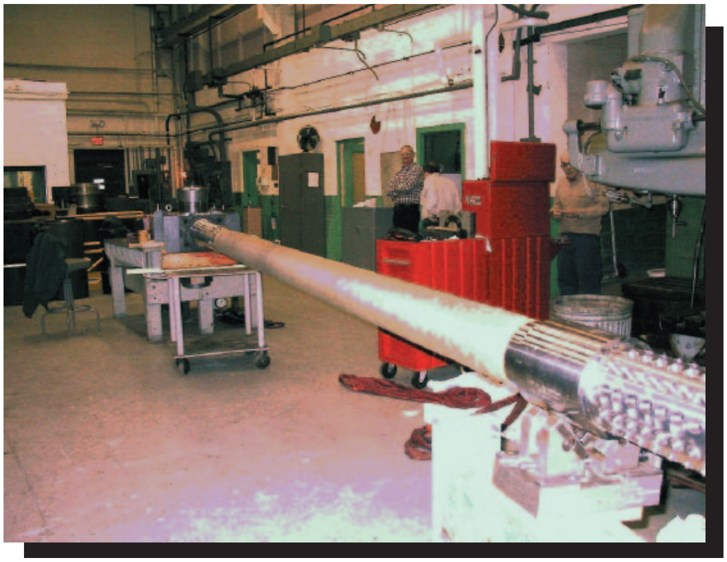

Figure 4. 105-mm Composite Overwrap Cannon.

IMPROVING BARREL LIFE

The US Armed Forces currently use chrome plating in their large caliber, direct-fire weapon systems to protect the barrel's bore surface against the harsh effects of hot propellant gases and from the mechanical wear of projectiles during firing. The electroplating process is used to deposit chromium onto these large caliber gun barrels. The process involves applying a chromium coating by passing an electric current through an electrolyte in contact with the gun barrel. The essential components of the electroplating process include the barrel (electrode to be plated), an anode to complete the circuit, an electrolyte containing the chromium metal ions to be deposited, and a direct current power source. The barrel and the anode are immersed in the chromium-rich electrolyte with the anode connected to the positive leg of the power supply and the barrel connected to the negative leg. As the current is increased from zero, a point is reached where chromium metal plating begins to occur on the barrel. The advantage of chromium electroplating is that it will deposit a relatively thick layer of chromium directly on the gun barrel's interior surface providing a surface with high wear resistance, a low coefficient of friction, and excellent hardness and corrosion resistance.

Unfortunately, recent advances in armament munition technology have deemed chromium electroplating as insufficient in protecting the bores of large caliber gun barrels. Increasing muzzle velocity and range requirements have forced the development of advanced propellant formulations that wear and erode current chromium plated barrels resulting in severe reductions in barrel life. The M1A1 Abrams tank main armament, 120mm M256 cannon, has lost significant barrel life throughout the evolution of the current family of 120mm car-

Figure 5. The M1A1 Abrams Tank's Main Armament: The 120mm M256 Cannon.

tridges (Figure 5). Recent candidate propellant formulations have condemned 120mm barrels after as few as 50 rounds were fired in them. Improvements in propellant formulation have been made so that the current barrel life is approximately 260 rounds but this still falls short of the earlier 400 to 500 round life. In addition, the chromic acid used in the electrodeposition process is a hazardous substance because it contains hexavalent chrome, a known carcinogen. Watervliet Arsenal, the producer of the 120mm tank gun, realizes significant annual environmental compliance costs associated with the chromium electroplating of 120mm barrels.

Chromium electroplating can no longer support these advanced propellant formulations for a number of reasons. Most notable is the fact that as-deposited electroplated chromium experiences a significant amount of cracking during the plating process. These cracks are a result of volumetric changes in the chromium layer when electroplating process contaminants outgas. This volumetric change results in a severe tensile load that is only relieved by the formation of micro-cracks. Further cracking occurs during the gun firing cycle when significant hoop strains are realized. These cracks offer a path for the hot propellant gasses to reach the steel substrate. These gases cause the steel, with its lower melting point, to convert to carbides and oxides further compromising the "foundation" to which the chromium layer is attached. As a result, the "compromised layer" spalls off revealing more unprotected steel and further propagating the erosion mechanism.

Advanced materials and application technologies are one way to provide adequate bore protection. A number of requirements must be met if an alternative material coating is selected. It must have a melting point higher than that of chromium (1875 °C). Such a requirement defines eleven refractory metals for consideration. In addition, it is desirable to have a coating material with an elastic modulus nearly equivalent to the steel substrate to prevent the on-set of cracking. Imposition of this constraint leaves three refractory metals for consideration – tantalum, rhenium, and niobium. For reasons of cost and reactivity, tantalum has been the primary coating material of choice amongst these three.

New Coating Processes

In addition to the investigation of new materials, significant effort has been devoted to developing a new coating process to overcome the inherent problem of cracking associated with the electro-plating process. The autofrettage process is followed by a thermal soak operation that aids in "normalizing" the stress variations (minimize thermal mismatch stresses) imposed during autofrettage. Exceeding the post-autofrettage thermal soak temperature (357 °C) will compromise barrel strength by reducing the beneficial residual stresses previously developed. Therefore, any coating deposition process must have a processing temperature less than the post-autofrettage thermal soak temperature. This eliminates consideration of many deposition techniques. Most spray, chemical vapor deposition (CVD), and laser-based technologies process at a far higher temperature.

Benet Laboratories has developed an ion-based physical vapor-deposition (PVD) process known as cylindrical magnetron sputtering (CMS) that is considered acceptable since it stays below the critical process temperature. CMS is a vacuum coating process in which positive gas ions are formed and accelerated to high speeds to strike a negatively charged target metal source (see Figure 6). The momentum of the gas ions is transferred to the metal atoms of the target in the form of energy, causing them to be ejected or "sputtered" from the surface. The substrate to be coated (the gun barrel) is placed in the direct path of the ejected neutral atoms and a film is formed as they strike the surface. This process produces high quality coatings with good adhesion and uniformity. It is limited by high cost, coating thickness, and line-of-sight restrictions for coating complex shapes. Sputtering is a non-aqueous, non-polluting coating process that is essentially benign, as only minor amounts of residue are produced from the vacuum systems associated with the equipment.

Explosive Bonding

Another technique for application of desirable refractory metal coatings is explosive bonding, commonly referred to as "cladding." It has been in use for over 40 years and has proven capable of joining any combination of dissimilar metals that are otherwise difficult to bond or metallurgically incompatible. The process involves the use of energy from a controlled explosive detonation to force a coating material or clad up

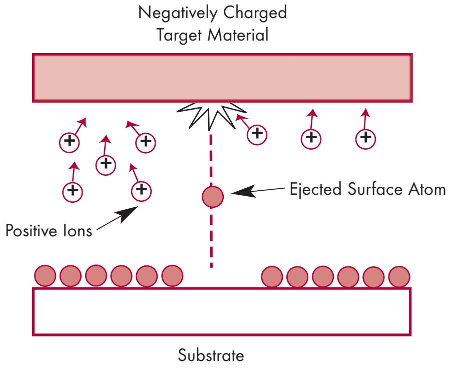

Figure 6. Schematic of a Physical Vapor-Deposition Coating Process.

Bradley Fighting Vehicle

M242 Bushmaster 25mm Gun

Figure 7. **The Bushmaster 25mm Gun is the Primary Weapon of the M-2 Bradley Fighting Vehicle.**

against the parent material at high pressures, causing a large amount of plastic strain and resulting in the formation of a metallurgical bond. Carpenter and Wittman [10] provide an excellent review of explosive bonding and identify four boundary condition requirements to produce an adequate bond, specifically the critical angles for jet formation, the critical impact pressure, the critical flow transition velocity, and a maximum impact velocity [11].

Explosive bonding has advantages over conventional chrome plating and physical and chemical vapor deposition techniques. The time duration for forming an explosive bond is seconds as opposed to the typical rates of 0.001 inch thickness per hour associated with the other techniques. Hydrogen embrittlement, a degradation process that can occur during the electrolytic chrome plating process, has caused numerous failures of gun tubes over the years and is not a concern with explosive bonding. Unlike physical and chemical vapor deposition processes, surface preparation is not a significant consideration for explosive bonding, where plasma is formed on the surface of the clad, and the parent material. The plasma is forced ahead of the collision front resulting in a scrubbing action on both surfaces, leaving behind virgin material free of undesirable oxides and debris that is conducive to providing an optimal bond.

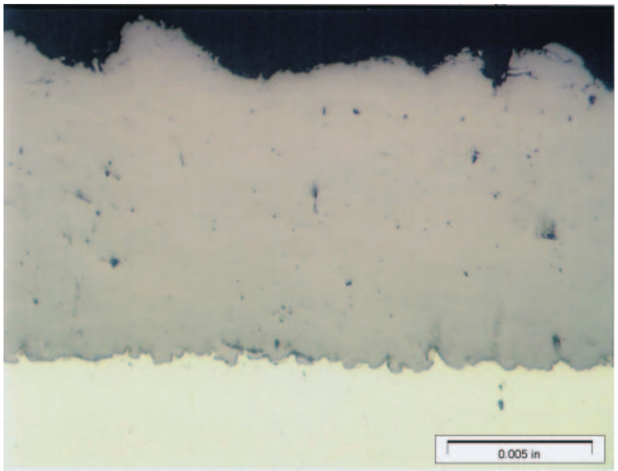

Figure 8. **Optical Micrograph of Ta-Deposited on 7075 Aluminum Using SPD.**

Over the past 25 years, tremendous advances have been made in characterizing and defining the important process parameters. TPL, Inc. has demonstrated the ability to explosively clad both a Ta-2.5W alloy and pure Ta to thicknesses of 0.027 inch and 0.063 inch, respectively, in a 120mm tube. In addition, they have employed the process to clad the inside diameter of both a rifled as well as a honed out, smooth-bore M242 Bushmaster 25mm gun barrel (Figure 7) with pure tantalum [12]. As a result of testing on a rifled barrel and the subsequent analysis, it has been determined that pure tantalum is too soft to withstand the forces exerted on the lands and grooves of rifled guns. Tantalum alloys with 5-10% tungsten are being examined as viable alternatives, as well as Stellite, a cobalt-based alloy.

Supersonic Particle Deposition

A third process under consideration for application of refractory metal coatings is Supersonic Particle Deposition (SPD) also referred to as "Cold Spray" because it is performed well below the melting temperature of the deposited materials. In the process, a metal powder (that can contain significant amounts of ceramic particles) is accelerated at supersonic velocities and propelled against a suitable substrate. The powder diameter is 1 to 45mm with velocities ranging from 300 to 1,200 m/sec. ARL has successfully deposited pure tantalum with desirable microstructural characteristics (see Figure 8) and is expecting to test and evaluate such coatings via vented combustion chamber tests at Benet Laboratories to simulate the 120mm tank gun environment. SPD generates no thermal stresses since there is no melting and re-solidification, and yet is still capable of forming a bond similar to explosive

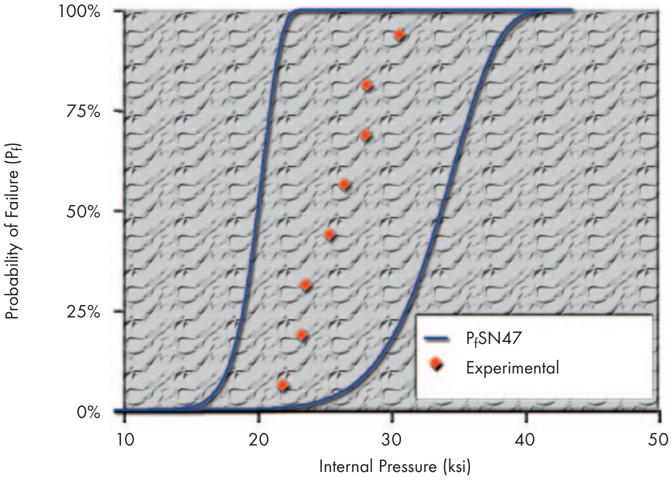

Figure 9. Experimental Results from an Internal Pressure Test of Ceramic Tubes with High and Low Failure Prediction Curves.

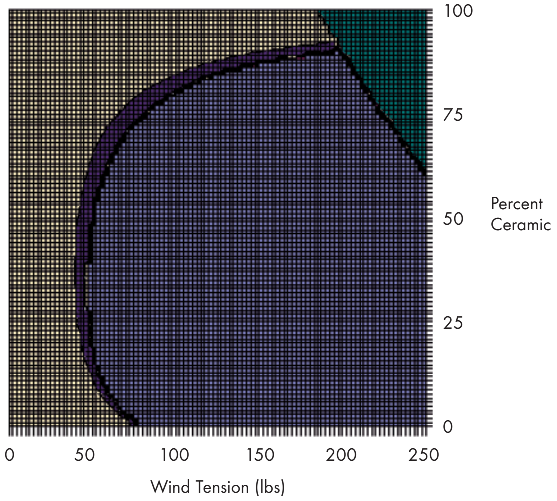

Figure 10. Optimal Design Surface for a 5.56mm Barrel.

bonding due to the intimate mixing of the clad and substrate material in what ARL has defined as "Super Plastic Agglomerate Mixing" or SPAM [13].

Ceramic Liner Research

Another approach to improving barrel life that has been attempted repeatedly over the past 30 years is to insert alternate materials for the bore surface, typically refractory materials, or ceramics. These materials exhibit superior melting temperatures and high temperature behavior (mechanical property retention, erosion/corrosion resistance, and hardness) when compared to gun steels. This leads to reduced rates of erosion and mechanical wear and makes them an obvious choice for gun barrel liners. Unfortunately, the limitations of these materials, and what has kept them from use in this application, are low tensile strength, brittle fracture, low toughness, a high degree of variability in the measured strength, and high cost.

Currently, ARL has renewed investigations into ceramic-lined gun tubes. Over the past three decades different refractory material lined gun designs have been attempted. In the 1970's, groups from each of the services developed gun designs using refractory liners to improve gun tube life [14-17]. Each of the programs identified the need to compressively pre-stress the liner material to minimize tensile stresses and overcome the material's low tensile strength. Different problems arose, ranging from poor thermal management to the inability to control precisely the liner pre-stress that led to failures in the programs [18, 19]. In the late 1980's and into the early 1990's, new programs were initiated that were more focused on finding the best liner materials and designing the system around the liner material selection [20-23]. As a result of this approach, it was demonstrated that silicon carbide, SiAlON, and silicon nitride all exhibited excellent erosion resistance and were capable of surviving the stresses and temperatures experienced during firing [20]. When subjected to erosion tests in a ballistic simulator, the erosion rate of the different ceramic materials was reported to be on the order of 1% of that of the steel samples investigated.

In each attempt, the programs met with varying degrees of success. Some systems successfully fired in excess of 1000 rounds without failure, while others failed due to unexpected excursions in temperature or by what was then an unexplained material behavior. Fortunately, over the past decade, ceramic materials, material failure modeling, and sheathing material technologies have advanced. Improvements in the ceramics industry have led to increased material quality, improved strength, and decreased cost.

Understanding the need for designing around a material with a high degree of variability in strength has led to the development of probabilistic modeling approaches that use statistical analyses to calculate the probability of failure for the ceramic liner when subjected to a specific load scenario. These models are used to analyze experimental results and will serve as tools for developing the optimal design for a ceramic-lined barrel.

Figure 9 illustrates two prediction curves that account for high and low values due to different combinations of flaw populations and shows data for the burst pressures from eight different experimental samples of a silicon nitride material (SN47) falling within the predicted strength range. Figure 10 depicts a plot of the optimal design surface for a 5.56mm barrel calculated using the probabilistic models. The yellow area indicates probable ceramic failure, green indicates failure in the composite sheath, and blue signifies a high probability of success and thus defines the design space. The x-axis is the wind tension applied to the composite sheathing material to pre-stress the ceramic and the y-axis is the ratio of the ceramic wall thickness to the total barrel wall thickness. Barrels fabricated with these designs are currently undergoing ballistic testing. The combination of improved materials and probabilistic modeling, coupled with sheathing techniques that ideally generate a triaxial compressive state, has positioned ceramic barrel technology as a viable alternative to coatings.

CONCLUSION

The combination of advanced materials and new innovative processes are being employed to develop cannons that have improved erosion and wear life, reduced weight, and improved structural and thermal capabilities that allow for the use of more energetic propellant charges. Higher performance cannons, across all calibers, continue to be a goal amongst the Army's armament community with the materials and processes currently under investigation serving as the foundation for advanced cannonry of the 21st century.

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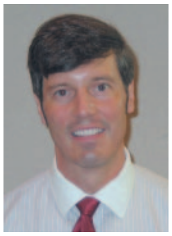
Dr. Robert Carter is a materials engineer with the Ordnance Materials Branch in the Army Research Laboratory's Weapons and Materials Research Directorate. He received his PhD in Materials Science and Engineering from Virginia Tech in 2001. Dr. Carter joined the Army Research Laboratory in 2002 after spending a year as a post-doctoral research associate in the ceramic gun barrel program. He is currently leading development of probabilistic modeling approaches for the design of ceramic-lined gun barrels and developing novel multifunctional material structures.



Mr. Victor Champagne is the Team Leader of the Materials Analysis Group at the Army Research Laboratory's Weapons and Materials Research Directorate. He holds a BS in Mechanical Engineering (1984) from Central New England College and an MBA (1986) from Anna Maria College. Mr. Champagne has served at ARL for nearly 20 years. His current areas of research are Supersonic Particle Deposition (SPD), ElectroSpark Deposition (ESD), and Metal Spray.

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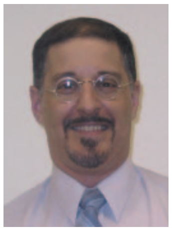
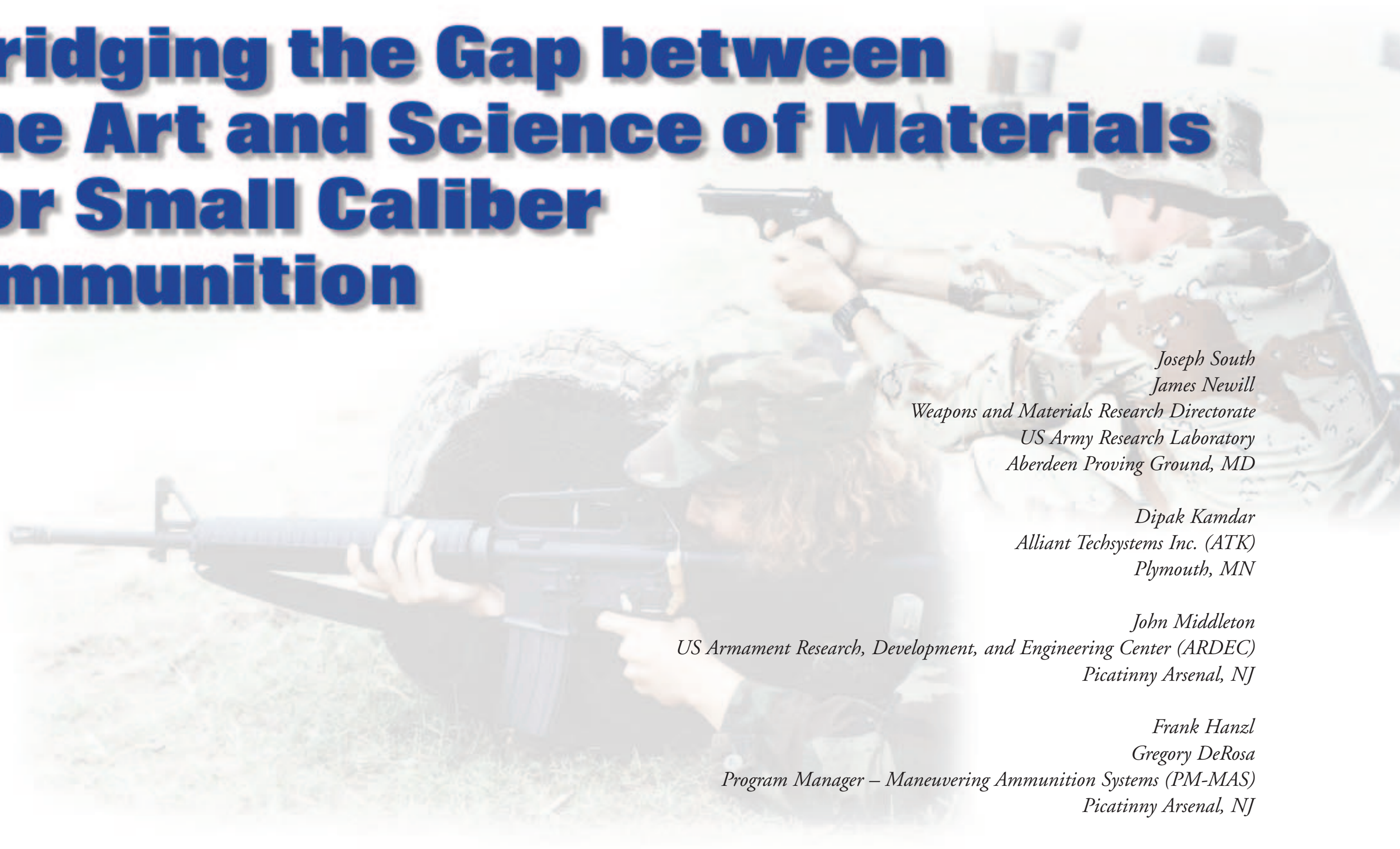
Mr. Michael Audino is presently the branch chief for the Protective Coatings Branch at Benet Laboratories (2000-present). Mr. Audino leads a group of scientists and engineers in the area of advanced bore coatings for large caliber gun barrels with emphasis on PVD-based processes. Mr. Audino earned a BS in Mechanical Engineering from Clarkson College and a MBA from the College of St. Rose. Mr. Audino has authored 22 government and open literature publications, and has presented much of his work at national symposiums and conferences. Mr. Audino is also the holder of one patent with a second currently pending in the US Patent Office.



Mr. Edward Troiano is presently a laboratory experimentalist with the Fatigue and Fracture Mechanics Team at Benet Laboratories. He holds Mechanical Engineering degrees from the University of Buffalo (BS, 1984) and Rensselaer Polytechnic Institute (MS, 1992). Mr. Troiano has been involved in testing and modeling of protective coating and hydrogen embrittlement for over ten years. He is an active member in the American Society for Testing of Material (ASTM) in both the Fracture Mechanics committee (elastic/plastic fracture mechanics) and Environmental Fracture Committee. Mr. Troiano has over 61 government and open literature publications, and has presented much of his work at national and international symposiums.

Bridging the Gap between the Art and Science of Materials for Small Caliber Ammunition



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INTRODUCTION

Small caliber projectiles, such as the M855 ball round, are some of the simplest munitions in the Army inventory. The M855 projectile depicted in Figure 1 is comprised of three components: a lead slug, a steel core penetrator and a copper jacket; and is similar to the ammunition that has been used for the last century. This ammunition is used in service and training for the M16A2/A3/A4, the M4, and the M249 weapons.

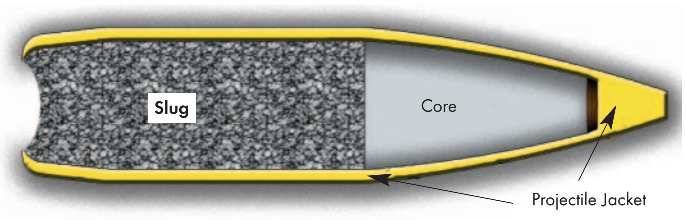

Figure 1. **M855 Projectile[1].**

Use of small caliber munitions during training and conflict leaves behind a significant amount of material from the projectiles in the environment. The US Army has a program to investigate alternative "green" materials, such as tungsten/nylon, to replace the lead slug in the projectile and effectively reduce the environmental impact of these munitions. The tungsten and nylon are particulate composites which are consolidated using cold compaction. The basic premise of this program was to develop a non-polluting "green" material that will match the performance of lead. This match would result in maintaining the mass properties, stability, and flight dynamics of the M855 projectile. These changes would be transparent to the soldier, and would therefore avoid potential costs and complications that result from introducing a new type of ammunition into the Army's inventory.

This program progressed for several years from small-scale testing to initial production. During the soldier qualification, it was noted that a significant percentage of the rounds were creating "key-holes" as they penetrated the target. Figure 2 shows that well-behaved projectiles penetrate the target with a circular hole on the order of the projectile diameter, but the shot labeled as 23050 had a very high yaw angle* as it passed through the target, thus creating an elongated hole. The implication from the target is that the projectile was gyroscopically or dynamically unstable as a result of the low spin rate as it exited the weapon.

The high yaw, demonstrated in Figure 3, causes the projectile to fly erratically and results in the round either missing the intended target or not having enough velocity to penetrate the target. Figure 3 illustrates the importance of controlling yaw. A projectile in proper flight has a uniform flow-field around it, thus ensuring accurate movement. Conversely, a projectile in the yaw condition will experience turbulent conditions and increased frontal area which decreases both the speed and accuracy.

In response to the soldier qualification issues, additional investigations were conducted. While Figure 2 showed only one unstable round, some of the follow-on testing produced a larger number. In contrast, other testing only periodically produced high yaw rounds. It was demonstrated that the projectile high yaw rate can go from 0% to 50% depending on the type of ammunition and weapon used. While M855 ammunition produced from lead will occasionally show similar erratic

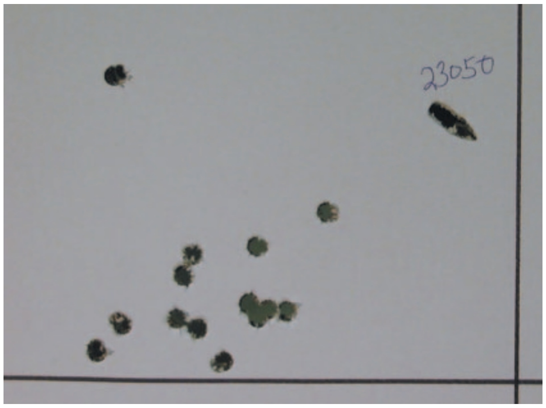

Figure 2. Target Showing Normal M855 Impacts and a Key-Hole Impact[2].

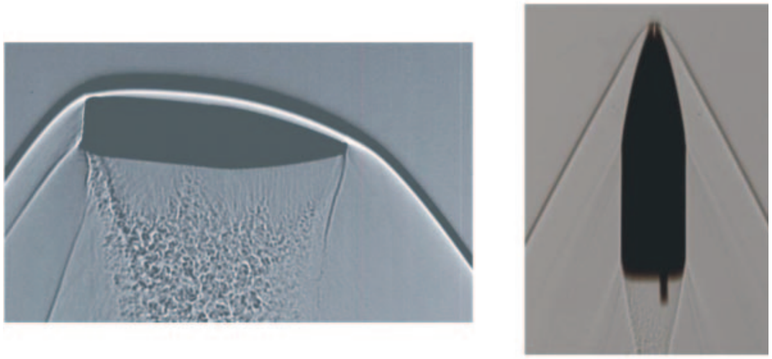

Figure 3. Shadowgraph of a High Yaw Projectile (Left) and Stable Projectile in Flight (Right)[2].

behavior, the percentage of these occurrences is very low, implying that the slug material change was responsible for the faulty behavior.

The data from these experiments implied that by changing the slug material the basic functioning of the system was modified. The testing in various weapons and using different lots of ammunition showed that even though the failure was intermittent, the functioning of the "green" material in the system was fundamentally different than lead. It should also be noted that the weapons variability and manufacturing likely also played a major role. This article identifies how the green slug material contributed to the failure, along with the approaches used to diagnose the issue to understand this "simple" ammunition system. In doing so, some of the critical materials issues associated with small arms ammunition are highlighted.

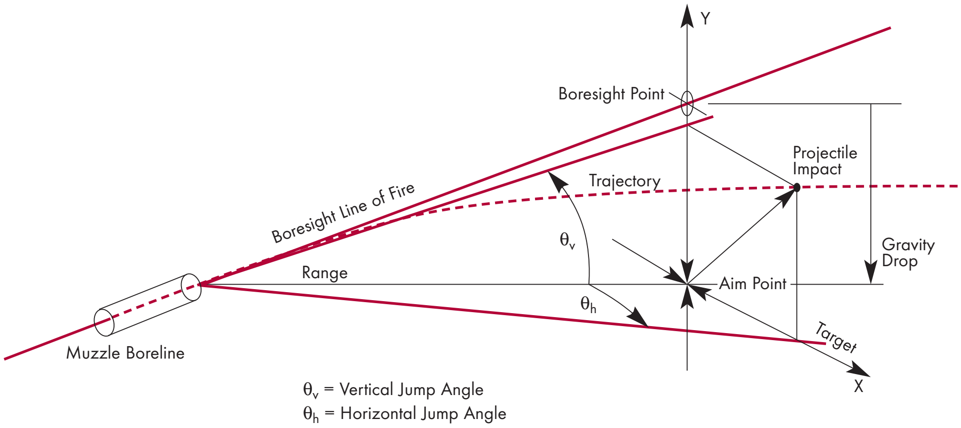

Figure 4. A Definition for Jump[3].

Approach

A team led by the Project Manager for Maneuver Ammunition Systems (PM-MAS) and comprised of the Joint Munitions Command (JMC), the Armament Research, Development, and Engineering Center (ARDEC), the Army Research Laboratory (ARL), and Alliant Techsystems (ATK) was convened to study and resolve the problems with the green M855 projectile. A Keppner-Trago (KT) process control decision-making analysis was used to diagnose the multi-variable problems. The KT analysis identified and eventually proved that a low spin rate was the cause for the rounds exhibiting a high degree of yaw. The flight instability resulted from gaps between the jacket and slug and was exacerbated by the high yield strength of the slug material, as compared to lead, which reduced the ability of the projectile to adapt to variability in both manufacturing and the weapons.

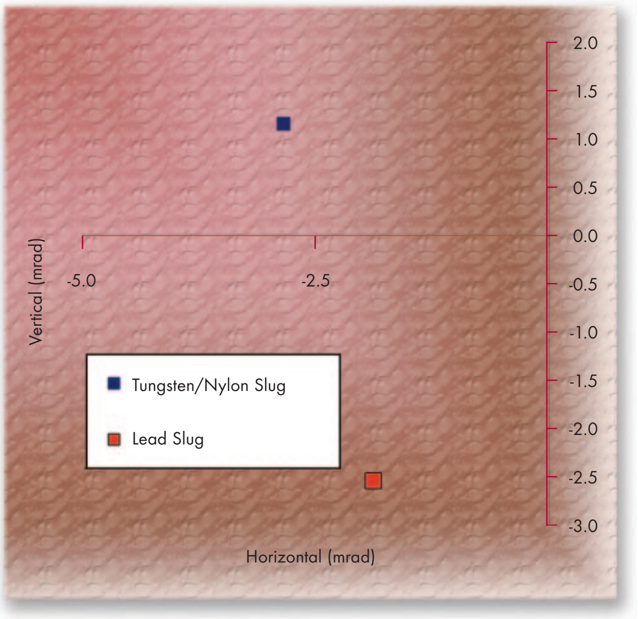

Figure 5. Average Jump from 60 Round Groups for Several Types of M855 Projectiles Fired from a Single M16A2 Barrel[3].

Table 1. **Breakdown of the M855 Components and Their Forces[4].**

	Mass (g)	% Mass of Projectile	Force (N)	% Force	Acceleration (m/s²)	Acceleration (g's)
Bullet	4.033	–	9073.56	–	2,249,828	229,340
Slug/Core	2.823	70.0	5996.12	66.1	2,123,765	216,490
Jacket	1.210	30.0	3077.43	33.9	2,544,061	259,333

As a result of the KT findings, ATK led the investigation into potential manufacturing problems, and ARL led the investigation into launch mechanics and material characterization. The results of these investigations are covered in the remainder of this paper.

Projectile Launch Mechanics

A simple ballistic experiment that characterizes the nature of projectile launch is to measure the projectile jump. Jump can be measured by sighting a gun, aligning the muzzle with the aim point on the target, firing a projectile and measuring the distance from the hole in the target to the original aim point, Figure 4. While jump is an indirect measure, it provides insight into the in-bore mechanics (gun/projectile interaction) of the system.

For a given type of cartridge coupled with a particular barrel fired under similar conditions, the jump is relatively constant. While the round will not impact the same spot each time, this spread, or dispersion, is a measure of precision, whereas the average jump for a group of projectiles fired from the same barrel can be compared to infer changes in in-bore mechanics. Figure 5 shows the results of two types of M855 projectiles, tungsten/nylon, and lead, shot from the same barrel. Each point on the graph shows the average jump obtained from sixty rounds.

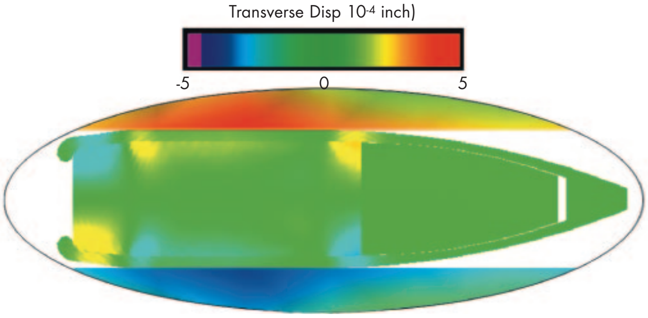

Figure 6. **Transverse Displacement of the Projectile at Peak Acceleration[5].**

It can be seen from the figure that the lead rounds jump in a downward direction, while the tungsten/nylon rounds jumped in an upward direction. The difference in jump is on the order of 4 mrad.§ This is a significant deviation in the behavior that is an order of magnitude larger than the system precision. The dispersion of the M855 projectiles is typically less than 0.3 mrad. While this type of testing does not show how the launch mechanics differ in the system, it does show that the mechanics changed with the slug material change.

IN-BORE PROJECTILE MECHANICS:

To obtain a better understanding of the change in mechanics, a more detailed insight into the initial portion of launch is necessary. The first step was to perform rigid body calculations to show the interaction of each projectile component during launch initiation. The mass, force, and acceleration that each projectile component would experience due to a 51 ksi peak pressure are shown in Table 1. The parts of the projectile are referenced in Figure 1.

While the force imparted to the jacket of the projectile is lower (33.9% of the total force) than the force transmitted to the slug/core, the mass of the jacket is only 30% of the total mass. This translates into the jacket "wanting" to accelerate faster than the slug/core; but the jacket is physically constrained in the boat tail region (tapered section at the rear) of the projectile. The net effect is that the jacket creates a seal against the slug which helps prevent pressure from leaking inside the projectile.

Implicit and explicit finite element simulations were used to study the initial portion of the projectile launch in more detail. Figure 6 shows the transverse displacement at peak acceleration. Several key features can be seen on this figure. The first is that the jacket in the rear portion of the projectile is clamping down on the back of the slug, and there is a slight gap in the front of the projectile between the jacket and the penetrator. The gap shows that the jacket is trying to ride forward on the back of the slug and that the penetrator is being carried by the

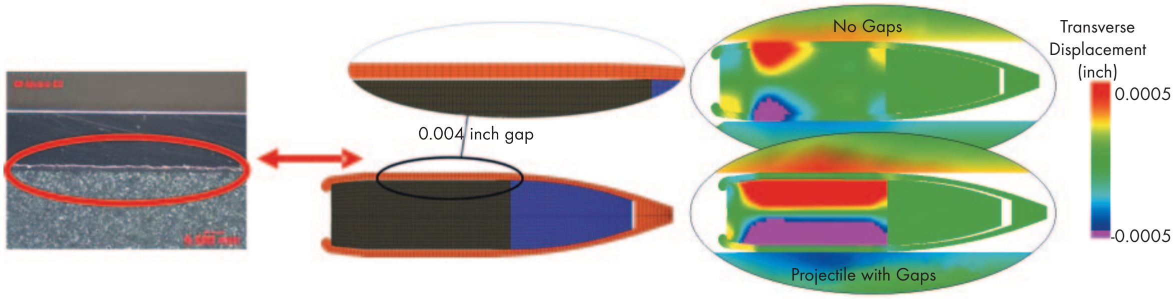

Figure 7. **Effect of Gaps between the Slug and Jacket[4].**

slug. The behavior confirms that the rear jacket/slug interface acts as a pressure seal. This is consistent with the relative accelerations shown in Table 1 as the jacket acceleration is greater than the slug/core acceleration thus creating the seal. Secondly, the figure shows that the cylindrical section of the projectile provides the projectile/bore gas seal known as obturation†. Both the front section and rear section of the cylindrical portion of the slug are expanding in the radial direction forcing the jacket into the bore of the gun barrel. In addition to obturation, this expansion provides the pressure necessary to cause the jacket to flow around the rifling as the projectile engages the lands‡ in the gun. It was hypothesized that low spin rate was due to projectile swaging (reduction in projectile diameter instead of the jacket material flowing around the lands)[5].

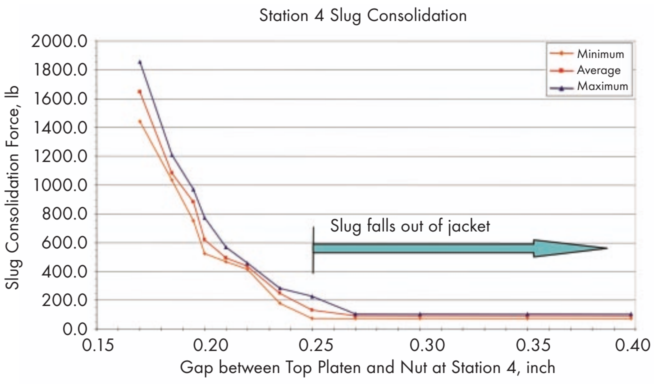

Figure 8. **Results of the Manufacturing Consolidation Study for Projectiles Made with Tungsten/Nylon Slugs[8].**

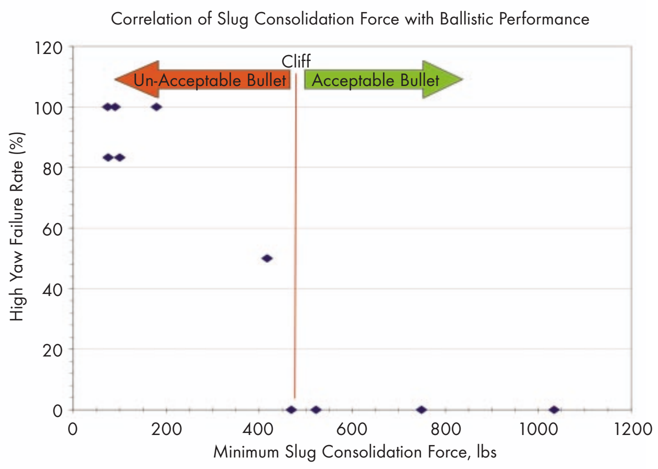

Figure 9. **Effect of Slug Consolidation Force on Bullet Performance[8].**

From the theory, two causes were determined to explain the differences between the ammunition made from tungsten/nylon and that made from lead. The first cause was that gaps between the slug and jacket, resulting from the manufacturing process, altered the amount of pressure, thus forcing the jacket into the lands of the rifled barrel. The second cause was that the mechanical properties of the slug also affect the expansion pressure.

The mechanism showing how gaps between the slug and jacket affect the projectile in-bore mechanics can be seen in Figure 7. The figure has a picture[6] of the cross-section of the projectile showing a gap between the jacket and the slug. From the results presented in the figure, it is easy to see large differences in the displacement state when the gaps are introduced between the slug and the jacket. The location where the jacket experienced the greatest expansion, at both ends of the cylindrical section of the projectile, is significantly reduced. This decreased expansion shows that the pressure available to force the jacket to engage the rifling was sharply reduced.

Manufacturing and Gaps

To demonstrate how these gaps could have been produced inside a projectile and how they can affect launch mechanics, a number of experiments were devised by ATK.[7] A series of projectiles used in these experiments were produced by a manufacturing process which applied varying amounts of load to consolidate the slug inside the jacket. This approach deviated from the current bullet assembly machine (BAM) process at Lake City Army Ammunition Plant (LCAAP) in Missouri, which utilizes displacement control during the consolidation process. The projectiles were produced at different displacement settings while generating real-time force data during consolidation. The results of this analysis showed that there is a critical consolidation condition (Figure 8). This condition is directly related to the amount of load exerted on the projectile. Projectiles consolidated below this critical consolidation condition had slugs that were loose and fell out of the jacket. Loose slugs, or slugs with incomplete consolidation, could result in gaps. Loads above this critical value would produce bullets with an acceptable degree of consolidation.

Ballistic tests were performed to determine the effect of the unconsolidated slugs on performance. Bullets were produced using consolidation loads that varied above and below the critical load. The projectiles were fired, and their performance was characterized by whether or not they resulted in a high yaw condition. Bullets that were manufactured with loads at or above the critical load did not result in failure, while bullets produced below the critical load demonstrated failure rates between 82 and 100%, as shown in Figure 9. These test firings confirmed that projectiles produced with gaps inside the jacket consistently exhibited high yaw during flight.

Mechanical Requirements for a Slug Material

A confounding issue to the gap is related to the mechanical properties of the slug materials. Lead slugs have been used in the current M855 manufacturing process for over two decades and have shown tolerance to the displacement controlled consolidation process. Introducing a new material with different mechanical properties affects the projectile's tolerance to both the consolidation process and the related problem of in-bore mechanics.

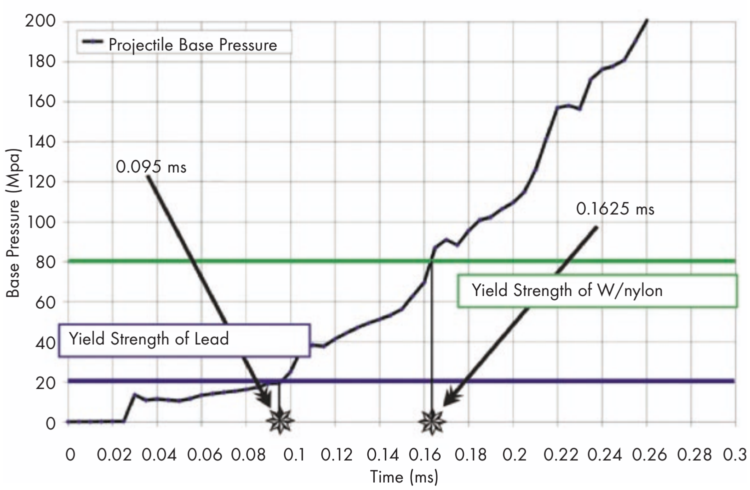

Figure 10. M855 Base Pressure Compared to the Yield Strength of the Slug Materials[9].

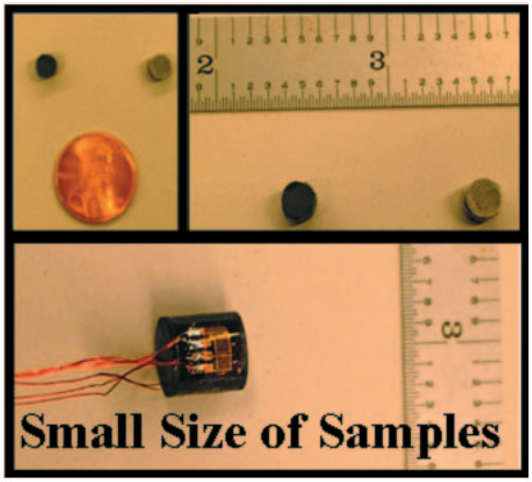

Figure 11. Size of Core Testing Samples[10].

Shown in Figure 10 is an approximate propellant pressure-time history for the initial portion of the launch cycle. Plotted on the graph are the points where the propellant pressure matches the yield strength for lead and also for tungsten/nylon. What is inferred from the graph is that as the yield strength of the material increases, the amount of time within the launch cycle necessary to reach the yield point also increases. The yield strength marks the beginning of where the material becomes incompressible. An incompressible material does not change volume when it is loaded. This is a driving attribute since it represents the maximum value of gas propellant pressure that can cause transverse displacement (same as radial displacement for cylindrical geometries) of the slug material, which was illustrated in Figure 7.

In order to determine the effectiveness of alternative materials for bullet components, the mechanical response of the materials must be determined. One of the critical attributes underpinning both understanding of material behavior and modeling is the selection of material properties. Due to the size of the slug materials, which has a diameter of 0.18 inches, testing techniques need to be modified and developed in order to obtain good material properties. Figure 11 illustrates how small the slugs are by comparing them to other small items.

A characterization study was conducted to determine the compressive stress – strain response of both the slug material and the sheathed slugs from manufactured bullets. Samples were strain-gauged with parallel and perpendicular gage orientations. Two axial gages were used at 180° positions to correct for any slight bending of the samples. Polymer-based samples required a plasma treatment in order to obtain adequate adhesion of the gage to the sample. To minimize damage, special grips were fabricated to hold the polymer-based samples during mounting of the strain gages. Results of the compressive testing are shown in Table 2 and plotted in Figure 12. The difference in the material response between the lead and the tungsten/nylon specimen is quite evident, particularly the yield point of the materials. The inset figures show the difference in the failure mechanisms between the two material systems. The lead specimen exhibits a ductile failure while the tungsten/nylon exhibits a brittle failure. Figure 12 shows the importance of materials to the performance of bullets. Both materials have approximately the same density and yield but their compressive behavior and ultimate failure are completely different.

Table 2. Averaged Compressive Mechanical Properties of Slug Materials[9].

	Modulus (Msi)	Compressive Yield (Ksi)
Tungsten/Nylon	1.2 – 1.4	9.7 – 10.2
Lead	1.5 – 2.0	~2.5

Another way of looking at this argument is to examine the behavior of a section of the slug/jacket material. A test was

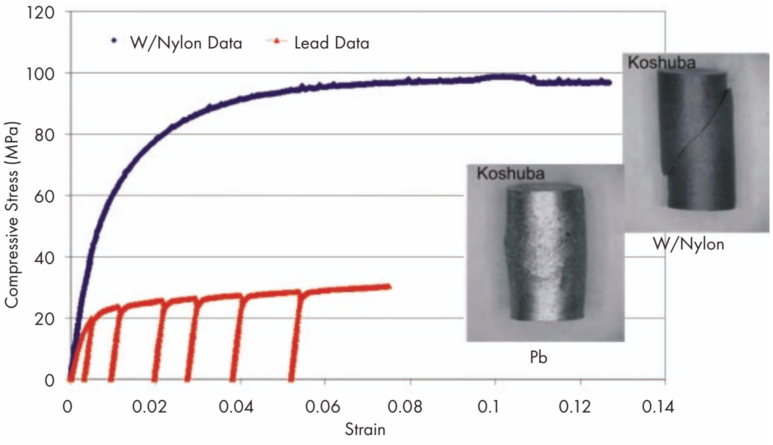

Figure 12. Stress-Strain Behavior of Lead vs. Tungsten/Nylon. The Inset Shows the Difference in the Failure Behavior between the Two Materials[12].

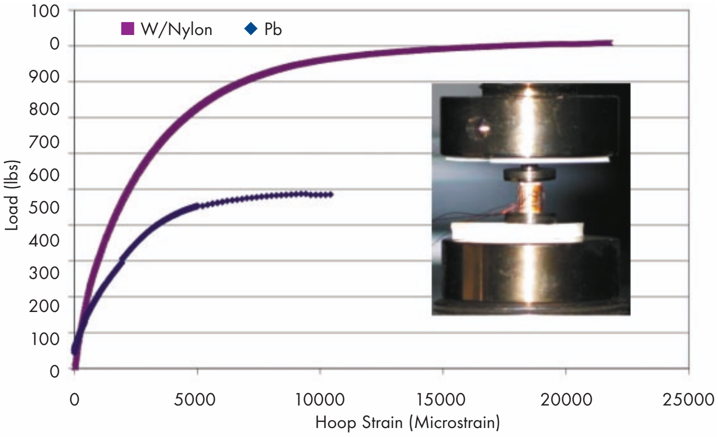

Figure 13. Results of the Sheathed Compression Testing. The Inset Picture Shows the Testing Arrangement[12].

developed to look at the unconstrained loading behavior of small sections of the projectile[11]. This is a non-conventional test method that was developed in order to evaluate the potential performance of the slug material on the inside of a bullet. Prior to testing, the boat tail and the tip of the bullet forward of the cannelure** were removed. The bullets were then ground to a final height of 0.375 inches. Strain gages were mounted in the axial and hoop directions. Only the slug material was loaded in compression, and the jacket was left as a free surface. Typical results from the sheathed compression tests are shown in Figure 13. The effect of yield strength on the performance of the slug material was quite evident, with tungsten/nylon exhibiting much higher loads during the test. For small strains, approaching those seen in a weapon system, the lead exhibited ten times more hoop strain than the tungsten/nylon slug samples. This difference is directly attributable to the yield strength of the material and the point the material achieves incompressibility. This testing arrangement can also further evaluate the effects of a gap between the slug and the jacket as the system would respond with a rapid increase in load without an increase in strain.

CONCLUSIONS

The M855 three-piece projectile represents a very basic design. A simple modification, a material replacement, was perceived as a benign change but resulted in erratic occurrences of high yaw rounds when fired. Through careful study, simulation, and experiments it was shown that the change in performance resulted from the manufacturing process and the basic mechanics of the materials. Once these issues are addressed and the problems corrected, the new “green” ammunition will become a suitable replacement for lead-based ammunition. The example illustrated in this article demonstrated that a thorough understanding of the interaction of the components within a system is required prior to implementing material substitutions.

NOTES & REFERENCES

* Yaw angle is the angle between the longitudinal axis and the direction of travel.

§ A milliradian (mrad) is 1/1000th of a radian.

† Obturation is the sealing of the gun barrel to prevent the propellant gases from escaping.

‡ Lands are the ridges inside a rifled gun barrel.

** The cannelure is the ring around the body of the projectile where the case is crimped.

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[6] Tim McFarland and Todd Botcher ATK
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Dr. James F. Newill currently serves as the small caliber coordinator for the Weapons and Materials Directorate at the Army Research Laboratory and where he's also the Deputy Chief of the Aerodynamics Branch. He has worked at ARL since 1995 on munitions research for a variety of systems; including tank munitions, electromagnetic rail guns, and medium and small-caliber munitions. He has authored over 50 publications on dynamics simulation of projectile gun interaction, accuracy of army systems, and other munitions related issues. He received his PhD in Mechanical Engineering from the University of Delaware in 1996.

Dr. Dipak Kamdar is a Senior Engineering Fellow at ATK Ordnance Systems. His area of expertise is in large caliber ammunition design. His recent work has contributed to a highly successful M829A3 kinetic energy tank round. His patented composite architecture and sabot design has resulted in the lowest parasitic mass ratio among all the tank rounds. Besides projectile design, his work on the spring disc (that holds the cartridge case to the case base) has resulted in large caliber ammunition that, for the first time in army history, has fulfilled army cartridge chamber and extraction requirements. He has also been involved in modeling and optimizing the manufacturing process. His work on a 5.56 mm 'Green Ammo' manufacturing process has contributed to a successful non-lead small caliber round.

Photo

Not

Available

Mr. John Middleton is the Team Lead for the Small Caliber Ammunition Production Team in the Mounted/Dismounted Infantry Munitions Division of RDECOM-ARDEC. He has been involved in small caliber ammunition since 1985. Mr. Middleton earned his BS in Mechanical Engineering from Clarkson University in 1981, and his MS in Mechanical Engineering from Stevens Institute of Technology in 1991. In addition, he is Level III certified in Systems Planning, Research, Development and Engineering and is a member of the Acquisition Corps.

Photo

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Mr. Frank Hanzl is currently assigned as the Small Caliber Engineering Team Lead for the Project Manager - Maneuver Ammunition Systems. He earned his BS in Mechanical Engineering from Manhattan College, and his MS in Management from Florida Institute of Technology. In addition, he is Level III certified in test and evaluation; systems planning, research, development and engineering; manufacturing, production and quality assurance.

Photo

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Mr. Gregory DeRosa is the Project Officer in the Small and Medium Caliber Product Office for the Project Manager – Maneuver Ammunition Systems. He earned his BS in mechanical engineering from New York Institute of Technology and his MS in Management from Florida Institute of Technology. In addition, he is Level III-certified in test and evaluation; systems planning, research, development and engineering; manufacturing, production and quality assurance.

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Material EASE

AMPTIAC 28

Robert Woodman
Weapons and Materials Research Directorate
US Army Research Laboratory
Aberdeen Proving Ground, MD

AMORPHOUS MATERIALS:

A Tutorial on Noncrystalline Solids

INTRODUCTION

Amorphous materials are an integral part of many of the current weapons platforms for the US Army, and have considerable potential for contribution to the Army's Future Force applications. The Army is engaged in efforts to further develop these materials and utilize the many benefits they offer. In general, amorphous solids consist of thermoset plastics, transparent polymers, elastomers, oxide glasses, and metallic glasses. This issue of *MaterialEASE* will explain at a basic level what amorphous materials are, how they relate to crystalline materials, some of their important properties and attributes, and give examples of how they are used in Army systems.

What is an Amorphous Material?

Amorphous – from the Greek for "without form" – refers not to materials that have no shape, but rather to materials with no particular structure. The atoms or molecules of amorphous materials are arranged in essentially the same manner as they are in a liquid. An amorphous material is still solid – the molecules are closely packed and chemically bonded, and the material exhibits an elastic response to shear stresses – but the spatial arrangement of the atoms is nearly random. In contrast, the building blocks of crystalline solids are arranged in orderly, 3-dimensional, periodic arrays. Figure 1 illustrates the difference between a crystalline material and an amorphous solid. A crystalline material is analogous to a formation of troops on parade, while an amorphous material is more like a crowd or mob. Just as formations and crowds are both groupings of people, amorphous and crystalline materials are both groupings of atoms. In both cases, the manner in which the components are arranged influences how the assemblage behaves.

Also known as noncrystalline solids, glasses, or disordered solids, amorphous materials are characterized by their structure rather than their composition. This is because, under the right conditions, any material can be prepared as an amorphous solid. All amorphous materials have crystalline counterparts. An important aspect of this is that of the two structures, the crystalline form will generally be more stable. This is because the crystalline solid is at chemical equilibrium, whereas the amorphous form is not. Preparing an amorphous solid requires rapid cooling to avoid crystallization. The cooling rate that constitutes rapid cooling varies with the type of material.

The structures of materials affect their properties, and the properties of amorphous materials are no exception. Metallic glasses exhibit mechanical properties outside the range observed in other materials, combining high strength with a high elastic limit, as shown in Figure 2. This leads to elastic recoil not seen in other materials. A dramatic demonstration of this is how long a steel ball bearing will bounce when dropped onto a plate of metallic glass [1]. A more familiar property inherent in amorphous solids is optical transparency, as exemplified by such materials as plate glass, acrylic (polymethylmethacrylate), and Lexan® (polycarbonate). However, atomic arrangement is not the sole determinant of properties. For example, metallic glasses are optically opaque.

Amorphous vs. Crystalline Structure

The telltale sign of an amorphous solid is its diffraction pattern. Whether x-rays, neutrons, or electrons, radiation which is short enough

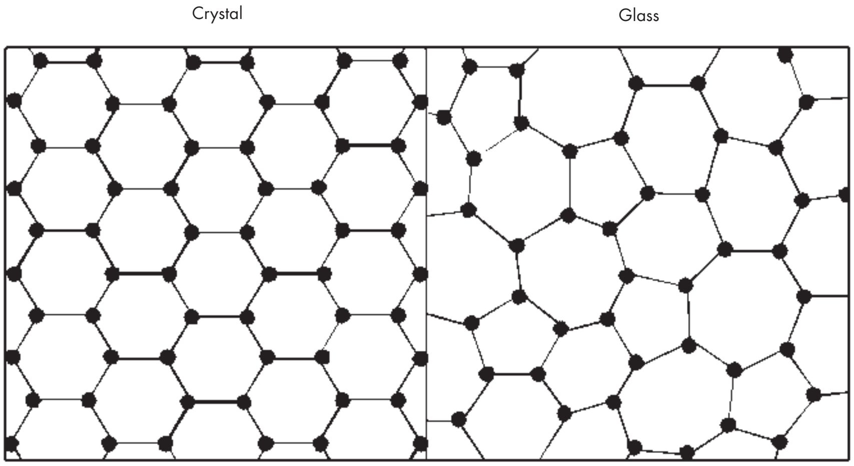

Figure 1. Schematic Illustration of the Structures of Crystals and Glasses.

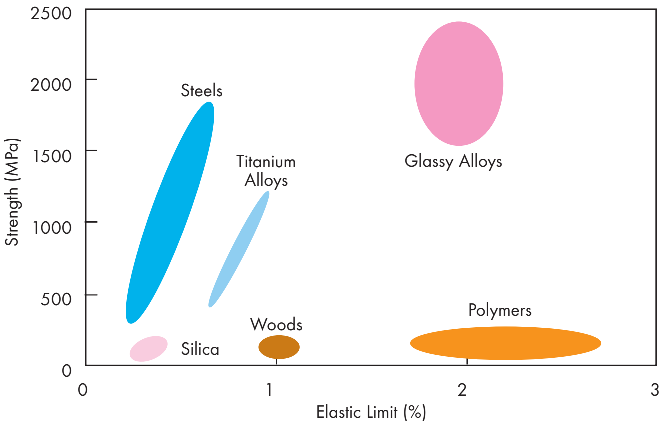

Figure 2. **Strength vs. Elastic Limit for Several Classes of Materials – Metallic Glasses Offer a Unique Combination of High Strength and High Elastic Limit [2].**

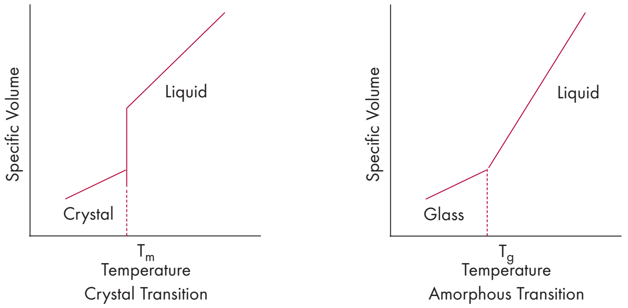

Figure 4. **Liquid-Crystalline Solid Transition (Left) and Liquid-Glass Transition (Right).**

in wavelength to pass between atoms will interact with the atomic structure in the same way that visible light interacts with a diffraction grating. Regions of constructive and destructive interference develop, and a pattern emerges. The location and intensity of peaks in the diffraction pattern is determined by the location and arrangement of atoms. For a crystalline solid, a diffraction pattern is analogous to a fingerprint, and can be used to identify the material.

The diffraction pattern is a direct consequence of the ordered nature of the structure of crystalline solids. Amorphous solids have no such order, and as a consequence, their diffraction pattern is diffuse as displayed in Figure 3. Consequently, the pattern can only be used to determine that a material is amorphous, but not to determine its chemical composition. For comparison, the diffraction pattern from a liquid is similar.

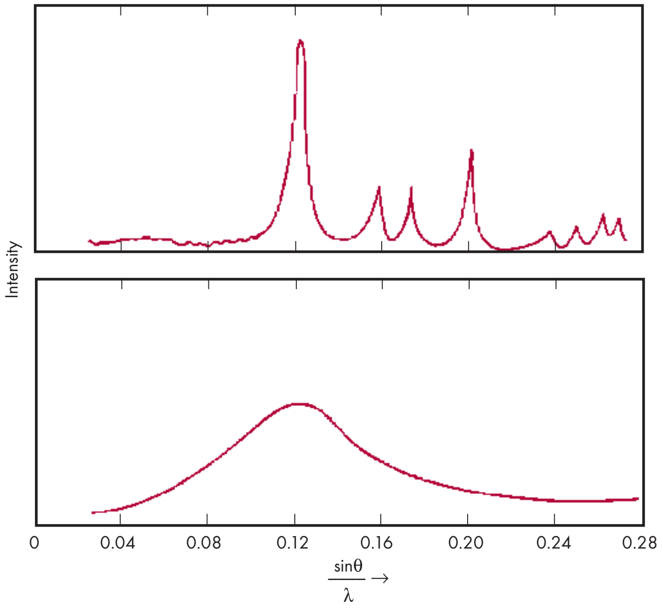

Figure 3. **Characteristic Diffraction Patterns from Crystalline Material (Top) and Amorphous Material (Bottom). [3]**

The Glass Transition

While amorphous materials are solid, they are often described as high-viscosity or supercooled liquids. Amorphous materials are also characterized by the absence of a pronounced discontinuity in their properties when the liquid solidifies and becomes a glass. This is in contrast to crystalline materials, which experience a distinct transition from liquid to solid as the temperature decreases to below the melt temperature (T_m), as shown in Figure 4. The physical process by which a liquid solidifies to form an amorphous solid involves more gradual changes than the crystalline solid, and is known as the glass transition. During the glass transition, there is a detectable change in the slope of properties, such as density, with temperature. The glass-transition temperature, Tg, occurs over a range of temperatures, and is often defined as the mid-point of this range.

Unlike well-defined transformation temperatures in crystalline solids, such as freezing points or boiling points, T_g is not uniquely defined, but varies with cooling rate. Typically, the slower the cooling rate, the lower the temperature at which the glass transition occurs (Figure 5).

AMORPHOUS MATERIALS – EXAMPLES AND PREPARATION TECHNIQUES

Theoretically, any material can be formed into an amorphous solid as long as the cooling rate is sufficient to prevent crystallization. However, some materials more readily form amorphous solids compared to others. Furthermore, there are often limitations on the size of the amorphous solid that can be formed by current techniques.

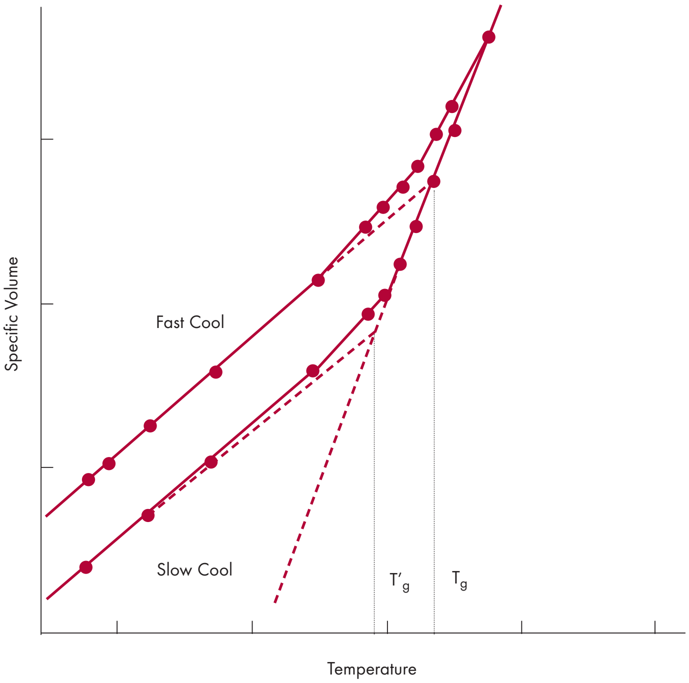

Figure 5. Schematic Representation of the Glass Transition. Note that the Glass-Transition Temperature (T_g) Shifts to a Lower Temperature with Slower Cooling (T'_g).

Amorphous Ceramics

Ceramic glasses are the oldest known and, not surprisingly, the easiest to prepare [4]. Alkali silicates, in particular, form glasses so readily that preparation of glass objects from alkali silicate melts came to be known as the glass industry. Ceramic glass production is a mature industry; a thorough discussion of the processes is beyond the scope of this article. The reader is referred to various reviews and textbooks, such as ASM handbooks [5].

Amorphous Polymers

Due to the size and configuration of the large, chain-like molecules of which they are made, most commercial polymers are amorphous materials. However, nearly all polymers have some degree of crystallinity. While the molecules of polymers are much larger than those in ceramics or metals, the essential features of amorphous structure and the glass transition are the same. Preparing an amorphous polymer is largely a matter of cooling a molten polymer blend through its glass transition. As with most oxide glasses, special equipment and techniques for cooling are not typically required.

Metallic Glasses

Metallic glasses are a greater challenge to make than oxide or polymeric glasses, and are the most recent development. In fact, for years it was argued that metallic glasses would be impossible to make for a couple of reasons. First, the crystal structures of metals are simple, and have a strong tendency to form (crystallize) near the solidification point. Secondly, molten metal near the solidification point has a low viscosity, facilitating rapid atomic rearrangement. Over the course of the middle decades of the 20th century, as more metallic glasses were prepared, it became evident that all solids have the potential to be prepared as glasses.

As mentioned earlier, the challenge to preparing metallic glass is to cool it at a sufficiently rapid rate. This rate for many metals can be as high as 10^6 °C/s. Unfortunately for the prospects of engineering with metallic glasses, the maximum rate at which an object can be cooled is limited by the thermal conductivity and heat capacity of the material. This, in turn, limits the maximum thickness of the material that can be prepared with an amorphous structure. The higher the critical cooling rate of the materials, the smaller the maximum thickness. So, while there are techniques for achieving rapid cooling – such as melt spinning and splat quenching – the amorphous product is often quite thin. Some metallic glasses can be prepared only in sheets or ribbons a few microns thick.

During the 1990's, several alloys were developed that had critical cooling rates in the range of 1-100 °C/s, with corresponding critical dimensions in the range of 1-100 mm [6]. Most of these alloys have chemical compositions with at least five components, and achieve their glass-forming properties from what has come to be called the "confusion principle." If the atoms in the melt must rearrange themselves into three or more coexisting crystal structures on cooling, then the probability of cooling them rapidly enough that the rearrangement becomes impossible is increased. The atoms can be said to be "confused" about where to go and, like the last person to sit down in a game of musical chairs, unable to find a place in the ordered structure. Arbitrarily taking 1 mm to be sufficiently thick to be considered "bulk", the new class of alloys came to be called bulk metallic glasses (BMGs). It is important to note that many of the BMG-forming alloys still require cooling rates considerably higher than those required to make oxide or polymeric glasses. Even the best bulk metallic glasses cannot be made with a critical dimension greater than 100 mm. Despite the vast improvement in metallic glasses that BMGs represent, the materials remain largely developmental.

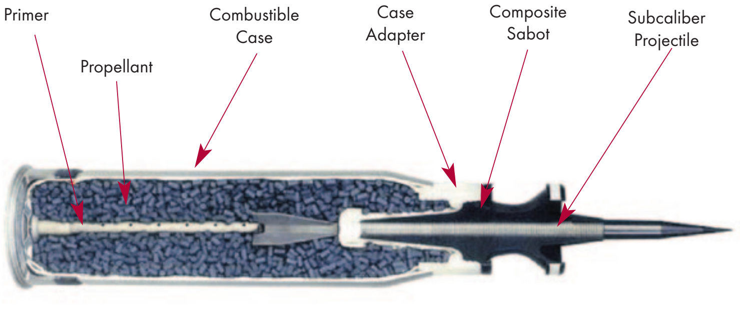

Figure 6. Anatomy of an M829 Tank Round.

APPLICATIONS

Amorphous materials have contributed substantially to the success of military technologies, and there is potential for further contributions. Substitution of an amorphous thermoplastic polymer matrix for a thermosetting polymer in a composite drastically reduced the cost of the sabots used in the M829A3 tank round. Tempered glass backed by amorphous polycarbonate has long served as transparent armor. Careful engineering of the degree of crystallinity of polyurethane makes possible lighter, more effective transparent armor. Metallic glass may be the key to achieving the lethality of a depleted-uranium kinetic-energy penetrator using a nonradioactive material.

Transparent Armor

Amorphous polymers are transparent and tough, making them effective against ballistic threats such as fragments and pistol rounds. The most commonly used transparent armor polymers are polymethylmethacrylate and polycarbonate. Polyurethanes belong to a class of polymers known as block copolymers. Blocks of hard and soft urethanes can be mixed to engineer optimum transparency, hardness, and toughness. Urethanes offer the opportunity for weight savings compared to polycarbonate, but have not been widely adopted because of their high cost.[7] When combined with a high-hardness strike-face plate like tempered glass, polycarbonate is effective against heavier ballistic threats, such as assault-rifle rounds.

Sabot Materials

A sabot is a composite structure used to hold a projectile (penetrator) in place (as part of a round) while in the barrel of a gun (Figure 6). Sabots also help to accelerate the projectile upon combustion of the propellant when the gun is fired. The sabot then falls away, leaving the projectile to fly in a ballistic trajectory (Figure 7).

Sabots are used in the US Army's M1 tank, where they support the use of dart-like depleted uranium penetrators. In this application, sabots are fabricated from composite materials. Composite materials are made by reinforcing either thermoplastic or thermoset polymers with fibers.

Figure 7. A Sabot Falling Away from a Projectile After Firing.

Because thermoplastics soften at higher temperatures, they are readily prepared for mechanical forming operations in a manufacturing setting. In contrast, thermosetting polymers such as epoxies form cross-linking bonds that create a rigid 3-D network when heated. The M829A2 kinetic-energy cartridge featured a sabot formed from graphite-reinforced epoxy. Use of the epoxy in a manufacturing setting required the use of freezers for epoxy storage and careful control of the time that the epoxy spends in processing. Substitution of an amorphous thermoplastic-based composite reduced the manufacturing costs, and is now implemented in the M829A3. The reduced costs were a result of increased shelf-life since the properties of thermoplastics don't degrade over time like they do with thermosetting polymers. Furthermore, less processing infrastructure (e.g. freezers, autoclave) is required to produce thermoplastic-based composites, which also led to a reduced manufacturing cost.

Kinetic-Energy Penetrators

Depleted uranium penetrators derive their superior penetration performance from an unusual erosion-and-wear mechanism that leads to self-sharpening during penetration. Due to their structure, bulk metallic glasses exhibit a similar mechanism during fracture. In order to match the penetration performance of uranium, a replacement material will have to be comparable to uranium in density (18.95 g/cm^3).

Penetrator development is directly affected by the critical-cooling-rate issue mentioned earlier. One of the best BMGs, $Zr_{41.2}Ti_{13.8}Cu1_{2.5}Ni_{10.0}Be_{22.5}$, has a critical cooling rate of ~1 K/s, and can be readily made into objects with critical dimensions as large as 12.6 mm.[8] Unfortunately, the beryllium content of the alloy makes it too hazardous to replace uranium. While alloys of similar composition have been developed, none has exhibited a critical dimension greater than 10 mm. Most importantly, a BMG composite penetrator which can be made to quarter scale or medium caliber cannot necessarily be scaled up to a full-scale, tank main-gun round in a straightforward way. Alternate alloys or fabrication techniques must be developed for the potential of BMGs to be realized in kinetic-energy penetration applications.

SUMMARY

Amorphous materials – whether metals, ceramics, or polymers – are characterized by a liquid-like structure. This structure is readily evident from a comparison of the diffraction pattern of an amorphous material to that of a liquid. However, amorphous materials are solid. They enter the solid state when a cooling liquid undergoes a change in its physical properties known as the glass transition.

Any material can be prepared as an amorphous solid if it is cooled quickly enough. For metals, the speeds of cooling limit the size of metallic glasses, even for the newly developed bulk metallic glasses. Many ceramics and many polymer blends are more easily prepared as glasses; some are ubiquitous and familiar.

The structure of amorphous materials leads to distinctive properties, such as transparency, plasticity, and elastic recoil. Their properties make amorphous materials useful to the Army's mission, particularly as transparent armor and in munitions manufacture. The Army continues to pursue the development of amorphous materials with desirable properties.

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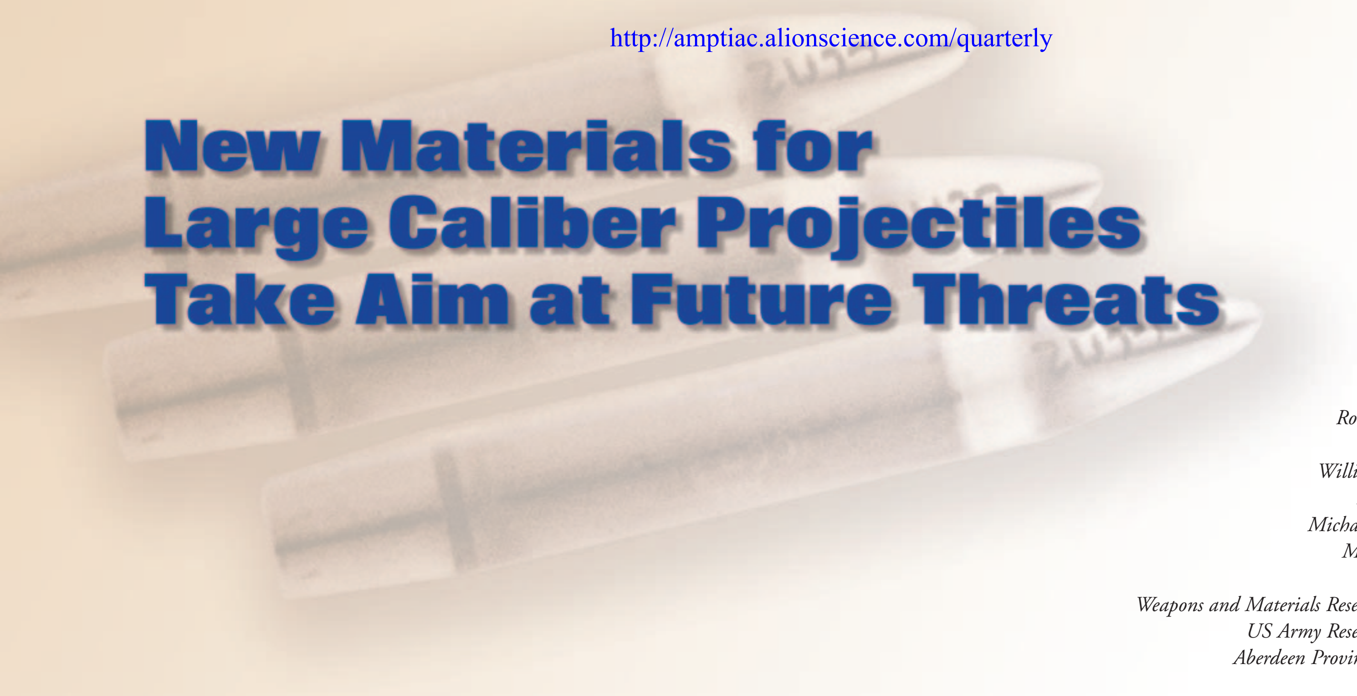

New Materials for Large Caliber Projectiles Take Aim at Future Threats

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INTRODUCTION

All materials used in large caliber projectiles share a common feature; their design and use requires knowledge of their deformation behavior up to and beyond failure at high strain and heating rates. Crucial to the development of these materials is the ability to describe the life of the material from its synthesis and process development to a complete description of the terminal ballistic performance, platform structural response, and ultimate structural failure under dynamic loading. Materials for this application include those used in kinetic energy penetrators, sabots, fins, cartridges (Figure 1), and liner materials for shaped charge and explosively formed projectile warheads. One will find that a complete spectrum of materials is used for these components, including metals, ceramics, polymers and composites.

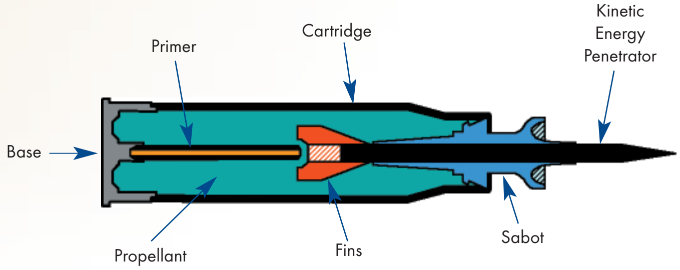


Figure 1. Typical Components of a Large Caliber Projectile.

Materials under current development for large caliber projectiles come from unique sub-classes of conventional disciplines. These include nanocrystalline metals, bulk amorphous metallic glasses, polymer matrix composites, and metal matrix composites. Also, beyond just materials selection is the consequent need to develop the processing of these materials so as to maximize the desired mechanical and physical properties, and thus optimize munition lethality. These materials technologies have been vital to past battlefield successes and will be essential to future victories.

KINETIC ENERGY PENETRATORS

The standard high performance material used for kinetic energy penetrators (KEPs) is a depleted uranium (DU) alloy. Its performance is attributed to its high strength and density (18.6 g/cm^3) and a localized flow softening behavior, more commonly referred to as adiabatic shear. This allows the DU penetrator, upon impact, to maintain a 'conical-nose' shape favorable for enhanced penetration. A longstanding goal of current research has been to replicate this deformation and flow behavior in non-DU materials. More recent processing technologies with nanocrystalline tungsten (W) and bulk metallic glasses (BMGs) have shown promise in reaching the desired performance levels of DU alloy penetrators.

Defeating armor requires that the maximum kinetic energy be delivered to a given area of armor, for the longest time duration, and at a velocity as high as possible. Geometrically, execution is via a long thin (high length-to-diameter, L/D ratio) high-density, high-strength rod striking the smallest armor area. The early use of uranium alloy penetrators was based on this understanding but not on the knowledge that additional performance is achieved by controlling the deformation and fracture modes of the penetrating rod. A high L/D ratio extends the time of penetrator-target interaction, but high strength alloys also extend the time of interaction by allowing more deformation and fracture of the target relative to the erosion loss of a higher strength penetrating rod. If the deformation and failure mode of the long rod is adiabatic shear (as opposed to stable deformation), a smaller diameter of penetrator/armor interaction occurs with a "sharpening" effect of the penetrator tip, allowing spent rod and target material to flow backward easier and escape the on-coming active rod, see Figure 2. Less kinetic energy per unit of rod length is consumed and the effectiveness of the munition is increased [2]. Use of uranium alloys as long rod KEPs is now governed by the following parameters: velocity, L/D ratio, and material properties of density, strength, hard-

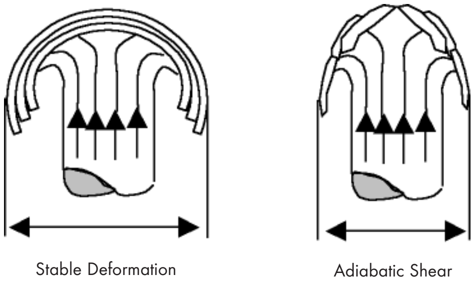


Figure 2. Penetrator Rod Deformation, after Magness [1].

ness, and propensity for adiabatic shear [3-7], which includes flow stress increase with strain (work hardening) [4,6], strain rate [4,6,7], temperature sensitivity of flow stress [4,5], volumetric specific heat[4], and flow localization parameter [4,5,6].

Uranium Alloys for Long Rod Kinetic Energy Munitions

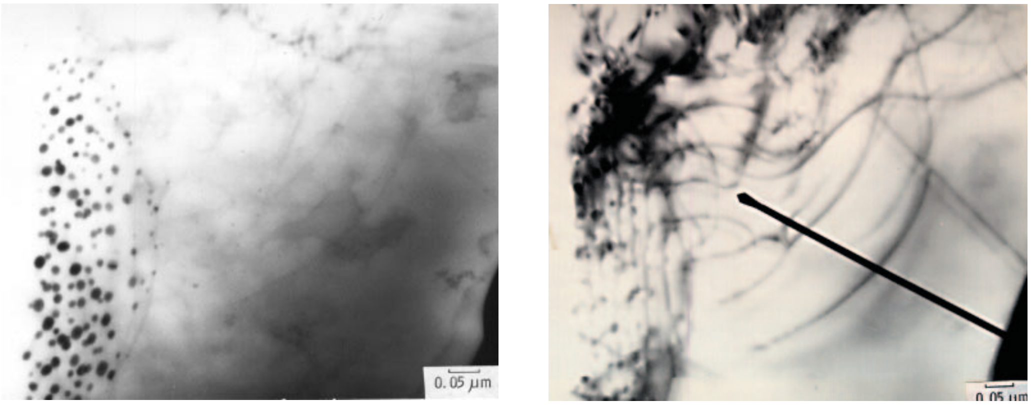
Uranium alloys, depleted of the highly fissionable U235 isotope are referred to as depleted uranium and if used as KEPs are called staballoy. Their radioactivity is 40% below natural uranium, which is already low enough to be handled and used safely with a few basic precautions. This includes minimizing the ingestion of air-borne particles, a safety precaution necessary for all heavy metals regardless of whether or not they are radioactive. Depleted uranium's low radioactivity does aid in locating finely divided metal particles easily with a Geiger counter during clean-up operations in ranges and post-battle fields. Cleaning-up other heavy toxic metals, after use, with or without target interaction, is virtually impossible.

Uranium must be alloyed and strengthened with other elements such as titanium, molybdenum, vanadium or niobium with a small alloying content near 1 or 2 wt% so that the density remains high. Uranium alloys have three allotropic phases referred to as α, β, and γ. Alpha uranium is a base-centered orthorhombic crystalline phase, existing below 668°C [8]. Beta uranium is a tetragonal crystal phase existing between 668 to 776°C. The gamma phase is a body-centered cubic crystal structure existing from 776°C up to uranium's melting point of 1135°C. The room temperature phase, α, and the highest temperature phase, γ, are the two most important. The intermediate temperature phase, β, is too brittle to be useful as a penetrator. Solubility of alloying elements is higher in the γ phase, and taken advantage of during heat treatments producing a supersaturated room temperature α' phase, strengthened either by pure solid solution or subsequent aging. Aging reactions often precipitate intermetallics of the form U_2M, where M is a solute element, such as titanium, molybdenum or niobium. These intermetallic precipitates are usually inherently brittle, but are effective in strengthening provided their morphology is small, spherical, and non-planar. Over-aging leads to a tradeoff of ductility for strength when U_2Ti, for example, grows preferentially along lenticular-shaped martensite (α') boundaries. Small U_2Ti, precipitates are observed preventing dislocation motion, Figure 3, resulting in increased strength [9]. However, deformation is predominately by twinning at high strain rates.

Texture development during deformation processing also plays a major role in strengthening uranium alloys [10]. The Army Research Laboratory and its predecessor, Watertown Arsenal, played a major role in developing and understanding uranium alloys[11], including the current production alloy, Uranium - 3/4 wt% Titanium (U-3/4 Ti), although Sandia[12] and Los Alamos National Laboratories also played major roles. New alloy development builds on the control of all the materials parameters influencing propensity for adiabatic shear of the projectile in addition to velocity, L/D ratio, and density. Ultra high strength and ductility must be maintained as well as low work hardening [3,4] and high flow stress-temperature sensitivity [4] and high flow localization parameter [4, 5] that allow early onset of adiabatic shear [13]. Present work on uranium alloys continues to refine our understanding of the crystalline phases and is leading to some revisions of phase diagrams [12, 13] and enhanced properties [13, 14].

Nanocrystalline Tungsten Penetrators

Tungsten has been researched quite extensively for the replacement of DU penetrators. It has a high density (19.30 g/cm^3) but has lacked the ability for adiabatic shear. Powder consolidation methods including microwave sintering and plasma pressure compaction (P^{2}C) followed by mechanical



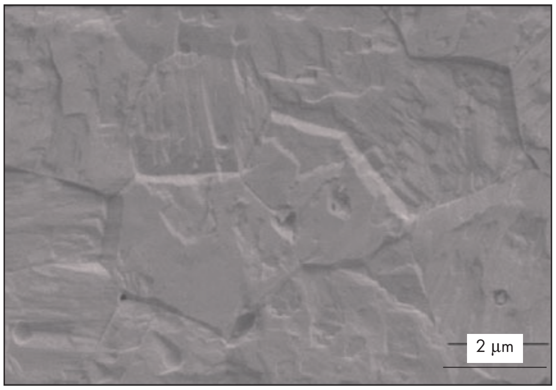
a) U_2Ti precipitates with Dislocations Slightly Visible Due to Diffraction Conditions.

b) Dislocations (More Visible) Interacting with U_2Ti, After Tilting the Foil.

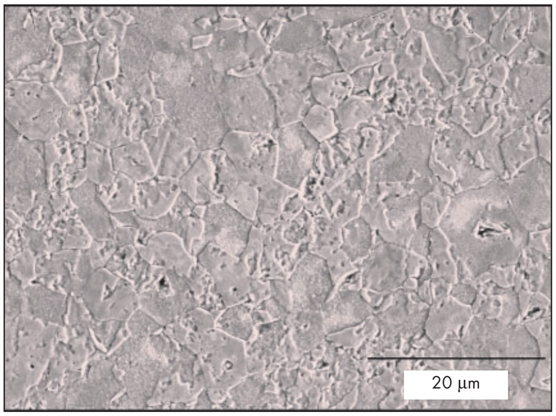
Figure 3. Transmission Electron Micrograph of U_2Ti in an ARL-Made U-3/4 Ti Alloy.

working, and an alternate approach using severe plastic deformation, are being investigated to produce ultrafine grain and nanocrystalline tungsten which have potential for a high performance KEP.

Particulate consolidation is a solid-state densification technique used to bond individual particulates or aggregates of particulates using thermal and sometimes mechanical energy to convert them into a solid load bearing structure. Particulates consist of small particles with wide ranges of shapes. In most cases, pure bulk tungsten is produced by a particulate consolidation technique followed by one or more post consolidation mechanical working methods such as swaging, forging, and rolling.



a) Microwave Sintering Technique



b) Plasma Pressure Compaction

Figure 4. **SEI of Consolidated Tungsten.**

In tungsten, or any other material, the conventional grain sizes are typically micrometers in size while for nanocrystalline materials the grain size is usually defined as 1-100 nm. Ultra fine grain sizes fall in the range of approximately 100 to 500 nm. A material's properties are dependent upon grain size with an abrupt change occurring in the nanoscale region referred to as the critical grain size.

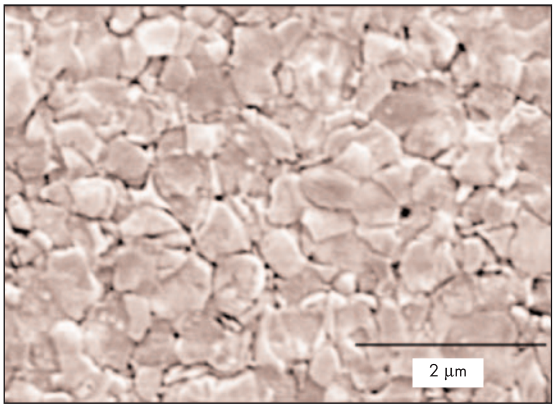


Figure 5. **SEI of Microwave Sintered Tungsten Doped with a Small Amount of HfO_2.**

It is widely considered that the critical grain size is a material characteristic. On the other hand, it is also well understood that materials with the same crystal structure have similar plastic deformation characteristics. Tungsten is a high density refractory metal with a body centered cubic (BCC) atomic unit cell structure. Micrometer grain size BCC metals, such as conventional tungsten and conventional iron, have extremely stable compressive dynamic plastic deformation behaviors (e.g., resistance to compressive plastic deformation is proportional to the cumulative compressive plastic strains at high strain rates). This behavior, known as stable plasticity, is not a desirable property for KEP materials. Unlike conventional iron, however, ultra fine grain iron and nanocrystalline iron have shown unstable dynamic compressive plastic deformation behavior accompanied by dynamic shear band formation at or below average grain sizes of 250 nm. Based on the results with iron, it has been widely postulated that ultra fine grained tungsten may show similar shear localization type plastic deformation characteristics at high dynamic compressive strain and strain rate regimes. Shear band formability in ultra fine or nanosize-grained tungsten would produce a high performance KEP.

Tungsten densification is mainly promoted by grain boundary diffusion that naturally encourages grain growth. In order to consolidate ultra fine grained tungsten and nanocrystalline tungsten, therefore, the densification processes should provide extremely rapid heating rates in order to minimize the grain growth. High applied pressure is also desirable as it provides additional driving force for densification. In general, shorter processing time and lower temperature is beneficial for retaining fine grain structure. Currently, two particulate consolidation techniques for nano and ultra fine grained tungsten are being examined. They are microwave sintering and plasma pressure compaction (P^2C). Both techniques utilize rapid volumetric heating which does not promote thermal diffusion and therefore should, in theory, prevent grain growth.

Tungsten particulates are not subjected to pressure during microwave sintering while in contrast, during P^2C, tungsten particulates are placed in a graphite die and pressure is applied through a set of graphite punches. Consolidation results from these processes can be seen in the secondary electron images (SEI) of nanoparticulate tungsten in Figures 4. Secondary phases can artificially pin the tungsten grain boundaries during the densification stage of processing. The grain boundary pinning agents may allow an elevation of the consolidation temperature to achieve full densification without sacrificing grain growth. An SEI of microwave sintered tungsten doped with a small amount of hafnium dioxide (HfO_2) is shown in Figure 5 and illustrates the pinning effects.

Severe Plastic Deformation

There are two approaches for making a bulk nanostructured material. The first is to build it from the bottom up using nanoparticles and consolidating them to a fully dense structure. Controlling grain growth, however, is a difficult task because of the heat involved. Often, particles that are initially less than 100 nanometers can grow to several microns in diameter. An alternate approach is to deform plastically the material to break down a coarse grain structure into a very fine nanocrystalline structure. The amount of cold work required is large and the total strain necessary can be 500% or more. The process of cold work and recrystallization is well known, and is commonly used in metalworking.

Equal channel angular pressing (ECAP) offers a cold working method that is unique, see Figure 6. It can impart very large amounts of cold work without changing the original cross sectional shape or area. In an ECAP die, two channels intersect at a predetermined angle, θ, where the work piece is processed in pure shear. This angle is usually 90° for ductile metals such as copper and aluminum. The angle is set at higher values for more difficult to work metals like tungsten.

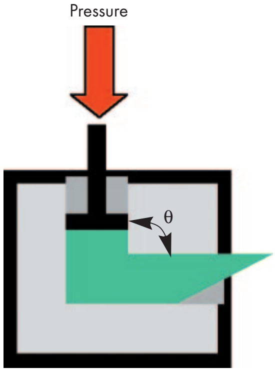


Figure 6. **Equal Channel Angular Pressing (ECAP) Die Schematic. Two Intersecting Channels of Equal Shape and Size Guide the Work Piece as it is Deformed. Multiple Passes Allow for Accumulation of Strain.**

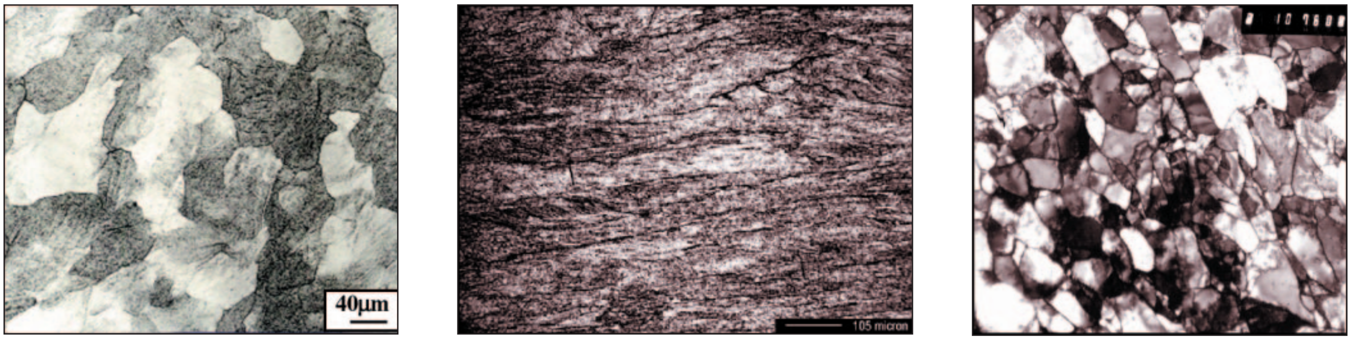
Recent ECAP of pure tungsten has shown that refinement of coarse grains to the nanoscale is possible. Commercially pure tungsten has a grain size of approximately 70 mm. After ECAP processing where the work piece was processed 16 times, the grain size was reduced to approximately 100 nm, Figure 7. A reduction in the ductile to brittle transition temperature of 80°C has been observed in nanostructured tungsten in comparison to conventional tungsten. It is reasonable to expect this structure will deliver properties previously unobtainable by other means.

Bulk-Metallic Glass-Matrix Composites

Conventional tungsten heavy alloy (WHA) penetrators are two-phase composites of nearly unalloyed tungsten particles embedded in a nickel alloy matrix. Because the tungsten phase itself is very resistant to adiabatic shear localization, efforts have primarily focused on replacing the nickel alloy matrix with one having a greater susceptibility to adiabatic shear failure. The Army has led a concerted effort wherein bulk metallic glass (BMG) alloys with unique shear deformation and failure mechanisms are being examined as candidate matrix materials for use in novel tungsten based composites. Unlike conventional materials, BMGs are amorphous, that is they do not have a long-range ordered crystalline structure. At ordinary temperatures, BMGs are in a deeply under cooled state. That is, below their glass transition temperatures (T_g), BMGs have an extremely high viscosity causing randomly dispersed atoms to be immobile. Above their T_g, there is a rapid decrease in viscosity. However, as atoms become mobile above a certain temperature, crystalline phases form and BMGs devitrify.

Typically, the formation of BMGs necessitates fairly high cooling rates to retain their disordered, amorphous structure. The best zirconium based BMGs have critical cooling rates of about 10 to 100 degrees/second and densities of about $7\ g/cm^3$. The disordered atomic arrangement also leads to mechanical properties that are quite different from those of ordinary crystalline materials. It is this distinct property of BMGs that is of greatest interest. Specifically, when subjected to a compressive mechanical load, they deform uncontrollably by shear localization, in a manner very similar to the way depleted uranium alloys deform and fracture.

Fundamental research has lead to a significant technical achievement in solving two simultaneous problems: (1) identify a BMG with higher than $7\ g/cm^3$ density and, (2) achieve control over the deformation mechanism. This was accomplished by concurrently attacking the problem with three approaches. First, a new high-density BMG was synthesized that nearly doubled the density of the previously available zirconium-based BMGs. This alloy, based on hafnium, was developed using first principles, modeling, and a semi-empirical experimental method [15]. Second, and just as significantly, using a liquid-infiltration technique, a composite was created that incorporated fine particulate tungsten powder which further raised the density and allowed for control of the shear banding. Lastly, intensive mechanical and ballistic characterization provided the proper path for the material and composite synthesis activities [16].



As-Received Tungsten
Grain Size 70 µm

6 Passes ECAP
Grain Size ~1 µm

16 Passes ECAP
Grain Size ~100 nm

Figure 7. **Pure Tungsten That Has Been Subjected to Severe Plastic Deformation.**

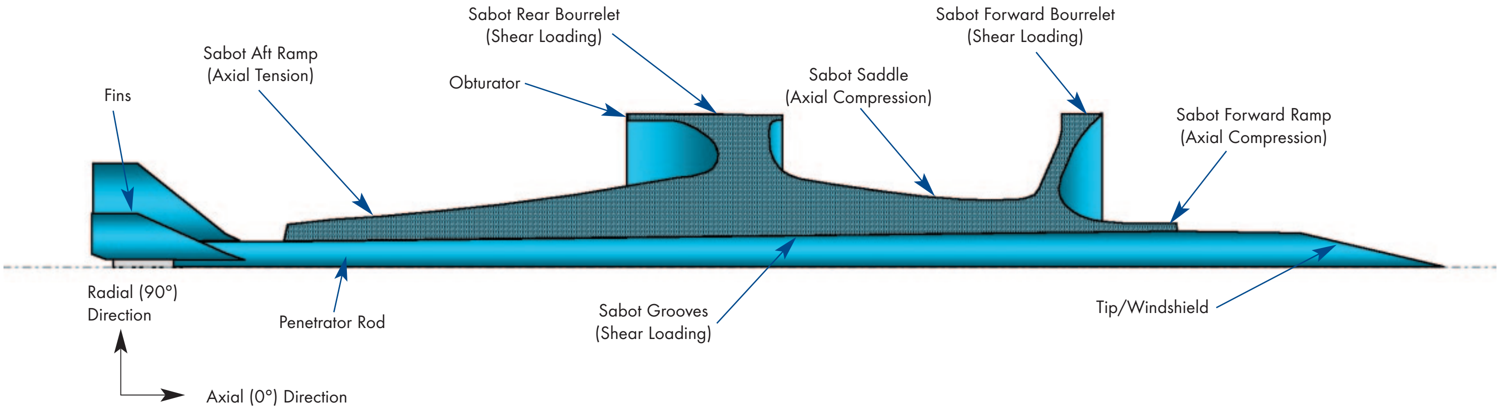


Figure 8. **Axisymmetric View of a Kinetic Energy Penetrator System. Major Regions of the Sabot and Their Loading Requirements Are Indicated.**

The ultimate discovery of the alloy, the processing methods, and a verification of the preferred ballistic deformation behavior achieved two things. First, it raised the density to an acceptable level for kinetic energy penetrators (about 17 g/cm^3) and second, it allowed for control of the shear localizations that are so important to the performance of the KEP. This new, hafnium-based BMG-tungsten composite provides new options in materials selection for KEPs. It performs substantially better than existing conventional WHAs and on a par with DU alloys.

Current and future efforts focus on developing a reliable process to produce large-scale composite structures beyond the dimensions of sub-scale projectile devices [17]. To address this issue, a powder metallurgy-based approach was invented that, in part, depends on a hot isostatic pressing (HIP) technique, equipped with a sensor system to monitor and optimize the consolidation process. Instrumentation allows real-time control of the HIP process, with adjustments to alter exposure time of the composite powder blend to pressure and temperature, in order to achieve full densification and bring about the proper evolution of the desired amorphous structure. Prudent control of the HIP and post-HIP processing are used to bypass detrimental conditions that otherwise would devitrify the composite.

COMPOSITES FOR LARGE CALIBER SABOTS

Advanced lightweight composites are being utilized or considered for large caliber munitions in both the direct and indirect fire modes. Increased armor penetration, lethal radius, effective range, and accuracy of the projectile are the major factors promoting the use of these engineered materials.

In the direct fire role, the primary anti-armor ammunition for current main battle tanks is the sabot-launched KEP. The sabot is the portion of the round which cradles the long rod penetrator. Its primary functions are to (1) support the dense, low structural efficiency penetrator during the high axial acceleration of launch, (2) to seal the gun barrel to hot, high pressure gas, (3) to protect the long, high length-to-diameter ratio rod from transverse balloting loads, and (4) to launch the flight penetrator or payload so that it may fly accurately to the target. Since the sabot is discarded at muzzle exit and does not fly to the target, any kinetic energy resident in the sabot was lost after firing. Thus the minimization of the sabot mass leads directly to increased kinetic energy in the penetrator. An axisymmetric view of a sabot-launched kinetic energy projectile is shown in Figure 8, which also indicates the stress state and primary loading of the different portions of the sabot. The obturator prevents explosive gases from escaping around the projectile, maximizing the load transferred to the projectile. The rear bourrelet handles the loads transferred to the projectile upon discharging the weapon. The forward bourrelet provides the loading surface for separation of the sabot from the penetrator rod after emerging from the gun barrel.

Since one of the functions of a sabot is merely to occupy volume (sealing the gun tube) a low density material is needed. Another of the design requirements calls for a high axial modulus to provide support for the rod. This combination of design criteria suggests a graphite fiber/ polymer matrix composite (PMC) material as providing the optimum combination of properties. The identification of zones of the sabot needing high shear strength then suggests a plus/minus off-axis laminate.

Analysis and design of projectiles that employ a PMC sabot is complicated by the lack of an accepted laminate failure criteria that considers thick sections and three dimensional (3D) loading. To meet this challenge, an assessment methodology was developed using LAMPAT modeling software. Besides providing a quick determination of relevant 3D elastic properties for use in finite element (FE) codes from unidirectional ply values, LAMPAT calculated the stress or strain in individual plies from the global 3D FE results, allowing a more rational failure assessment.

Using these analysis techniques, two generations of composite sabot KEPs have been fielded. The first, the M829A2, reduced the sabot mass from the comparable aluminum sabot M829A1 by 35%. The second generation, using a more optimum lay-up in the laminate, resulted in an additional 30% equivalent sabot mass reduction for the M829A3 projectile. These are the only composite sabots successfully fielded.

An additional savings that occurred in the evolution of the M829A2 to the A3 was in the area of cost. The A2 version used an epoxy matrix sabot. Epoxy resins used for sabot applications, and many others, require storage freezers and special monitoring of the material on the factory floor. The A3 version switched to a thermoplastic matrix sabot, which made possible the use of an induction laminator as well as the elimination of special storage needs. The laminator was the result of the joint Army Research Laboratory/University of Delaware Center for Composite Materials (CCM) program. By using inductive currents in the graphite fibers to heat the prepreg plies and then immediately compacting them with consolidation rollers, an eight ply laminate of the basic lay-up building block of the sabot was rapidly fabricated at less cost.

METAL MATRIX COMPOSITES FOR HIGH PAYLOAD MUNITIONS

A slightly different set of requirements are needed for the Beyond-Line-of-Sight and Non-Line-of-Sight projectiles, more similar to traditional artillery rounds. Here, light weight is still desired, but the crucial need is for increased cargo volume. Since the diameter of the round is strictly curtailed by the cannon caliber and the length is limited by cartridge compatibility, any means of increasing interior volume for the explosives, propulsion, or guidance components adds directly to the effectiveness of the munition. While PMCs can deliver very competitive projectile sidewall weights, the more than double wall thickness cuts unacceptably into payload volume. Steel sidewalls represent an acceptable material solution for the shell from consideration of payload volume; however they are excessively heavy compared to metal matrix composite (MMC) materials. One such material is the system of alumina ceramic fibers in an aluminum metal matrix. The tensile strength of this material is similar to high strength steel; the compressive strength of uniaxial plies is phenomenal, approaching 800,000 psi, all at a density similar to aluminum.

Besides their extraordinary specific strength advantages, laminated MMCs are superior to isotropic materials in their ability to modify the material to best handle the stress distribution for the application. For example, one possible configuration for an extended range cargo round has the sidewall for a rocket motor buried deeply within the propellant bed. When the propellant burns, the external pressure acts to collapse the sidewall as well as accelerate the projectile. The resulting stress state can have hoop stresses which are several times larger than the axial stress. Conversely, for a more conventional artillery shell where the projectile is seated in the gun and the propellant separately loaded, the resulting stress state is almost entirely axial. By changing the ratio of hoop to axial plies in the composite lay-up used for the projectile sidewall, the differences in strength requirements are easily satisfied.

Projectiles designed for the standard configuration projectile were fabricated and tested in a 105 mm smoothbore gun, see Figure 9. The MMC sidewall had the same thickness but less than half the weight of a steel design. All tests have been successful for the new material. The MMC tubes used for the sidewalls in the successful firing tests were fabricated by infiltration of molten aluminum into a mold containing the ceramic fiber lay-up. A joint program to develop other potentially cheaper fabrication techniques is being pursued by ARL and CCM. This effort begins with an MMC tape, thin ribbons of ceramic fibers already encased in an aluminum matrix, and develops an analogy between this material and thermoplastic tape for use with robotic tape laying processes. The CCM has developed extensive software to simulate the fabrication of large parts by thermoplastic tape laying methods, including models of various means of applying heat to the interface, heat lost to conduction into the part and to the consolidation rollers, effects of consolidation pressure, etc. Depending on time at temperature and pressure, the degree of consolidation of the tape can be predicted.

In extending the simulation to MMC tapes, several key differences appear besides the obvious similarities. The melting or softening temperature of aluminum is much higher than thermoplastic polymers. Additionally, the rate of heat conduction away from the joining interface is much higher in aluminum (polymers act almost as insulators). Both of these differences indicate the need for more robust heat deposition for MMC tape placement. Inductive heating is currently being studied for this very application. A patent application has been submitted for the robotic induction head/compaction roller developed from the MMC simulation.

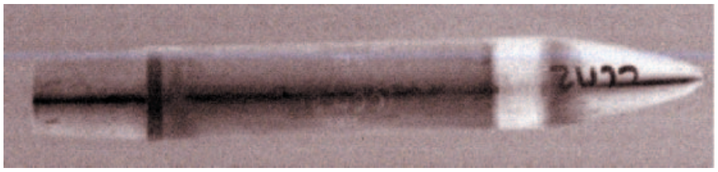


Figure 9. Photograph of an MMC Projectile just after Exiting the Muzzle.

ENABLING MATERIALS FOR FRANGIBLE PROJECTILES

United States military forces are increasingly finding themselves in situations where the use of non-lethal weapons is desired. Shaping the battlefield with non-lethal payloads delivered by these weapons is considered to be an essential option in future conflict scenarios. To be a truly non-lethal weapon, both the delivery vehicle (aeroshell) and the payload must be non-lethal. Non-lethal weapons are designed to disable a vehicle or personnel without excessive physical damage or fatality. ARL has determined that fragmenting the aeroshell mass in a manner that produces high aerodynamic drag staves is an attractive solution for achieving a non-lethal large caliber weapon.

ARL has demonstrated that an adhesively bonded bimetallic nano-layered composite, with a designable level of electrical or thermal initiation, can completely and quickly separate two adhesively coupled surfaces. Unlike other de-bonding approaches, this method allows for remote and virtually instantaneous, on-command separation of structurally bonded materials [18]. This rapid de-bond technology enables the development of a frangible non-lethal artillery aeroshell.

Typically, these reactive nanocomposites are made by sputter deposition of alternating bilayers 10-100 nanometers thick of metallic and/or intermetallic materials. An illustration of the nanocomposite is shown in Figure 10. The bilayer constituents and thicknesses can be chosen on the basis of their reaction temperatures and their propagation rates (typically 1-10 m/s). The propagation rate is typically inversely proportional to the bilayer thickness [19].

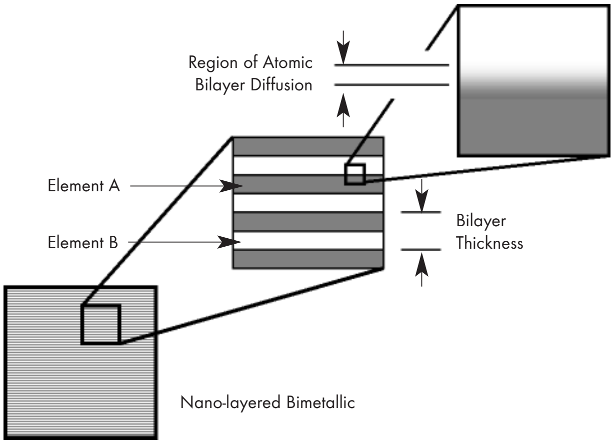


Figure 10. **Nanocomposite Illustration Showing Composition, Bilayer Thickness, and Bilayer Diffusion Region.**

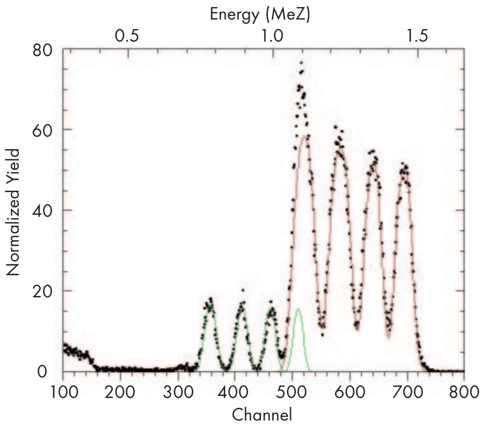


Figure 11. **RBS Spectrum of ARL 4-Period Array of Sputtered Ni [85 nm]/Al [45 nm] Nano-Composite Stack.**

Nanocomposite stability appears linked to the sharpness of bilayer interfaces on the nanometer scale. Typical bilayer systems are aluminum/nickel or aluminum/titanium with the total bilayer thickness in the 0.1-0.2 mm range. ARL has investigated atomic diffusion at the bilayer interface and its effect on propagation velocity and initiation sensitivity. Figure 11 is an energy spectrum of 2 MeV helium ions elastically backscattered via Rutherford Backscattering Spectrometry (RBS) from a four period bilayer stack of Ni/Al nanocomposite. The periodic variation in yield is directly due to the two element composition of the nanocomposite and can be converted into their relative thicknesses and interfacial diffusion, which governs exothermic rates and initiation sensitivities.

SUMMARY

Research and development of materials fabricated through newer processing methods will produce the next generation of large caliber projectiles and produce non-lethal weapon technologies. These processing techniques, in some cases, open the door for alternate materials due to the enhanced performance that may be achieved, especially for nanostructured materials. The Army Research Laboratory is leading the way to develop materials and technologies for large caliber projectiles that will result in a more effective force for future operations.

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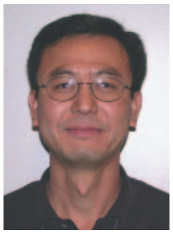

Mr. Kyu C. Cho is a Materials Engineer at the Army Research Laboratory in Aberdeen Proving Ground, MD. He holds a BS in Mechanical Engineering, and a MS in Materials Science and Engineering, both from Worcester Polytechnic Institute (WPI). He joined the Army in 1994. His current work includes development of refractory metals for ordnance applications with a particular emphasis on synthesizing bulk nanocystalline refractory metals by particle consolidation. He has coauthored more than 35 publications.

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Dr. William Drysdale has been employed by the Army Research Laboratory and, prior to that, the Army's Ballistic Research Laboratory for a total of 30 years. His specialty has been structural integrity and integration of projectiles during launch and flight. He has a PhD in Aeronautical and Astronautical Engineering from the University of Illinois.

Since 1985, Dr. Laszlo Kecskes has been a Research Physical Scientist with the US Army Research Laboratory, Aberdeen Proving Ground, MD. His primary responsibility relates to the development, evaluation, and use of novel amorphous alloy materials in advanced kinetic energy penetrator concepts. Dr. Kecskes is the lead for a multidisciplinary team of scientists and engineers from government, industry, and university, utilizing fundamental physics, chemistry, and materials science principles that recently demonstrated a new ballistically superior tungsten (W)-based composite, based on the use of amorphous alloys.

Mr. Michael Minnicino currently works on a number of programs; including nano-layered bimetallics for debonding, frangible munitions, and other munition structural analyses related to interior ballistics at WMRD. From 2002-2004 he was employed as a Geo-Centers, Inc. contractor and was subsequently hired as a mechanical engineer at the ARL Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD. He earned a BS (2000) and a MS (2002) in Mechanical Engineering, both from Pennsylvania State University.

Dr. Michael R. Staker is a registered professional engineer, a registered patent agent and patent law practitioner. He works at ARL in the Ordnance Materials Branch conducting basic research on various topics of interest to the Army including advanced armor, kinetic energy munitions, high strain rate behavior of materials, uranium metallurgy, metal hydrides, thermodynamics, phase diagrams, calorimetry of phase changes and low energy nuclear reactions. He has published over 50 papers and reports; and holds several patents related to failure analysis, armor and kinetic energy penetrator materials and their behavior at high strain rates. Dr. Staker earned his PhD from the Massachusetts Institute of Technology.

Advanced Materials Bring Electromagnetic Gun Technology One Step Closer to the Battlefield

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INTRODUCTION

Electromagnetic (EM) launch has the potential to revolutionize a wide range of defense applications including tank gun, artillery, and aircraft launch. The EM launch concept has been demonstrated as the Army and other services have recently fabricated and tested several prototype gun systems. Advanced materials and manufacturing techniques played a major role in this achievement [1]. The engineering development necessary for a fieldable system is considerably more difficult than the laboratory systems. The design of the current laboratory system is not fully optimized from a mechanical and materials performance aspect. Application of advanced materials with innovative design concept in various critical components of the system is in progress under the current program at the US Army Research Laboratory (ARL) and Armament Research and Development Center (ARDEC).

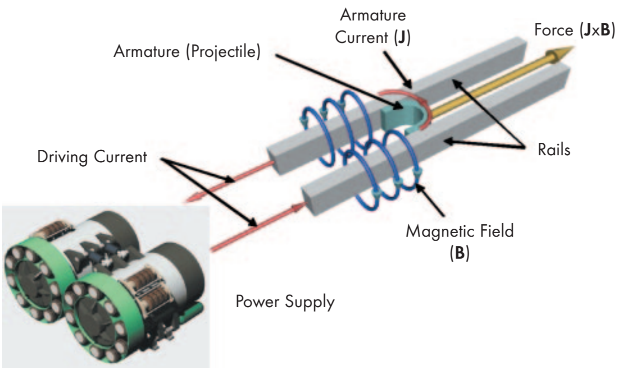


Figure 1. A schematic of an Electromagnetic Gun. Current Flowing in the Rails Creates a Magnetic Field That Interacts with the Current in the Armature to Generate a Lorenz (JxB) Force. The Force Acts to Accelerate the Projectile Forward.

ELECTROMAGNETIC LAUNCH TECHNOLOGY

The schematic in Figure 1 illustrates the essential components of an electromagnetic gun system, including a pulsed power supply, a rail gun, and a projectile package. A current level of one million amps is generated from the pulsed power supply, a capacitor bank, or a rotating machine, providing propulsion energy for the gun system. The current flows from the gun breech through one rail, across the armature (part of the projectile package), and then returns through the other rail. As a result, an intensive magnetic field is generated perpendicular to the plane of rail/armature. Accordingly, the current flowing through the armature and rails interacts with the magnetic field and results in an electromagnetic (Lorenz) force. The forces generated during operation act to accelerate the projectile forward and push the rails apart. In theory, the projectile can be accelerated to any velocity, but it is limited by the physical constraints of material strength and structural design.

Rotating machinery has been identified as the most feasible solution to provide pulsed current at several million amps. The machine converts kinetic energy into electrical current over a short duration equivalent to interior ballistic cycles of traditional guns. Within weight and volume design constraints, the machine has to store energy as well as deliver enormous power. Figure 2 shows the progress of pulsed-power devices resulting from recent engineering design and materials advancements. One is an extremely large homopolar generator and inductor built in 1985, which stores 60MJ of energy. The other is a subscale compulsator that stores 20MJ energy and was developed by Scientific Applications

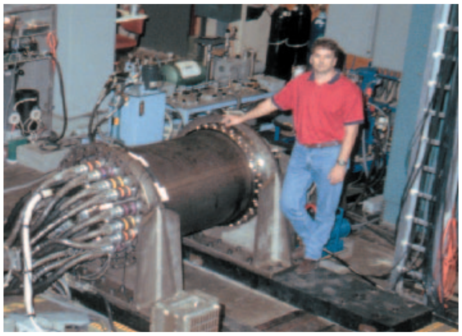


Figure 2. Homopolar Generator (1985) and Subscale Compulsator (1998) Developed under Army Contracts at the Center for Electromechanics, the University of Texas in Austin.

International Corporation and the University of Texas under the Army Research Laboratory's electric gun program in 1998. The compulsator achieved most of the performance as predicted, although this required many iterated modifications of design and engineering development. In terms of mechanical performance, the machine was spun up to 12,000 rpm and 1.0 J/g energy density, defined as energy delivered divided by total mass of the system. For an objective system, however, it will need a much higher energy density and storage capability. This will require a higher spin rate, packing ratio, and material performance due to high stress and strain developed in the machine.

There have been many EM rail launchers built in the past two decades. Most of them were built as laboratory launchers and designed mainly from an electrical performance aspect. Figure 3 shows the test fire of a 90-mm rail gun developed by Maxwell Corporation, sponsored by the Defense Nuclear Agency in 1989. Like most EM guns built in the past, the rails were supported by a massive laminate steel containment with a very large breech (not shown in Figure 3). The muzzle blast caused by electrical short as the projectile passed through the muzzle needs to be further reduced for a tactical application. A few tactical weapon-like guns were developed in the last fifteen years. Composite containment and lightweight insulator materials were used to enhance gun designs. However, they either lacked performance or were short in service life. Currently, a tactical EM launcher is being developed at ARL. Advanced polymer composites, lightweight reinforced metals, and various cladding and coating materials are considered for the gun tube, breech, and muzzle shunt construction. In addition, manufacturing techniques and assembly procedures are being investigated.

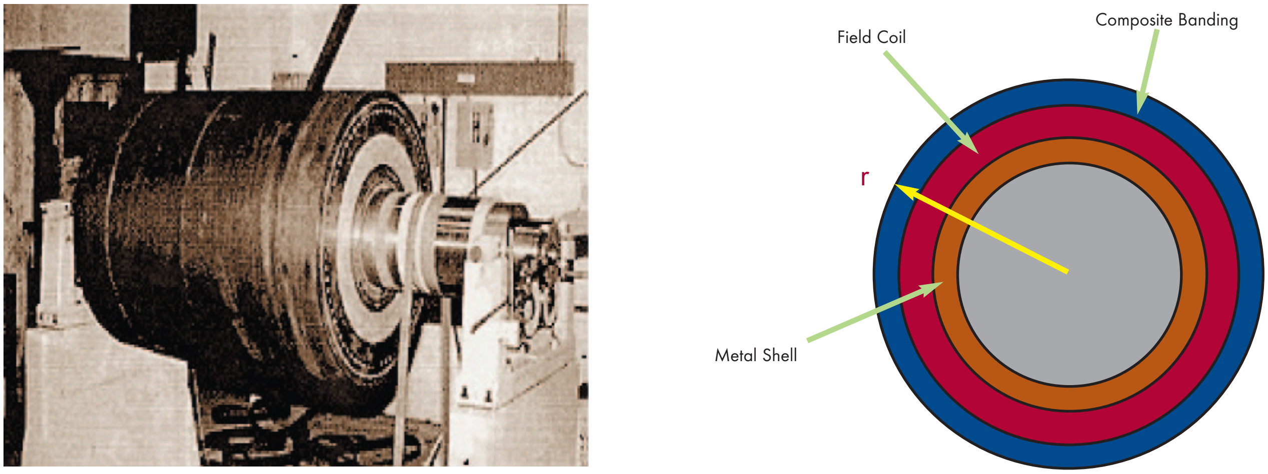
Figure 3. 90-mm Rail Gun Test.

Figure 4. An EM Projectile for Rail Gun Launch.

Figure 4 shows an EM kinetic energy projectile. A major difference between an EM launch package and a conventional projectile is the armature that allows current to pass through the projectile package by connecting two rails electrically. The interface between the projectile and rails has been the focus of recent research. The rapid change of material properties due to the high intensity of current, heat, and stress does not occur in conventional material applications and is a challenging materials research issue.

PULSED POWER MATERIALS

As an energy storage device, the rotating machine must be operated at high speed to achieve the required energy density. Centripetal forces from high-speed rotation cause significant stresses and deformations in the rotor. During discharge, the stored energy is extracted to generate electric current for launching projectiles from a rail gun. Magnetic forces are also not trivial,



a)

b)

Figure 5. a) Rotating Machine. b) Schematic of Rotor Cross Section.

as millions of joules of energy are extracted from the rotating body within a few milliseconds. Additional stresses are generated from the deceleration. It is a considerable challenge for advanced materials and machine design, especially since a long service life span is required for the rotor, stator, and converter.

The rotor in Figure 5(a) is composed of three parts from the aspect of mechanics as shown in Figure 5(b). From the inner to the outer radius of the cylinder, there is a strong metal or composite substrate, a relatively compliant field coil (FC), and composite banding that provides the essential structural integrity. The FC is generally made of a soft electrical conductor insulated and embedded in a fiberglass epoxy composite. Structurally, it is mostly a parasitic mass supported by the composite cylinder and the substrate. The composite cylinder is primarily reinforced in the circumferential direction to provide strength and stiffness to the rotor that is subjected to centripetal and EM forces. In order to achieve the required performance, the rotor has to operate at high stress and strain in comparison to a utility generator. The mechanics of the composite rotor have been investigated and reported previously [2].

In order to overcome the strength requirement of the FC, the rotor is designed with significant built-in prestress through a "press-fit" procedure during fabrication. Accordingly, the composite band is in a state of tension prior to rotation, while the FC is under a state of compression. The pre-compressive stress in the FC can compensate part of the tensile stress while the rotor is at speed. This is a key process of the design to enhance the mechanical performance and fully utilize the tensile strength of composite materials. However, centrifugal force from high-speed rotation can be large enough to generalize tensile stress, deformation, and radial growth in the FC even though it is pre-stressed in compression.

High-strength and high-temperature materials with innovative design methodologies are currently being developed to enhance machine performance. For example, high strength carbon fibers, such as T1000 and IM9, and high strength conductor materials are considered for construction of the composite shell and the FC conductors, respectively. Table 1 illustrates recent developments to achieve high strength composite shells. A composite cylinder with various fiber volume fractions was fabricated and hydro-burst tested. High circumferential strengths can be obtained by packing more fiber (high fiber content) in the composite cylinder. Additional tests were also performed to evaluate shear and transverse properties of composite cylinders, since composite materials are anisotropic in nature. A high fiber volume fraction generally degrades these properties. The goal of future development is to achieve the maximum hoop strength with balanced shear and transverse properties.

Table 2 illustrates the properties of potential conductor materials for EM gun applications. The 6061 aluminum alloy, with moderate electrical conductivity and mechanical properties, is considered as the baseline material for the field conductor. It is a very complex materials problem to determine a suitable conductor material. Electrical conductivity, mechanical properties, densities, materials availability, and manufacturing

Table 1. Hydroburst Test Results Showing the Relation of Strength and Translation Efficiency to the Fiber Content of Composites [2].

Banding	Material	Fiber Content (% vol)	Burst Strength (ksi)	Theoretic Max Strength^a (ksi)	Translation Efficiency^b (%)
Standard	T1000/epoxy	60	475	540	85.6
Medium Fiber Vol.	IM9/cyanate ester	67	518	620	83.5
High Fiber Vol.	T1000/cynate ester	76	585	703	83.2

[a] Theoretic strength = 925 ksi (high fiber volume for each banding); 925 ksi is a general number (T1000) used for comparison.

[b] Translation efficiency = burst strength/theoretic strength.

Table 2. Mechanical and Electrical Properties of Potential Conductor Materials.

Material	Yield Strength (ksi)	Ultimate Strength (ksi)	Modulus (msi)	Density (g/cm^3)	Conductivity (IACS)* (%)	Resistance (10^{-9} Ohm-m)
6061 T6	40	45	10.0	2.70	43	40
7075 Al	73	–	10.2	2.85	33	–
Gigas 30 Al	102	110	10.3	2.85	(25)	–
Gigas 24 Al	75	–	12.8	2.95	(25)	–
Al/Al_2O_3 (45%)	–	180	24.0	3.4	34	66
Al/Al_2O_3 (30%)	–	120	20.0	3.2	43	–
Cu/Ultra SiC (30%)	–	(300)	(20.0)	(8.0)	(70)	–
Cu/Al_2O_3 (1.1 wt%) particle	80	–	–	8.9	78	–
Pure aluminum	–	–	–	–	65	26

Parentheses indicate theoretical values

feasibility are parameters to be evaluated for the potential conductors in terms of the final machine performance.

The 7075 series aluminum has high strength and is commercially available but it is slightly low in conductivity (33% IACS*). Recently, a relatively new aluminum alloy 7055 was considered for the application because of its high strength (90 ksi) and high conductivity (38% IACS). Efforts continue to enhance the conductivity of these high-strength aluminum alloys while maintaining excellent mechanical properties.

Non-conventional materials such as fiber- and particulate-reinforced metals (composite conductor) are also being evaluated. The aluminum oxide (Al_2O_3) fiber-reinforced aluminum can be fabricated by protrusion, press-molding, and press-infiltration. The properties of a composite conductor can be tailored by varying the fiber and matrix contents to meet the mechanical and electrical requirements simultaneously. For example, for an Al_2O_3-reinforced conductor, the aluminum oxide fiber content can be varied from 45% down to 30%. The electrical conductivity then increases from 34% to 43% IACS while the mechanical strength decreases from 180 to 120 ksi. The composite conductor gives the engineer flexibility to design a machine. However, manufacturing processes for large scale and complex components still need to be developed for the composite conductors.

Rate of fire is a critical performance metric for any tactical gun system. The pulsed power supply will need an active cooling mechanism and efficient thermal management. However, the thermal capability of materials drives the operating temperature of the machine. The most thermally-sensitive component in the rotating machine is the electrical insulation, which is a polymer-based materials. Research has been conducted on high temperature polymers and their composites to replace the baseline material of glass/epoxy. Particularly, the study emphasized thermal degradation, creep, and durability of the potential insulation materials. The objective is to push the operating temperature up and ease the design difficulty of the machine cooling system. Similar efforts were conducted for the armature and supporting structure of the stator.

The alternating current output from the rotating machine is converted into direct current by a converter. Switch materials development is another area that has great potential to impact the machine size, weight, and performance. It is a considerable challenge to convert several million amps of current, even for a short pulse using solid state switches. Silicon (Si) is the baseline and the state-of-the-art switch material produced at a reasonable cost. Resources have been invested in building a compact and efficient converter with silicon switches.

Silicon carbide (SiC), a wide bandgap semiconductor, has been frequently mentioned as a candidate switch material for the EM gun application. Compared to the current Si switches, SiC switches can be operated at a relatively higher temperature. Accordingly, there is a significant weight savings (vs. Si) with improved performance at a higher operating temperature and breakdown voltage although it is currently limited by the wafer size and materials cost. A research effort to leverage other DOD programs was conducted in two areas related to SiC switch development including durable high-power ohmic contact materials design and surface-smoothing techniques to reduce the cost of a SiC wafer. A nickel/tungsten-silicon/titanium/platinum composite contact for n-SiC (doped SiC having free electrons which carry electric current) was investigated with the annealing temperatures up to 1000°C. Results showed the composite contact maintains the desirable electrical properties and possesses excellent interfacial, compositional, and surface properties required for high-power and temperature applications. A surface-smoothing process for SiC wafers was investigated by using a gas cluster ion beam. The technique may be applied to smooth low-cost SiC epitaxial layers cleaved from costly SiC wafers. A successful development of this process can allow production of SiC wafers at a significantly lower cost.

LAUNCHER AND PROJECTILE MATERIALS

Three EM rail gun designs built in the past are illustrated in Figures 6. They are a laminated steel barrel [3], a 90 mm 9 MJ range gun [4], and the Cannon-caliber electromagnetic launcher [5], respectively. Many similarly laminated barrels have been designed and used in the laboratories because they are electrically efficient and easily assembled and disassembled (for replacing rails, insulator, etc.). The laminated steel construction provides good circumferential stiffness and confinement for the rails and insulator. However, it lacks strength in the longitudinal direction and is too heavy for a tactical application. The 90-mm, 9-MJ gun in Figure 6(b) is another version of a laminated steel core structure utilizing a compos-

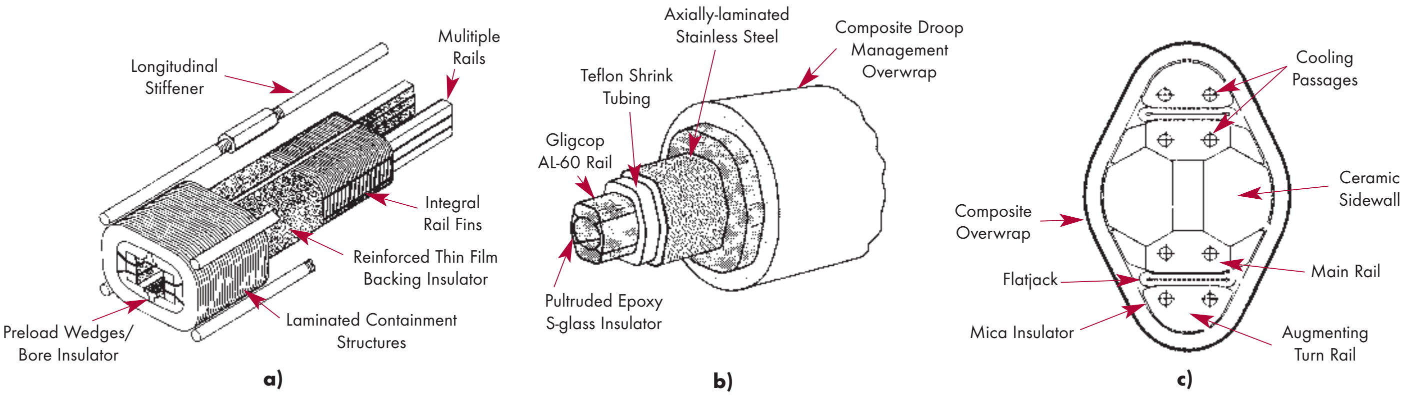


Figure 6. a) Laminated Steel Rail Gun [3], b) 9MJ Range Gun [4], c) Cannon-caliber Rail Gun [5].

ite overwrap for axial stiffness and strength. The Cannon-caliber gun uses a steel flatjack as a prestress mechanism to keep the components in intimate contact during launch. Concerns for this type of design are the possible loss of preload over time and the feasibility for a tactical weapon system.

Based on the lessons learned from the previous design, the Army has recognized a need to develop an integrated structure that provides electrical insulation, support, and stability of the rails within a weight limit [6]. The electromagnetic force in rail guns is not axisymmetric, such as those in conventional guns that use propellants. Instead, the forces concentrate only on the rails and part of the containment/support structure. The electromagnetic forces and possible plasma pressure typically vary in time and space along the length of the rail gun during launch. During a hypervelocity launch, the dynamic response of the gun is highly transient in nature. Accordingly, rail guns cannot possibly be constructed from a single material and a simple geometry due to the severe electrical and mechanical requirements. It is therefore a significant challenge to design the individual components and the interfaces between components in a rail gun, particularly to optimize the material selection to achieve balanced electrical and mechanical performance.

The previous rail guns all had a relatively short service life compared to conventional cannons. Test results show that most

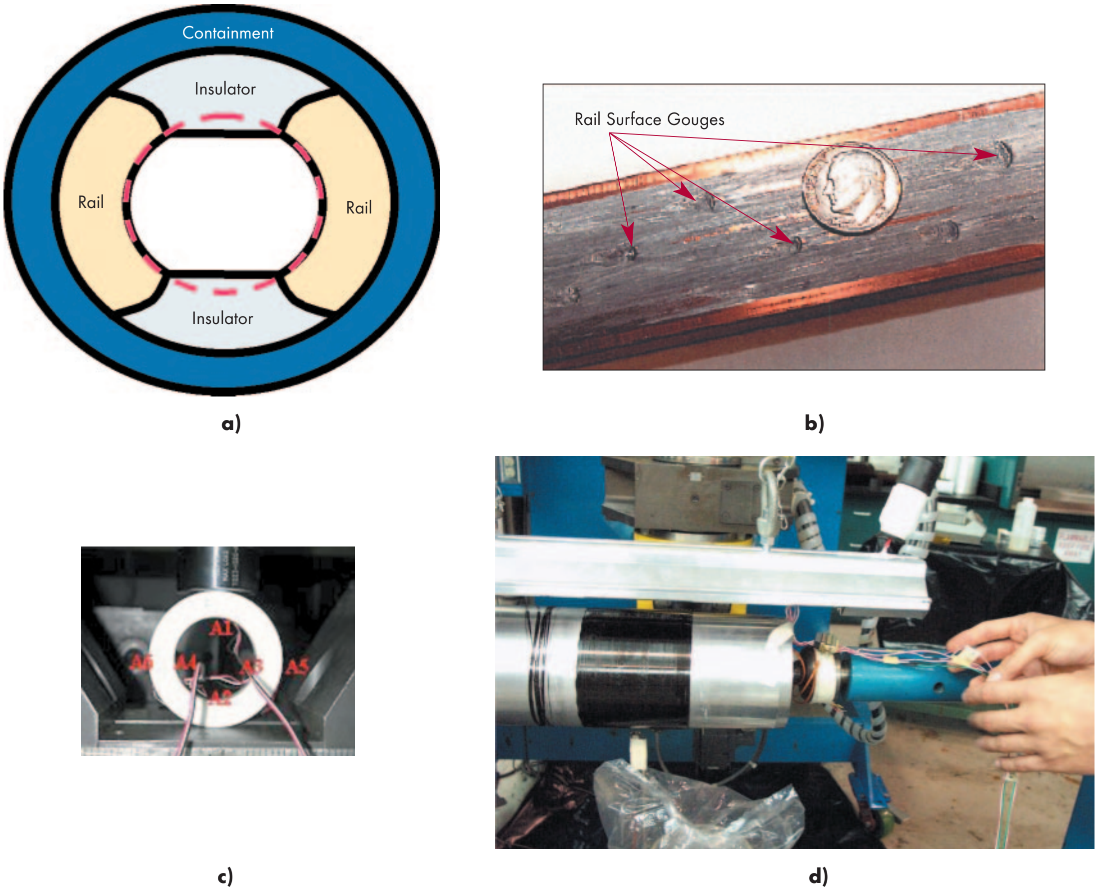


Figure 7. a) Schematic of a Rail Gun Cross Section, b) Copper Rail Gouging, c) Ring Test of Insulation Material, and d) Tension Winding Experiment [7].

failures occur in the rails and insulators, such as gouging and melting of the rail surface, cracks developing in the ceramic insulator, delamination in the glass insulator, and transition-associated failures. These failures are influenced by material performance (i.e., strength, melting temperature, hardness, etc.), as well as structural support from the containment.

A schematic of the rail gun cross section is shown in Figure 7(a). Three major components including rails, insulators, and containment have to be integrated. Figure 7(b) shows gouging of a copper rail due to thermal, electrical, and mechanical loads resulting from armature/rail interaction. Extensive tests have been performed on the rail materials such as copper, aluminum, alloys, and metal composites. There is no single conductor material so far that can satisfy all requirements in various rail sections. One approach is to build the rails with different materials for various sections. Figure 7(c) show a ring-test setup for evaluation of insulator material. Various non-conductive polymers and composites have been evaluated. High-strength composites have been identified as possible candidates for the containment. Figure 7(d) illustrates the tension winding of the composite overwrap. The test setup measures the radial pressure that can be utilized for the application of the preloading mechanism.

The projectile armature, which current passes through, interacts with the rail surfaces. Heat and stress resulting from electrical resistance, friction, and concentrated magnetic fields cause the material degradation at the surface of the armature. Aluminum alloys are commonly used for the solid armature of a projectile because of high electrical conductivity and strength. Various metals and alloys are being evaluated in addition to the configuration of the armature and current distribution in the projectile. A continuous study is needed to explore new alloys or multi-material integrated conductors.

An EM projectile can be designed as a base push (artillery type) or a mid-ride as in a conventional kinetic-energy projectile. Accordingly there are supporting materials, such as sabots, to provide structural support and reliable accuracy to hit the target just like conventional projectiles. These supporting materials have property requirements similar to those for conventional projectiles.

SUMMARY

Electromagnetic launch railguns require the development of advanced materials and material processes in order to scale-up prototype technology demonstrators into fielded systems. Significant challenges must be tackled to design components able to meet the combination of material properties required. The Army Research Laboratory and the Armament Research and Development Center are developing new technologies in an effort to solve these challenges.

NOTES & REFERENCES

* IACS stands for International Annealed Copper Standard. It is a measure of conductivity used to compare electrical conductors to standard copper-wire and expressed as a percentage. Standard copper wire is 100% IACS which equals a conductivity of 58 megasiemens per meter (MS/m).

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Dr. Jerome T. Tzeng joined US Ballistic Research Laboratory/Army Research Laboratory in 1991. He works in the area of composite material for ballistic applications, such as advanced projectiles and gun systems. His current research has concentrated on the electromagnetic rail gun including pulsed power machine and rail gun since 1995. Prior to the civil service, he worked with DuPont and Bechtel Corporation. Dr. Tzeng is also actively involved in the basic research, as a journal editor and an adjunct professor at Drexel University. He has authored about 100 technical publications. Dr. Tzeng received his PhD in engineering mechanics from Virginia Tech and Master in civil engineering from Rice University.

Dr. Edward A. Schmidt received his PhD from the Polytechnic Institute of Brooklyn in 1969. Since that time he has worked for the Army, either on active duty or as a civilian. His areas of technical interest are unsteady flow, aeroballistics, tank ammunition, and recently electric guns. Currently, he is the Manager of the ARL Electromagnetic Gun Program.

Novel Energetic Materials for the Future Force:

The Army Pursues the Next Generation of Propellants and Explosives

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INTRODUCTION

The changing nature of international conflicts requires the development of new war-fighting capabilities within the Department of Defense. It is recognized by the US technology community that advanced energetic materials with substantially enhanced performance, reduced sensitivity, and controlled (or manageable) energy release will be critical enablers for precision weapons. In the past ten years revolutionary breakthroughs in munitions technology were made through aggressive development of advanced energetics by the worldwide community.

Much of the synthesis effort over the past 50 years has been directed toward compounds that contain only carbon, hydrogen, nitrogen, and oxygen (CHNO explosives). For most of the past 40 years the benchmark against which high energy CHNO ingredients have been compared was cyclotetramethylenetetranitramine (HMX).

In 1987, a new compound, hexanitrohexaazaisowurtzitane (CL-20) was synthesized for the first time by the Navy. It is more energetic than HMX and does not have most of the instabilities of other high energy compounds that have precluded their use. The traditional procedure for formulating new materials such as CL-20 has been largely guided by intuition, experience, and testing, relying heavily on trial and error. The ever-increasing need for rapid deployment of emerging weapons systems dictate a streamlining of the development process of advanced high-energy insensitive materials tailored for optimal performance in advanced weapons.

Developments in computational chemistry and physics based modeling using High-Performance Computing (HPC), chemical synthesis and formulation, and materials science are providing the key factors that will provide breakthroughs in the performance of energetic materials. The DOD HPC network and advanced modeling science and technologies afford a critical means to rapidly close the technology gap and expedite the design and prediction of new revolutionary advanced energetic materials (Figure 1).

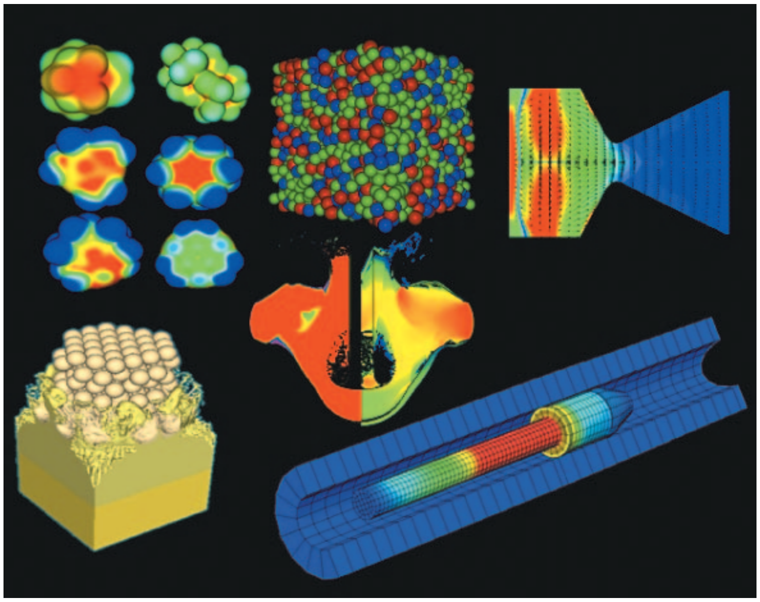


Figure 1. **High-Performance Computing Modeling and Simulation of Energetic Materials and Advanced Propulsion.**

ADVANCED GUN PROPELLANT MATERIALS

The Army initiated a significant effort in the design, formulation, and fabrication of future insensitive high-energy materials for Future Force weapons and is extensively leveraging science and technology from the national energetics community. A key objective is to develop advanced gun propellants having high energy release, increased burning rates, improved mechanical and environmental properties using nanomaterials and other novel high energy ingredients, while ensuring compliance with insensitive munitions requirements. The reduction in carbon content is also favorable as it reduces degradation and wear of steel gun barrels. Recent work in synthesis and characterization of new novel energetic materials has centered on the following energetic materials:

- Nano-particulates (metals, crystalline solid organics)
- Metal hydrides
- CHNO and CHNOF compounds
- All-nitrogen species
- High-nitrogen species
- Boron containing compounds (e.g., carboranes)
- Energetic liquids with potential as monopropellants

Gun propellants in layered disk geometries are of interest for applications in which an outer, slower burning layer is sandwiched with a center, faster burning layer to produce what commonly is referred to as “fast-core” propellant using chemical progressivity. The advantage of the fast-core concept is that at times early in the ballistic cycle before the projectile has moved significantly, a lower volume of gas is generated by the slower burning layer, so that pressures do not exceed the maximum pressure sustainable by the gun system. However, once the projectile begins to move and the volume available for expansion of the propellant gases increases, the inner, faster-burning core provides a greater level of gas to maintain work against the projectile for improved performance over that achievable with a uniformly-burning material. In practice, with energetic materials currently available, realization of this concept requires charge designs for which aspect ratios (length/diameter) are an order of magnitude less than in conventional charges and the individual layers are nominally 2-3 mm thick. This makes the mechanical properties requirements much more stringent than for colayered propellants.

Figure 2. **Advanced Gun Propellant Formulations with Energetic Nanomaterial Ingredients.**

High Nitrogen Compounds

High nitrogen compounds, including azo-tetrazolates, dinitramide salts, tetrazine derivatives, amino-azo-furazans, guanidine salts and diazido-nitrazapentane, have been investigated as burning rate modifiers for energetic formulations. Formulations using high nitrogen compounds have increased the burning rate differential to 3:1 between inner and outer colayered formulations required for performance improvements by chemical progressivity. Additionally, these formulations result in lower gas temperatures during expansion into high flow areas and increased ratio of nitrogen to carbon monoxide in the combustion products, compared to conventional propellants. Thus, wear and erosivity is reduced, increasing gun barrel lifetimes by reducing the dissociation of carbon monoxide and subsequent adsorption/absorption of carbon into the steel barrel [1].

New Energetic Binder Components

Energetic thermoplastic elastomers (ETPEs) are being considered for a wide range of applications, including binders for large caliber gun propellants. In addition to the fact that they can be processed without the use of solvents that pose health problems, they also offer potential performance improvements in weapon systems. The oxetane chemistry has been the basis for the polymer backbone, to which energetic pendant groups have been attached, including nitro, nitrate ester, nitramine, and in particular, the azide group. The ETPEs enable compositions with different energetic crystals to be readily processed into a stable layered geometry with good adhesion and without problems associated with plasticized propellants, such as diffusion between layers of different compositions, and oxidizer migration to and crystallization on the outer surface. The azido-ETPE polymers are of particular interest because of potential for high burning rates afforded by the azide group, and also the higher nitrogen content has been shown to help reduce the adverse effects of gun erosion.

Plasma Ignition Technologies

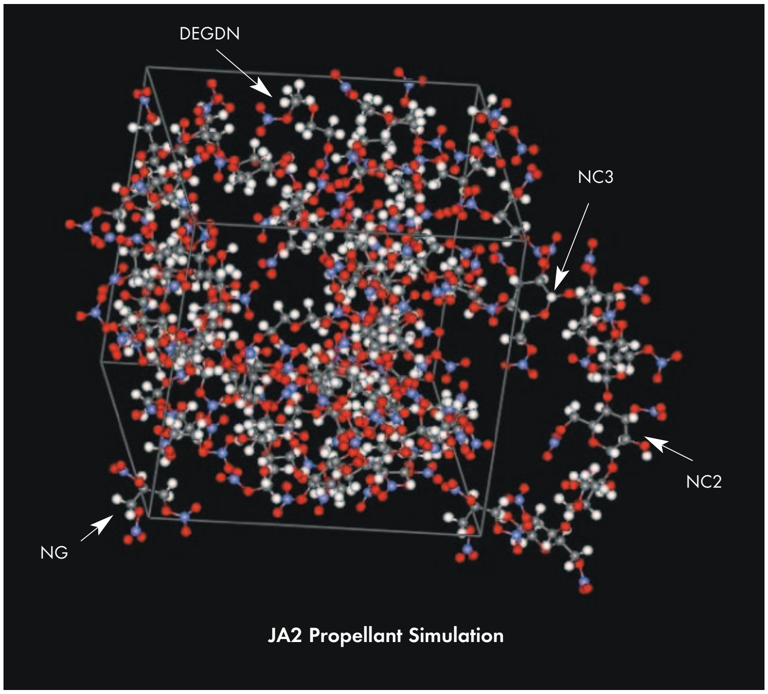
Electrothermal-chemical (ETC) and electrothermal ignition (ETI) gun technology is an advanced gun propulsion concept that utilizes both chemical and electrical energy for initiation of high-energy, high-loading density propellants to provide increased performance, lethality, and range. ETC gun propulsion technology utilizes electrical energy to form a high-temperature, high-energy plasma that augments the control and release of chemical energy stored in advanced high-performance propellants, in order to achieve significant performance enhancements over existing conventional guns. ETC technology offers many advantages over conventional gun propulsion including:

- An ability to tailor the pressure (thrust) of the propulsion gases of the chemical reaction through the electrically generated superheated plasma and propellant gases, resulting in increased projectile range or reduced acceleration-loading on the projectiles.

- An extremely reproducible ignition, providing precise and predictable muzzle velocities and gun tube dynamics, culminating in increased ordnance on target and less ordnance required to achieve a given hit probability, and gun recoil mitigation.

Nanoenergetic Materials

Energetic nanomaterials offer the potential of extremely high heat release rates, extraordinary combustion efficiency, tailored burning rate, and reduced sensitivity. However, exploiting these possibilities requires an understanding of: (a) properties of the individual nanoscale material, (b) the interaction of the nanomaterial with the matrix; (c) the interface behavior of the nanomaterial and the matrix; (d) energy release and dynamics of combustion and initiation processes on such short length scales (e) high-rate synthesis and practical scale-up of nanomaterials. Nanoscale energetic materials are currently being exploited to improve the combustion efficiency of advanced gun propellants, Figure 2.



(DEGDN – Diethylene Glycol Dinitrate, NG – Nitroglycerin)

Figure 3. **The First Molecular Model of JA2 Advanced Gun Propellant.**

Nanometals

The primary nanometals being considered for energetic material applications are aluminum and boron. Aluminum has long been an important burn rate accelerator for rocket propellants, especially in the nanoparticle form. The hope is that burning rate promotion obtained at modest pressures in rocket propellants will be realized for the high pressure regime of gun propellants. An oxide coating naturally forms on aluminum which detracts the energy available to the system. Ultra-high resolution microscopy techniques have enabled the imaging of an oxide surface 2.5 nm thick, mainly amorphous, but with crystalline layers which appear to exfoliate[2,3].

Prompt gamma neutron activation analysis has revealed greater levels of hydrogen and water present in nano-aluminum than for flake aluminum, which could enable porosity. Additional elements, which may also modify the initiation and energy release of aluminum, have been detected in nano-aluminum by X-ray Photoelectron Spectroscopy. In fact, since manufacture of nano-aluminum relies on recrystallization and quenching of aluminum from the high temperature plasma condition, doping of the bulk aluminum and/or oxide surface offers a tool for tailoring the atomic scale structure of nanometals.

Boron hydride compounds demonstrated great potential as burning rate accelerators, but spontaneous ignition of these materials rendered them too hazardous for practical application. Recently, ARL produced the ability to synthesize boron-based nanoparticles [4]. Future efforts will address coating particles of boron with other energetic materials which offers promise for taking advantage of the high heat of combustion and potential for burning rate promotion of nanoboron.

Extended Carbon Structures

Extended carbon structures, such as carbon nanotubes (CNTs) are being investigated for application to controlled performance (through burning rate modification and the increased energy of strained structures), and improved insensitivity (by encapsulation to control particle size and to buffer the effects of accidentally applied stimuli). The structure of CNTs gives them unique properties, including high thermal and electrical conductivity, and a very high aspect ratio, since their diameters are nanoscale while their lengths can be micro-scale. Their high conductivities and aspect ratio make them attractive candidates for serving as a type of “mini-fuze” distributed throughout energetic materials, yielding the potential for burning rate and combustion tailoring with very little parasitic mass.

Through the use of carbon nanotubes it may also be feasible to enhance the specificity of a propellant formulation to initiation due to the high electron density and conductance localized on the nanotube walls. Moreover, because of their unique structure, they may be used for confining energetic molecules in a nano-matrix with a positive effect on sensitivity properties.

Nano-Crystalline Energetic Materials

Anti-solvent recrystallization techniques, in both the liquid and supercritical phases, as well as rapid expansion of supercritical solutions, are being used for preparing nanocrystals of energetic oxidizers. Ultimately the goal is to prepare ultrafine particles with tunable particle size and morphology as well as a uniform size distribution. Crystals with fewer voids and uniform morphology are expected to yield decreased sensitivity results through the reduction of sites for possible hot spot formation that can lead to energetic material initiation. Nanocrystals of energetic compounds including, but not limited to cyclotrimetylenetrinitramine (RDX) and CL20 have been prepared and characterized [5]. Although optimization of process-

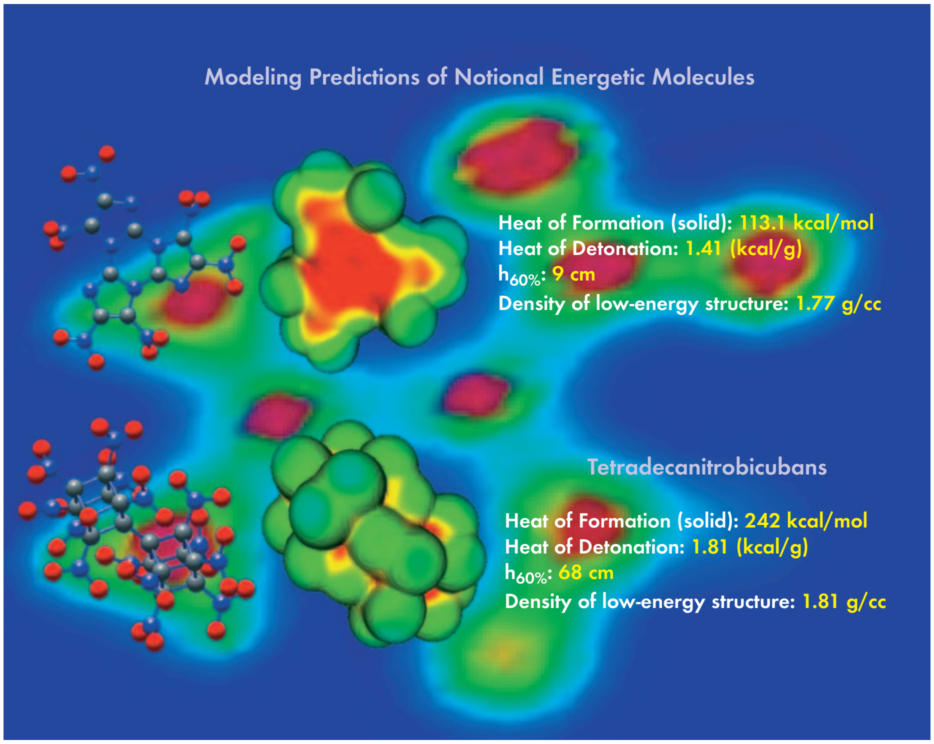


Figure 4. Theoretical Chemistry Predictions of Novel Energetic Molecular Properties.

ing variables of the various techniques is ongoing, preliminary characterization of the products generally show fewer irregularities and lower void content.

Smart Design of Energetic Materials Using Theoretical Chemistry

An accurate and reliable predictive capability can provide the information and insight needed for the intelligent design of energetic materials. The refinement and implementation of key computational chemistry methods are being used in a model-based design process for new energetic materials to achieve a process for atomistic model-based screening of notional materials. Included are methods that involve quantum mechanical predictions of properties of isolated and condensed phase explosives that are related to their performance and vulnerability. Other methods involve the utilization of intermolecular interaction potential energy functions that can be used in molecular simulation to explore the response of a material to initiation events. The methods and software are being developed within the Army Research Laboratory mission program and in conjunction with the DOD HPC Modernization Common High Performance Computing Scalable Software Initiative to provide an automatic and seamless set of procedures for the simulation and screening of potential energetic materials. In addition, molecular models are being developed to predict chemical and physical properties of propellant formulations such as JA2 used in 120 mm tank ammunition, Figure 3.

Quantum Mechanical Predictions of Properties of Notional Materials Associated with Performance or Sensitivity

Computational tools have been developed that are based on quantum mechanical calculations that describe relationships between the quantum mechanical properties of an isolated molecule and its behavior on the macroscale [6-8]. The predictive methods all use quantum mechanical predictions of the electrostatic potential that surrounds an isolated molecule. The first two computational tools that were developed have reasonably predicted Heats of Formation [6] and Detonation [7] for a large variety of CHNO explosives. The most recent application of quantum mechanical predictions of isolated molecules has shown that the electrostatic potentials for surfaces of equal electron densities surrounding CHNO explosive molecules are useful guides in assessing the degree of sensitivity of a CHNO explosive [8].

Crystal Structure/Density Prediction Using Molecular Packing

The property of solid-state density, required to assess accurately the ideal performance of gun propellants in current interior ballistics calculations, is not obtained from computer calculations but rather from known experimental values. The reliance on external sources for something as important as density is, of course, an unacceptable situation for a practical and widely applicable modeling system. A procedure for the prediction of possible crystal structures for an unknown compound has been developed [9], which accounts for factors such as the structure and conformation of a molecule, probable crystal packing arrangements and packing efficiency. The so-called "model-MOLPAK-WMIN" procedure consists of three steps: (1) construction of a reasonable three-dimensional model for the compound of interest (the search probe) followed by ab initio quantum mechanical geometry optimization; (2) determination of a number of possible crystal structures for the search probe (MOLPAK program); (3) refinement of the unit cell parameters (WMIN program[10]), search probe orientation and position by lattice energy minimization for the best of the crystal structures derived in Step 2, using a model function to describe interatomic interactions. The model being employed has been shown to reproduce the crystallographic parameters of over 80 crystalline systems, whose molecules contain functional groups common to explosives [11]. The suite of molecular simulation tools are now being employed to a priori predict properties on notional (new) candidate energetic materials, Figure 4.

SUMMARY

Novel energetic materials hold the promise of providing the following payoffs: (1) mission-enabling lethality at range by enhanced lethality and effectiveness and (2) crew survivability under ambush for the full range of Future Force weapons. The increased energy and efficiency of new energetic materials concepts will enable increased lethality through additional propulsion energy or impulse on the target. Alternatively, the same amount of energy as delivered by existing systems could be delivered to the target using less energetic material or a multipurpose energetic material, thus minimizing logistics burdens.

Decreased sensitivity of energetic materials will significantly reduce platform vulnerability. By managing the energy release of specific systems, it will be possible to maximize ballistic efficiency in advanced gun systems while also increasing the performance of compact rockets/missiles. In addition, it may be possible to minimize collateral damage with the use of powerful precision strike weapons against hard targets or targets surrounded by noncombatants, and also maximize effectiveness against soft yet distributed targets by spreading impulse and heat over time and distance. Finally, it seems reasonable that these new energetic materials may enable novel and efficient methods for eliminating incoming threat munitions, or they could be utilized as multi-purpose energetics (e.g. to provide thrust and/or detonate on target).

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Reducing Weight:

Multifunctional Composites Integrate Power, Communications, and Structure

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INTRODUCTION

The increasing complexity and mission requirements of US Army materiel systems, over a range of platforms, require a corresponding increase in the efficiency with which these systems utilize their mass and volume. For example, individual soldiers are required to wear an array of armor, sensors, communication equipment, and power sources. Limits on the total load that an individual soldier can carry, directly limits the mass of these subsystems. This constraint incurs measurable penalties on system efficacy, such as the ballistic resistance of the armor or the range and operating time of the communication system.

Ground vehicles currently under development are required to maintain survivability and lethality while reducing total system weight. Achieving this goal requires efficient implementation of all of the vehicle's subsystems, including armor, power systems, sensing, and communication. Smart munitions are designed to sense targets, adjust trajectory, and communicate with remote control interfaces. These additional subcomponents must be incorporated into the munition in a way that does not significantly degrade payload mass or volume.

Conventional design approaches address system performance issues by maximizing individual subcomponent efficiencies through the use of advanced materials or new performance technologies. A different approach is to create materials which have the capability to perform more than one function simultaneously. This article discusses a number of promising multifunctional material concepts including structural batteries, fuel cells, and capacitors, as well as data and power wiring, and antennas.

DESIGNING FOR MULTIFUNCTIONALITY

While various definitions and interpretations of "multifunctionality" have been proposed [1-3], here we define a multifunctional material as one which individual material elements are simultaneously participating in distinct, beneficial physical processes. As a simple example, consider high tension power lines. These cables are required to both support their weight across a large span while simultaneously transporting electrons. Conventional designs utilize aluminum conductors wrapped around a steel core. The relatively high resistivity of the steel core limits its ability to conduct electricity, so it primarily serves as structural support. Newer designs utilize metal matrix composite cores, which offer higher specific conductivity and specific strength than steel cores [4]. Because this novel core material is providing significant structural and electrical functions, the overall system efficiency is improved and cabling weight is reduced considerably.

For US Army applications, subsystem functionalities include structural support, ballistic protection, energy storage, power generation, power and data transmission, and communication. To utilize multifunctional design to reduce system mass, the heaviest subsystems must be addressed first. Over a range of platforms, such as the soldier and vehicle applications cited above, the most burdensome components consistently include structure, armor, and energy-power components. Multifunctional materials that combine structure and armor functions, in fact, have already demonstrated significant weight savings (refer to the article "Protecting the Future Force: Advanced Materials and Analysis Enable Robust Composite Armor" that appears in this issue). We believe that similar system-level performance enhancements are possible by combining structure and armor functionalities with power and energy functions.

Consider a future ground vehicle with a hybrid power system. The vehicle structure consists of 2000 kg of polymer composite material. The hybrid power system, with a combined output of 750 kW (1000 hp), includes 750 kg of batteries. We define a structural mass efficiency, σ_s, to represent some structural property (e.g. stiffness or strength) relative to the conventional polymer composite material, for which $\sigma_s = 1$. Similarly, the conventional battery material is described by an energy mass efficiency factor, or energy density, of $\sigma_e = 1$. In the nominal design, the battery is non-structural ($\sigma_s^{batt} = 0$) and the structure has no energy density ($\sigma_e^{struct} = 0$). If instead the battery material is allowed to contribute structurally to the overall

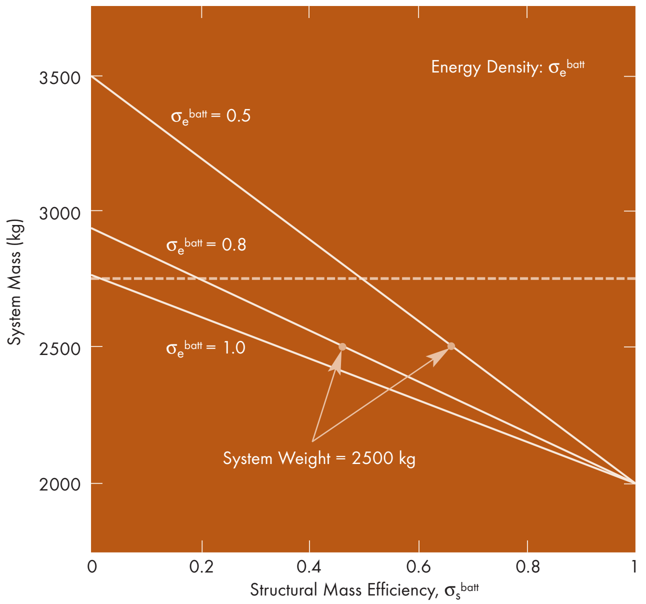


Figure 1. **System Masses for Designs Utilizing Structural Batteries with Various Structural Efficiencies (σ_s) and Energy Densities (σ_e).**

system, the total system mass is governed by the relation

$$\text{system mass} = 2000 \text{ kg} + (1 - \sigma_s^{batt})\cdot(750 \text{ kg} / \sigma_e^{batt}) \quad (1)$$

where we assume that $\sigma_s^{struct} = 1$ and $\sigma_e^{struct} = 0$. Figure 1 shows the resulting system mass for various structural and energy efficiencies. In the nominal design ($\sigma_s^{batt} = 0$, $\sigma_e^{batt} = 1$), total system mass is 2750 kg. If the battery has full structural and energy performance ($\sigma_s^{batt} = \sigma_e^{batt} = 1$), total system mass is reduced to 2000 kg, since 750 kg of structure can be removed and replaced by the 750 kg of structural battery. The performance gains for this design are unrealistic, since they require the synthesis of a "perfect" structural battery. However, reasonable performance gains are possible for more compromised systems. For example, 250 kg of system mass can be eliminated for structural batteries with $\sigma_e^{batt} = 0.8$ and $\sigma_s^{batt} = 0.47$, or $\sigma_e^{batt} = 0.5$ and $\sigma_s^{batt} = 0.67$. Note that, in these examples, the performance efficiencies of the structural battery fall significantly below those of the monofunctional materials. However, beneficial system-level mass savings are possible because the structural battery material elements are performing multiple functions simultaneously.

MULTIFUNCTIONAL ENERGY AND POWER STRUCTURES

Three potential multifunctional energy and power structures are currently under consideration: structural batteries, structural fuel cells, and structural capacitors.

Structural Batteries

As outlined in the Introduction, structural batteries could find application in ground vehicles or soldier systems. For example, in a ground vehicle, panels of structural batteries could be integrally fastened behind structural armor plates, providing enhanced stiffness and penetration resistance for the structural armor. For soldier applications, it may be possible to replace the conventional polymer composite used for helmet construction with a composite battery with both ballistic protection and power storage capabilities.

Batteries store energy and produce power through an electrochemical reaction. The electrochemical half-reactions take place at the electrodes, which are bridged by an electrolyte that conducts ions but not electrons. The reagent materials contained in the electrodes determine the maximum voltage of the cell. The speed at which ions travel through the electrolyte impacts the current of the cell. Polymer lithium ion (PLI) battery chemistries, utilizing lithium ion chemistry and polymer gel electrolytes, are one of the highest energy density batteries commercially available today.

Efforts are underway to produce structural PLI batteries based on the design shown in Figure 2a. The battery consists of a metal mesh cathode doped with a lithium donor salt, a carbon fiber fabric anode, a glass fabric separator layer, and a structural polymer electrolyte. The metal and carbon fiber electrodes both carry load and conduct electrons. The glass fabric separator layer provides structural support and acts to ensure electrical isolation of the anode and cathode layers. The structural electrolyte both conducts ions and provides load transfer between the reinforcement phases.

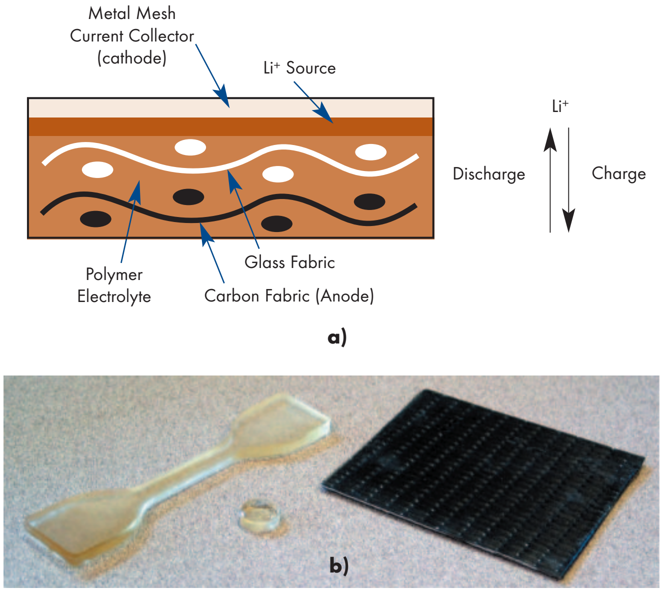


Figure 2. **a) Schematic of a Structural Battery Composite, and b) Photograph of Structural Electrolyte Polymer and a Structural Battery Composite.**

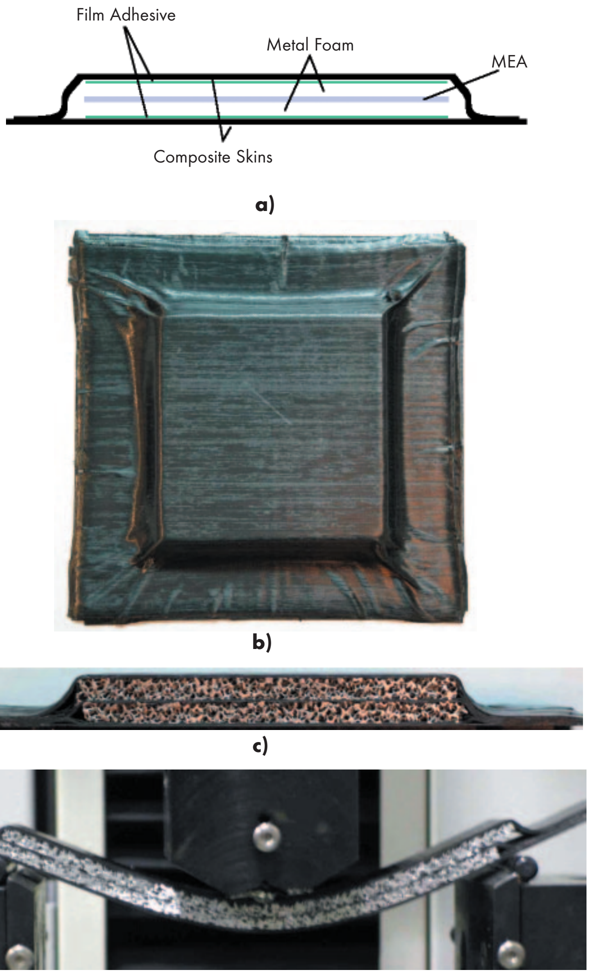
The main barrier to structural battery development is formulation of a structural electrolyte polymer. Typical routes for improving polymer structural properties, such as increasing crosslink density, lead directly to decreases in ion conductivity. However, through careful design, acceptable compromises in properties may be achievable. We have chosen to focus our study on resins that include oligo(oxyethylene) units owing to the known ion conductive properties of poly(ethylene oxide), PEO, and the ease with which lithium salts may be dissolved into PEO oligomers. To balance mechanical and electrochemical properties, partially crosslinked polymer electrolyte matrices that combine monofunctional and difunctional resin monomers have been synthesized, as well as interpenetrating networks of difunctional resins and linear PEO. To further improve mechanical properties of the electrolyte, we are investigating the addition of sub-micron fillers such as colloidal silica and alumina whiskers. Some studies indicate that such reinforcing fillers may also enhance ion conductivity. Figure 2b shows a demonstration (non-functional) battery composite fabricated from one of these structural electrolyte polymers.

Processing and packaging of such structural batteries also pose challenges. Many polymer electrolytes are extremely sensitive to moisture. This restriction requires careful handling of fiber preforms and resins during processing, and development of integral barrier layers to protect the electrolyte during its lifetime.

Structural Fuel Cells

Similar to the structural battery concept, a structural fuel cell could find use in a ground vehicle power system while simultaneously providing additional rigidity to armor and vehicle structures. Another concept would be to utilize a structural fuel cell within the wing of a powered unmanned aerial vehicle (UAV) [1].

Proton exchange membrane (PEM) fuel cells generate electricity through the controlled reaction of hydrogen and oxygen. The hydrogen source, such as hydrogen gas or an aqueous dilution of methanol, is separated from the oxygen source, typically air, by a membrane electrode assembly (MEA). The MEA consists of a thin PEM combined with conductive and catalytic electrode surface layers. The PEM allows for the selective transport of hydrogen ions to the oxygen source, which generates an electrical potential across the electroded surfaces. Commercial fuel cells typically consist of a series-connected stack of individual fuel cells. Each fuel cell contains an MEA assembly sandwiched between permeable layers, such as machined carbon plates, which allow for the circulation of fuel and air sources.



a)

b)

c)

d)

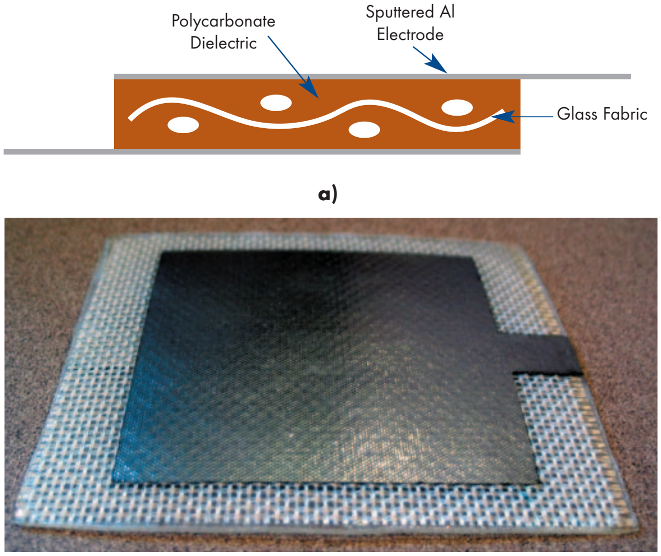
Figure 3. a) Schematic, b) Top View, and c) Cross-Sectional View of a Structural Fuel Cell. d) Structural Fuel Cell Undergoing Bending Test.

Figure 3 shows a structural fuel cell prototype. The sandwich-structure composite consists of thin carbon fiber composite skins with a fuel cell core. The core consists of a conventional MEA between layers of open-cell aluminum foam. The foam core provides the shear and compression properties necessary to achieve high sandwich stiffness, while simultaneously allowing for the circulation of air and hydrogen sources to the MEA. A critical shortcoming of this design is the low shear strength of the MEA, which greatly limits the overall bending stiffness of the structure. To overcome this limitation, novel structural MEAs and core architectures are under development. The foam pore size, density, and layer thickness must also be optimized to reconcile mechanical properties with air and methanol flow permeability.

Structural Capacitors

Army systems such as electromagnetic armor or electromagnetic rail guns require banks of capacitors to provide power conditioning or rapid electrical discharge. Structural capacitors could enable a reduction in system mass by storing electrostatic potential while carrying vehicle static loads.

Capacitors consist of dielectric layers, such as polymers and ceramics, with integral electroded surfaces. A simple structural capacitor can be constructed by metalizing a glass fabric-reinforced polymer composite, as shown in Figure 4. In this



a)

b)

Figure 4. a) Schematic and b) Photograph of a Structural Capacitor Composite.

example, the electrodes consist of 30 nm thick sputtered aluminum surface coatings, while polycarbonate is used for the composite matrix. The energy density of such a structure is fixed by the dielectric constant and dielectric strength of the polymer composite. The capacitance of the structure is governed by the number and thickness of the dielectric layers.

The principal hurdle in composite capacitor development is maintaining high dielectric strength in the polymer composite. Composite fabrication must ensure low void, moisture, and inclusion content to prevent premature dielectric breakdown of the dielectric layer. Some flaw tolerance is enabled by the use of thin "self-healing" aluminized electrodes. Arcing from dielectric breakdown causes the aluminized coating to sublimate in the vicinity of the short, insulating the breakdown region from the rest of the electrode area.

A second challenge is achieving sufficiently high levels of capacitance. In commercial capacitors, high capacitance is achieved by using thin (~1-100 μm) dielectric layers, significantly thinner than typical polymer composite ply thicknesses. This restriction does not limit overall composite electrostatic energy density, but will influence discharge times and circuit conditioning characteristics.

MULTIFUNCTIONAL COMMUNICATION AND BUS STRUCTURES

Integrating communication components, data busses, and information busses into structural materials are unlikely to result in significant weight savings, due to the relatively low weight penalty associated with these systems in typical US Army platforms such as ground vehicles. However, integration of these structures can provide secondary benefits, such as increased durability, simplified manufacturing, redundancy (for improved reliability and damage tolerance), and increased coverage.

Data Wiring

Data wiring consists of low power analog and digital signals transmitted within a system, such as a ground vehicle or rotorcraft. Optical fibers provide the highest information density, but are more susceptible to damage and harder to connect than metal wiring. To overcome these limitations, optical fibers can be directly integrated into the composite structure. For example, optical fibers can be directly woven into conventional glass fabrics, and processed like conventional composites [5].

Embedded optical fibers are more durable than traditionally clad and hung optical fibers. Furthermore, due to their small size and mass, these optical fibers can be pervasively integrated into the vehicle's primary structure. This strategy provides a high level of communication redundancy, and eliminates the need for structural cut-outs or channels for passage of cabling. Direct physical connection to these embedded optical fibers is difficult, and introduces potential flaw initiation sites. We are instead pursuing embedded line-of-sight optical transceivers, so that non-invasive, non-contact links can be established between the integrated data network and the external sensing and control elements. One such device is shown in Figure 5. A dual photovoltaic element is directly coupled to a light emitting diode (LED). Light incident on the photovoltaic, such an external LED or laser source, powers the LED which then couples into an embedded optical fiber. This particular prototype device is around 1 cm in size, but the package can be significantly reduced by using smaller integrated elements.

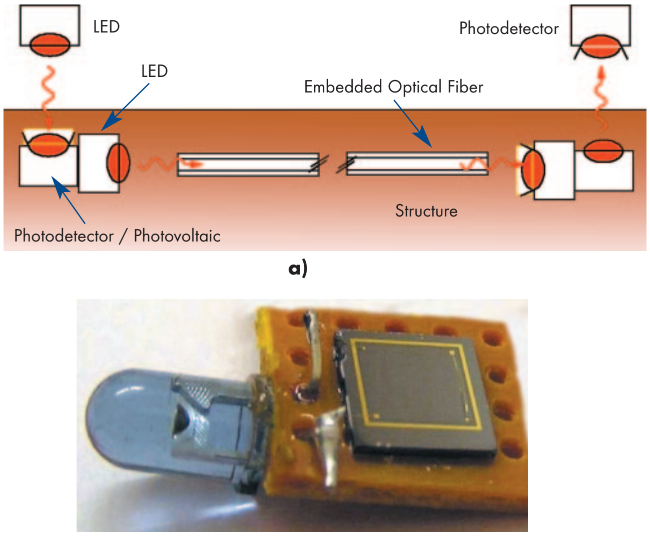


Figure 5. a) Schematic of Integrated Optical Communication Bus Concept. b) Photograph of Prototype Self-Powered Dual Photovoltaic Optical Transceiver.

Power Wiring

Power wiring often presents a more serious system-level mass penalty, as compared with data wiring, due to the large areal cross-sections required to transport power at high current and voltage levels. It may be possible to directly embed metal elements, such as aluminum ribbons, directly into composite structures. For some weight-critical structures, such as satellites or rotorcraft, these conductors could be engineered to act as structural elements. This approach is truly multifunctional, as the electrical conductors also carry loads, while the structural polymer composite provides electrical insulation between metal elements.

As with data wiring, special techniques need to be developed to enable efficient and safe connectorization* to the embedded metal conductors. Processing will also require special engineering, as the differences in thermal expansion between a polymer composite and embedded metal element could introduce significant internal residual stresses during processing.

Antennas

For ground vehicles, antennas typically account for only a small fraction of total system mass. However, integrating antennas into structural materials could provide secondary performance benefits. For example, embedding antennas provides more rugged packaging than traditional exposed antennas. If antenna elements can be integrated transparently into the manufacturing and design process, these elements could be ubiquitously positioned over the entire surface of the vehicle. This approach provides full coverage and line-of-sight capabilities, as well as a high level of system redundancy.

A potential structural antenna design appears in another article published in this issue: "Manufacturing a More Affordable Army Through Low Cost Composite Processing." Designing such integrated antennas introduces many complexities, as the high frequency dielectric properties of the structural and ballistic materials must be compatible with the antenna design. These radiating elements also must be reconciled with shielding and signature layers in the structure. Connection of the antenna to the system wiring also must be performed without degrading the structural or ballistic properties of the surrounding materials.

CONCLUSIONS

Multifunctional structural materials offer the potential for significant savings in system-level mass and volume, or performance benefits such as improved durability or redundancy. This design approach is in its infancy, and faces significant design and material synthesis challenges. Disparate material properties, such as structural and electromagnetic properties, need to be engineered and optimized simultaneously. These technical challenges require the close coordination of interdisciplinary teams.

Beyond multifunctional material design, manufacturing and repair also present difficult barriers to implementation. Fabrication approaches must allow for incorporation of many different material types and form factors, without introducing prohibitive cost or complexity. Repair of such structures could be difficult or impossible, since many critical functional elements are likely to be permanently embedded within structural materials. For some applications, these concerns could be addressed through modular design. For example, structural batteries or fuel cells could be mechanically fastened or reversibly bonded to other structural elements. Other sustainability strategies are also possible, such as redundant elements or self-healing systems. In some cases, single-use designs (such as munitions or disposable UAVs) are acceptable.

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* *Connectorization* is a technical term specifically pertaining to connecting data and power components. Within the field, the term is customary and preferred to *connected.*

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Chemical Agent Resistant Coatings Reach Higher Levels of Performance

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INTRODUCTION

The US Army employs a wide variety of equipment for tactical applications. Notable items are tanks, trucks, missiles, aircraft, artillery, and shelters. Less obvious equipment includes water purification units, generators, and high mobility forklifts. This tactical equipment is usually painted during the original manufacture and repainted as necessary at facilities ranging from large-scale Army depots and small "touch up" operations to unit level organizations. The same coatings systems, defined by their military specifications, are used at all facilities under many different environmental conditions.

The coating systems used to paint Army equipment are highly engineered materials that are formulated to meet multiple performance requirements. The selection of coating ingredients, formulation conditions, application methods, and curing conditions can influence the final properties of the coating, see Figure 1. Generally, Army coatings are formulated using polymer binders, a variety of solvents, pigments for tinting, extender pigments for control of gloss, and functional additives. In this paper, we discuss recent research findings and product developments that have led to the next generation coating systems for Army applications.

CHEMICAL AGENT RESISTANT COATINGS

Chemical Agent Resistant Coating (CARC) systems represent an important category of products that are researched, developed, and implemented by the Army. Finishes under this umbrella resist penetration by chemical warfare agents and can be readily decontaminated. This threat, identified in the early 1970's, led to the development of the Army's first generation CARC (MIL-C-46168) in 1974[2]. In 1983, the Department of Army required implementation of CARC systems for combat, combat support, tactical wheeled vehicles, aircraft, and essential ground support equipment (i.e. tactical equipment) beginning in Fiscal Year 1985. The Army Research Laboratory leads the research and development of CARC systems and also is the approving authority of CARC products for DOD.

The chemistry of the initial CARC finishes in the early

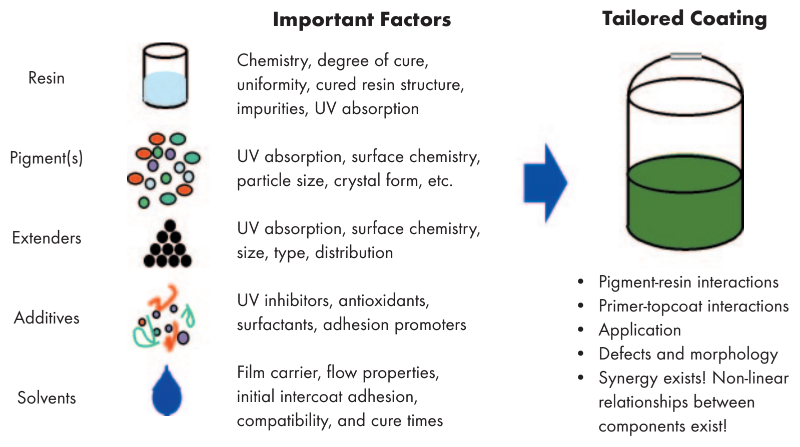

Figure 1. CARC Ingredients [1].

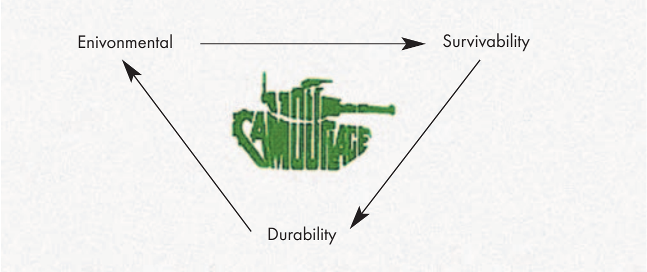

Figure 2. Guiding Principles for CARC System [1].

1970s and 1980s were alkyd enamels that were modified depending on their application. Primers utilized heavy metal pigments, in particular lead and hexavalent chromium and inert iron oxides to arrest and prevent corrosion. CARC topcoats employed a variety of organic and inorganic pigments to mimic woodland or desert surroundings; and silica and talc were used to lower the gloss of the coatings. The first generation polyurethane based CARC topcoat (MIL-C-46168), proved to be a tremendous improvement over the enamel finish it replaced (MIL-E-52798). However, while the high pigment content and low resin volume met the Army's low gloss requirement, it did so at the expense of long term durability, mar resistance and flexibility.

The Army's current topcoats are based on aliphatic polyurethanes that meet requirements of MIL-C-46168, MIL-C-53039 or MIL-DTL-64159 military specifications [2, 3, 4]. These coatings provide excellent performance characteristics, such as exterior durability and excellent chemical resistance. They also withstand decontamination procedures and provide camouflage properties in the visible and near infrared regions of the spectrum.

When assessing the inherent balance of properties found in the CARC coating system, the Army's coatings research program began embracing three principles to guide and assist in formulation, scale-up, and final implementation of new coating products to the field. The three primary principles are *Durability, Environmental Compliance, and Survivability*, Figure 2. The approach has produced products that ensure the best durability, meet or exceed current or proposed environmental and user safety laws, and meet survivability requirements for camouflage coatings. Survivability requirements drive two military unique technical challenges: camouflage that blends with a given background, while also providing resistance to live chemical warfare agents.

Figure 3. Elimination of HAPS in CARC Primers is a High Priority.

AMMUNITION COATINGS

Soldiers Loading a Mortar Round.

The Army also utilizes coatings on munitions. Recent research has resulted in a universal ammunition coating (UAC) with improved performance [1]. Prior to the development of this coating system, ammunition coatings were subject to premature and severe film failures, offered poor corrosion resistance, were incompatible or reactive with energetic materials, and failed to meet National Emission Standards for Hazardous Air Pollutants (NESHAPs). To improve coating performance, a new class of corrosion-inhibiting pigments was incorporated into an alkyd polymer system consisting of durable fast-drying chain stopped alkyd (drying oil modified polyester).

In addition to meeting the requirements for substrate adhesion and long-term storage stability with energetic materials, the UAC provides vastly improved corrosion resistance, eliminates the primer coats on certain munitions applications, and is "a drop in replacement" for existing materials. After extensive laboratory evaluations, the UAC was qualified on artillery and mortar projectiles at the Scranton Army Ammunition Plant (AAP) and the Crane Army Ammunition Activity (AAA) munitions manufacturing and maintenance sites. The benefit of this new coating to the Army is superior single-coat performance, enhanced durability, environmental compliance and elimination of production rejects and reworks. The UAC is being employed in the production of 120-mm and 155-mm projectiles at AAP and AAA. Implementation of the UAC will allow these facilities to meet local environmental regulations during the renovation of artillery projectiles.

[1] P. Smith and K. Chesonis, *Recent Advance in Ammunition Coatings*. ACS Preprint Aug 2004

Figure 4. Army Vehicles Painted with the MIL-DTL-64159 CARC [1].

A variety of environmental regulations and worker safety issues has motivated our research to develop environmentally compliant CARC coatings. For example, Federal and local regulations resulting from the Clean Air Act and its amendments restrict the amount of volatile organic compounds (VOCs) emitted during the application of protective coatings, and Occupational Safety and Health Administration (OSHA) regulations on worker safety restrict exposure to many of the materials used in their manufacture. To address these regulations, the coating has been reformulated to be lead and hexavalent chromate free, low in VOC content, and in many instances free of hazardous air pollutants (HAPs), Figure 3. This is significant since recent National Emission Standards for Hazardous Air Pollutants (NESHAPS) from the Environmental Protection Agency (EPA) are working to restrict and specifically regulate these materials.

From a historical perspective, the two main avenues to VOC reduction in coatings are formulations with lower molecular weight polymers and the use of waterborne, water-dispersible, or water-reducible polymers. Reducing a polymer's molecular weight usually reduces its viscosity, and introduces the need for solvents to control the system viscosity during application. This is the traditional high solids solution to VOC problems. The high solids versions of the CARC topcoats did not meet VOC regulations in certain localities, and a new technology was needed to develop a CARC to solve current and anticipated VOC problems. Alternatively, systems in which water can be used for this viscosity control can greatly alleviate the need for solvents altogether. Until recently, water-compatible coatings did not match the performance of solvent based analogs, but recent developments in polymer technology have enabled the development of high performance polyurethane systems with excellent performance and chemical agent resistance.

The recent development by our group of a water-reducible, two-component polyurethane CARC topcoat has been a significant achievement. This product employs water-dispersible hydroxy-functional polyesters and water-dispersible polyisocyanates. Traditionally, the presence of water must be eliminated in non-aqueous two-component polyurethane formulations due to the unfavorable reaction with isocyanate. The reaction forms an unstable carbamic acid, which quickly decomposes to generate carbon dioxide and an amine (Reaction 1). The amine then reacts with further isocyanate to yield the substituted urea (Reaction 2).

$$\mathrm{RNCO} + \mathrm{H_2O} \rightarrow [\mathrm{RNHCOOH}] \rightarrow \mathrm{CO_2}\uparrow + \mathrm{RNH_2} \qquad (1)$$

$$\mathrm{RNH_2} + \mathrm{RNCO} \rightarrow \mathrm{RNHCONHR} \qquad (2)$$

This reaction may inhibit or adversely affect the stoichiometry and development of crosslinking that is crucial to the integrity and performance typical of two-component polyurethanes [5, 6]. Developments in waterborne polyurethane technology have enabled high performance coatings to be formulated using water-dispersible polyisocyanates and hydroxyl-functional polyurethane dispersions [7]. While there is a competing reaction occurring with water, the kinetics, raw materials selection, and proper indexing of isocyanate (NCO) to hydroxyl (OH) groups can ensure that sufficient crosslink density is established. Dynamic Mechanical Analysis, Fourier-transform infrared spectroscopy and desorption-gas chromatography/mass spectroscopy has shown the role of indexing on final physical properties of these polyurethane materials [8].

Figure 5. ARL Continues to Develop Field-Ready Coatings with Improved Properties.

The research on water-dispersible urethanes has resulted in a new CARC coating system [9] that will replace the first generation MIL-C-46168 CARC with the water-dispersible technology and one component solvent based technology. The VOC of the regulated solvent is less than 180 g/L (a 60% reduction) and contains zero HAPs. At the same time through careful selection of pigmentation, the survivability and durability of this environmentally compliant coating is outstanding.

Chemical agent resistance is provided by the aliphatic polyurethane binder and the camouflage properties are provided by the appropriate selection of tinting pigments for visual color and near-infrared reflectance, plus extender pigments for gloss control. Camouflage requirements complicate development of Army coatings because of the need for low gloss that leads to proportionally higher pigment to binder ratios. Higher binder content in the formulation enhances chemical agent resistance while high pigment content reduces gloss. ARL has replaced the solvent borne polyester and polyisocyanate binder components of the current CARC with the water-dispersible system. At the same time, an improved pigment package has been developed to reduce the problems (such as marring and reduced flexibility) resulting from high pigment content required for low gloss. The resulting coating formulation survives decontamination and provides chemical agent resistance. The use of novel pigmentation has improved the low temperature flexibility, mar resistance, and weathering durability of this coating.

The selection of binders and pigments also affects the degradation of CARC coatings [10]. Research has demonstrated that replacing diatomaceous silica and talc with polymeric based extender pigments enhances the durability of CARC systems. Alternate pigment materials such as a blend of urea resin containing negligible quantity of free methlylol groups have been explored. The primary particles with an average grain diameter of 0.1-0.5 µm form agglomerates of approximately 4-5 µm. This results in a high pore volume and a steep grain distribution, two important factors that form the precondition for excellent matting effect. As a result of the almost ideal spherical form of the particles, the coating rheology remains unaffected, opposed to the more needle shaped silica particles. The other active flattening agents used are ones that have a polyurethane composition with a medium particle size of 18 µm. Most are spherical vesiculated type materials that have enhanced matting properties and are extremely chemical resistant as well. The combination of these materials provides a very dynamic and active flattening package. Currently, MIL-DTL-64159, water-dispersible CARC using polymeric beads is readily used by many weapon platforms in the DOD, as shown in Figure 4, the Canadian Armed Forces, and for preservation efforts in non-military applications.

CURRENT RESEARCH DIRECTIONS

Working throughout the DOD with Program Managers, the acquisition community, end users, paint vendors, and raw material suppliers, ARL continues to develop field ready coatings with improved properties (Figure 5). One current focus is developing formulations with minimal solar loading. These coatings are expected to exhibit slower degradation by minimizing ultraviolet (UV) absorption. Also, reduced solar loading will reduce equipment temperatures and lessen the need for cooling of interior compartments. Low solar loading coatings will provide tremendous enhancements to the field.

Additionally, we continue to work on the prevention and early detection of corrosion to maintain readiness and minimize equipment life cycle costs. Our corrosion research and expertise in the area of pretreatments, primers, and material substrates have enabled advances to lessen the need for heavy metals such as hexavalent chromium while enhancing durability and performance. Most recent, ARL in collaboration with paint suppliers has evaluated and identified viable alternatives to DOD-P-15328, a wash primer high in VOC content and containing hexavalent chromium [11].

SUMMARY

ARL is a leader in CARC materials technologies, developing coating formulations to meet both performance requirements and environmental regulations. In addition, today's CARCs function as camouflage and have increased environmental degradation resistance. These newer CARC systems meet the Army's current design strategies of providing durability, survivability, and environmental compliance.

ACKNOWLEDGEMENTS

The Coatings and Corrosion Team of ARL would like to thank and acknowledge our colleagues within the Tank-Automotive and Armaments Command (TACOM), the Aviation and Missile Command (AMCOM), the General Services Administration (GSA), and the various Armament Research, Development and Engineering Centers (ARDECs). The team would also like to acknowledge the paint vendors, raw material suppliers, and end users who collectively have enabled and assisted our effort to provide durable and robust products to the field.

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Mr. John A. Escarsega is a research chemist and leader for the Coatings and Corrosion Team in the Materials Application Branch for the US Army Research Laboratory. He received his BS in chemistry from the University of Mary Washington. He is the Commodity Manager for chemical agent resistant coatings (CARC) for the Department of Defense for military tactical vehicles, aircraft, and support equipment. He has been active in coatings research for the Army since 1981, and is the primary patent holder for the novel water dispersible coating, which is currently being implemented on Army and Marine Corp assets. He is the author of over fifty publications. He is an active member of the American Chemical Society as well as a member of the Federation for Coatings Technology.

Mr. Kestutis Chesonis is in the Weapons and Materials Research Division at Aberdeen Proving Ground. He received his BS in Chemistry from Johns Hopkins University and began his career in industrial coatings. He was involved in the formulation, manufacture, and application of various mil-spec coatings. In 1986, he started working for the Army at Fort Belvoir in the Organic Chemical Coatings Group. He has specialized in developing camouflage and ammunition coatings. Among the awards he has earned are The Commander's Award for Technological Achievement, the ARL Associated Achievement Award for Technology Transfer, the Cross Functional Teaming Award, and the Army R&D Achievement Award for outstanding scientific and technical achievement.

Dr. Dawn M. Crawford has served as a Research Materials Engineer in the Army for 20 years. Presently Dr. Crawford serves as the project leader of the Permselective Membranes program at ARL-APG in the Multifunctional Materials Branch, where she has been instrumental in developing a novel selectively permeable polymeric membrane for protective clothing applications. Dr. Crawford is a co-inventor on three patents, has been awarded two Army R & D Achievement awards and has authored numerous journal articles. In addition to her work in membranes, Dr. Crawford has also made contributions to Army programs in the areas of elastomer and coatings research. Dr. Crawford holds a BS in Materials Engineering from Virginia Tech and a PhD in Chemistry from Virginia Commonwealth University.

Mr. Jeffrey L. Duncan is a materials engineer in the Coatings and Corrosion Team of the Materials Application Branch. He holds a MS from Carnegie-Mellon University and has performed R & D in protective coatings for the US Army for over 30 years. He is a principal investigator for the research, development and implementation of protective coatings with environmental compliance and performance improvements within the chemical agent resistant coating system used by the US Army on all tactical equipment, including topcoats and corrosion resistant epoxy primer systems. Over that time, he has managed and/or participated in a number of Army, Tri-Service, and NATO task groups to develop, test, and standardize CARC-related technologies. Mr. Duncan retired in the fall of this year.

Ms. Pauline M. Smith is a Research Chemist and a member of the Coatings Technology Research Team at ARL. Her activities are primarily to formulate and design novel coatings for all types of Army equipment, with particular emphasis on tactical vehicles and ammunition. Her research has focused in four primary areas: Chemical Agent Resistant Coatings (CARC); Corrosion Resistant Ammunition Coatings, Camouflage Coatings, and Pollution Prevention/VOC-Compliant Coatings; all of which are being developed for the direct support of current Army assets and the Army-After-Next. Ms. Smith is the author of numerous publications.

Small Features Enable Big Results:

The Army's Latest Developments in Polymer Nanotechnology

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Some nanotechnology applications have been briefly mentioned elsewhere in this Special Issue, but this article and the next, "Small Features Enable Big Results: Nanotechnology Research Uncovers New Multifunctional Materials for Future Army Systems", focus solely on the development of nanotechnology to support the Army's Transformation. These articles provide updates and describe additional activities that are ongoing in the Army nanomaterials research that was first presented in the AMPTIAC Quarterly *Special Issue on Nanotechnology in 2002. [1] This article presents an introduction to the control and manipulation of the functionality of polymers at the nanoscale and the resulting applications for this technology. The next article describes various efforts involved in developing multifunctional nanomaterials and nanocomposites. We open with an introduction to nanotechnology and provide some background information suitable for both articles that address the impact of these ongoing efforts to the Army Transformation.* - Editor

INTRODUCTION/BACKGROUND

Nanomaterials technology offers tremendous potential for reducing weight and increasing performance of the materials used in Army applications. While nanotechnology, and specifically nanomaterials research, are still nascent in their development, there are trends emerging and applications becoming realized.

The nanomaterials technology discussed here and in the following article "Small Features Enable Big Results: Nanotechnology Research Uncovers New Multifunctional Materials for Future Army Systems" is focused on synthesizing and processing materials that exhibit unique and often tailored properties at the nanometer scale (1-100 nm). Characterizing, controlling and utilizing these nanoscale properties in practical ways are some of the challenges that scientists and engineers face in developing nanotechnology to solve relevant problems for the Army. It is a challenge for scientists, for example, to modify materials at the nanoscale with great uniformity without using complex, time-consuming methods such as nanolithography.

Ongoing nanomaterials research within the Army includes the synthesis and assembly of new nanomaterial building blocks, as well as the development of nanoscale characterization and metrology tools that can probe the structure and response of nanoengineered materials. Potential Army uses for nanomaterials can broadly be classified into structural and functional applications. Inorganic and organic nanomaterials are being explored in lightweight structural applications, and potentially for personnel and vehicle ballistic protection concepts. The ability to control the microstructure and response of materials at the nanoscale can lead to new mechanisms for load bearing and energy dissipation. As seen in the article on composite armor in this issue of the *AMPTIAC Quarterly* one such effort involving the application of nanotextured fiber coatings for composites applications is described. Likewise, transparent polymer nanocomposites are being explored for use in transparent armor and scratch-resistant transparent coatings.

Functional nanomaterials can improve performance of existing applications or enable new uses or capabilities. These two articles describe several research activities involved in developing nanofunctional materials and understanding and utilizing their unique properties. They further explain how these properties may be exploited to address the needs for new Army materials.

NANOFUNCTIONAL POLYMER MATERIALS

The fundamental units of organic materials are ideally suited for the development of nanofunctional materials. Synthetic chemists have developed numerous tools to create new nanoscale materials from the "bottom-up." Recently these tools have been applied to create materials with unique and desired characteristics and properties at the nanoscale. Nanofunctional organic materials are of particular interest to the Army, with specific examples described later in this article.

Introduction to Dendritic Polymers

In the field of polymer chemistry, the dendritic polymer architecture has been established as the fourth major class of macromolecular topology. These materials have earned this distinction based on a unique set of properties that are observed in this class of polymers. [2, 3, 4]. Dendritic polymers can be described by the level of control of their structure. Dendritic polymers are comprised of building blocks with characteristic branching units. The synthesis and assembly of these building blocks determines the type of dendritic polymer

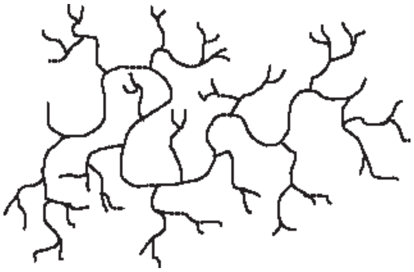

Figure 1. **Illustration of a Hyperbranched Polymer.**

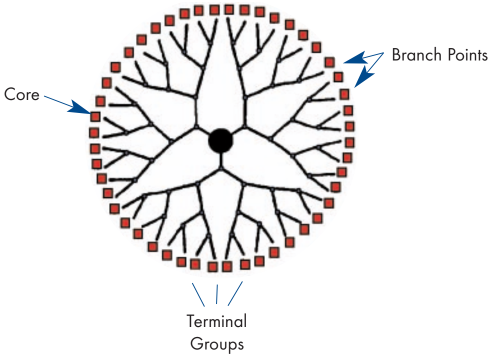

Figure 2. **Symmetrical Structure of a Dendrimer [2, 3, 4].**

that is produced. Hyperbranched polymers (HBPs) have the least controlled structure and consist of random branch points and are usually synthesized in "one-pot" reactions. Figure 1 schematically shows a random hyperbranched polymer structure as a tree-like structure, as shown in Figure 1. Hyperbranched polymers are often of interest in chemistry and materials engineering because they are easily synthesized and can possess a number of functional groups depending on the length and composition of the building blocks. The terminal groups in a hyperbranched polymer (located at the chain ends) are very important because to a large extent they determine the characteristics including reactivity and properties of the hyperbranched polymer as a whole.

Dendrimers and dendrons also possess a highly branched structure, but dendrimer structures are very precisely controlled resulting from the careful synthetic routes that are used to produce these materials. These polymers are precise core-shell materials that have been intensely studied in recent years [2, 3, 4]. An elementary schematic representation of a dendrimer illustrating its highly branched symmetrical structure around a core is shown in Figure 2. Polyamidoamine (PAMAM) dendrimers developed by Tomalia have received a great degree of attention and derive their precise structure and chemistry from a highly controlled polymerization scheme [2, 3]. Unlike their hyperbranched relatives, dendrimers can be synthesized to be monodispersed, even at very large molecular weights. This feature makes dendrimers very attractive nanoscale building blocks for materials scientists, chemists, and biologists.

While dendritic polymers have many properties that are similar to the traditional linear, cross-linked, and branched polymers, they possess certain properties that are significantly different from these other conventional polymers. A significant advantage of these types of polymers is the large number of terminal units (end points of polymer chains) available for chemical modification and the controllable degree of branching within the polymer. Traditional linear polymers possess very few branch points in the polymer backbone, and their physical properties are derived largely from entanglements between adjacent-polymer chains. Dendritic and hyperbranched materials, however, possess chains that have branches upon branches (analogous to a tree limb), and results in a number of chain ends that scales with the degree of polymerization. Because of their branched nature, they form negligible chain entanglements. These features make dendritic polymers attractive candidates for a number of applications ranging from structural composites to biosensors.

Dendritic polymers have precise and tunable nanoscale features that, when manipulated or controlled, can be used to tailor their properties and performance. Properties and characteristics such as molecular weight, geometric dimension, shape, and chemical functionality can be controlled using suitable initiators (compounds used to begin polymerization reactions), reagents, and reaction chemistry at the nanoscale. Unlike other macromolecules, the architecture (structural design) of dendritic polymers includes a distinct core, interior, and exterior [2]. Control of the chemistry, size, and geometry of these architectural features creates a very diverse set of nanomaterial building blocks. These features have led to great interest for dendritic polymers in widespread Army applications related to chemical and biological agent defense, multifunctional protective coatings and finishes, adhesion promoters, additives for polymer compounds, energetic materials, electronics, and optoelectronics.

Dendritic Polymers for Polymer Matrix Composites Applications

Dendritic polymers have been examined for several composites applications. Due to the large number of terminal units, the chemistry of dendritic polymers can be tuned to become a very effective coupling agent (a chemical agent that facilitates the adhesion of two components) for fiber-matrix combinations that have been considered incompatible or troublesome to composites engineers. For example, composite materials fabricated using liquid molding methods and vinyl-ester resins are attractive in a number of military applications. However, the use of higher performance carbon fibers in these vinyl-ester composites has been hindered by less than optimal bonding between vinyl-ester resin and carbon fibers. The use of dendritic polymers as adhesion promoters can improve the bond between the carbon fibers and the vinyl-ester matrix.

Dendritic polymers can be incorporated into vinyl-ester carbon fiber composites as fiber sizings (coatings on individual fibers) applied from aqueous solutions to the fibers directly, or alternatively, via a self-assembly method. Self-assembly is a nanoscale process where molecules are inserted into a system and assemble themselves naturally at a desired location. Thus, when the terminal units of dendritic polymers are configured with the proper functional groups at the nanoscale they can be added to the vinyl-ester resin and will naturally migrate to the fiber-matrix interphase* via self-assembly.

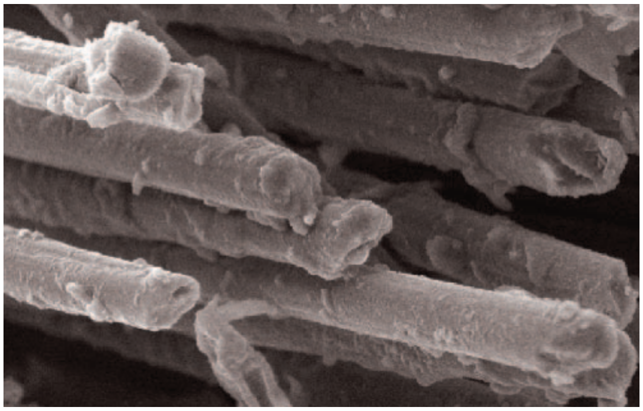

Figure 3. Electron Micrograph of Carbon Fiber Vinyl-Ester Composite That Has Used Dendritic Polymers to Modify the Fiber-Matrix Interphase. The Presence of Resin on the Fiber Surfaces Indicates Excellent Fiber-Matrix Adhesion.

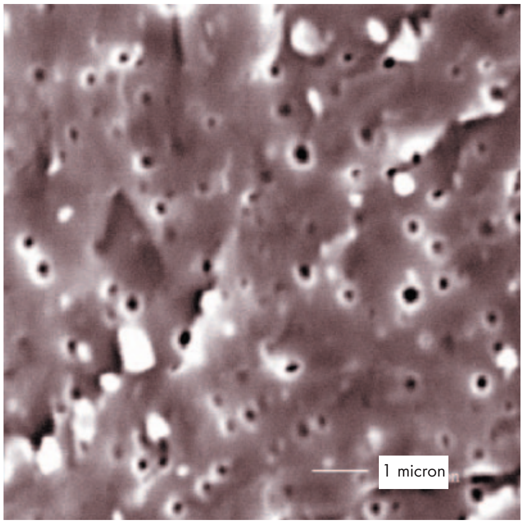

Figure 4. Micrograph of Dendritic Polymer-Toughened Epoxy Resin.

Figure 3 shows a scanning electron micrograph of a composite failure surface from a modified vinyl-ester carbon fiber composite. In this case, the carbon fiber was coated with a modified polyamidoamine (PAMAM) dendritic polymer, containing several different types of functional groups specifically tailored for this application. The failure of the composite occurred in the vinyl-ester resin; well-removed from the interface, indicating that the fiber-matrix interface maintained optimal adhesion. The resulting short-beam shear strength of this composite was improved by 40% through the use of the dendritic polymer based sizing.

Another application of dendritic polymers for polymer matrix composites is in creating low-viscosity toughened resins. Cost-reduction efforts in composites manufacturing have led to an increased use of liquid molding techniques for composite materials, and also created a need for low-viscosity toughened resins. Traditional tougheners, including rubbers and thermoplastic polymers, increase resin viscosity to levels that prohibit their use in many of these low cost liquid molding manufacturing methods. Since dendritic polymers have less of an impact on the viscosity of the resin than the traditional tougheners, their judicial use as tougheners in thermosetting resins results in relatively low-viscosity resins that perform comparably to higher-viscosity rubber-modified systems. During cure, micron-sized phases comprised of dendritic polymer-rich material separate from the bulk resin resulting in a toughening mechanism similar to rubber-modified systems. This microstructure is shown in Figure 4 where a polyester-based dendritic polymer has been added to a low viscosity epoxy resin resulting in a significant increase in polymer toughness without significantly increasing resin viscosity.

Dendritic Polymers for Surface Modification

The functional groups on a dendritic polymer can be modified in such a fashion as to create a macromolecule that exhibits self-assembly. For example, these dendritic polymers can be intentionally designed such that when added to an uncured polymer resin system, they migrate to the surface and orient themselves preferentially. An example of where this is useful is in the surface modification of polymer matrix composites to create a specific set of properties on the exposed surface of the material system without sacrificing the composite's bulk properties. This natural migration and orientation of dendritic polymers can be achieved by making some of the functional groups of the dendritic polymer branches incompatible (insoluble) with the resin matrix. Likewise, other functional groups on the same dendritic polymer would be made compatible (soluble) with the resin matrix.

An example of a self-segregating dendritic polymer is schematically shown in Figure 5. Proper control of the functional groups creates a dendritic material that remains soluble in the uncured resin, while creating a thermodynamic driving force for the incompatible functional groups to migrate the dendritic polymer to the surface of the resin. After curing, there exists a high concentration of dendritic polymers at the surface.

Dendritic materials with very strong surface migration tendencies have been developed by modifying the terminal units with low surface energy, perfluorinated functional groups[†]. The aliphatic functional groups[‡], which are compatible with the bulk matrix, permit the homogeneous mixing of the additive and bulk material, and the entire assembly serves to transport the delivered group[§] to the surface in significantly higher concentration than in the bulk material.

A practical example utilizing nanofunctional dendritic polymers for surface modification is the creation of a self-assembling catalytic layer on the surface of polymers, which could be used to make thin film catalysts, that could potentially be painted onto other surfaces. For instance, a polyethyleneimine dendritic polymer with perfluorinated functional groups and aliphatic chains containing a catalytic metal center can be mixed within a polyurethane resin. The catalytic dendrimer migrates to the surface of the polyurethane, and upon curing forms a polymer with a catalytic surface layer. At a cast polyurethane surface, the surface properties are dominated by the dendritic polymer additive and the composition of its functional groups. The modified dendritic polymers, complexed with a catalytic metal center, serves as a nanodelivery system, bringing the catalyst to the polymer surface. The polymer-metal complex has been observed

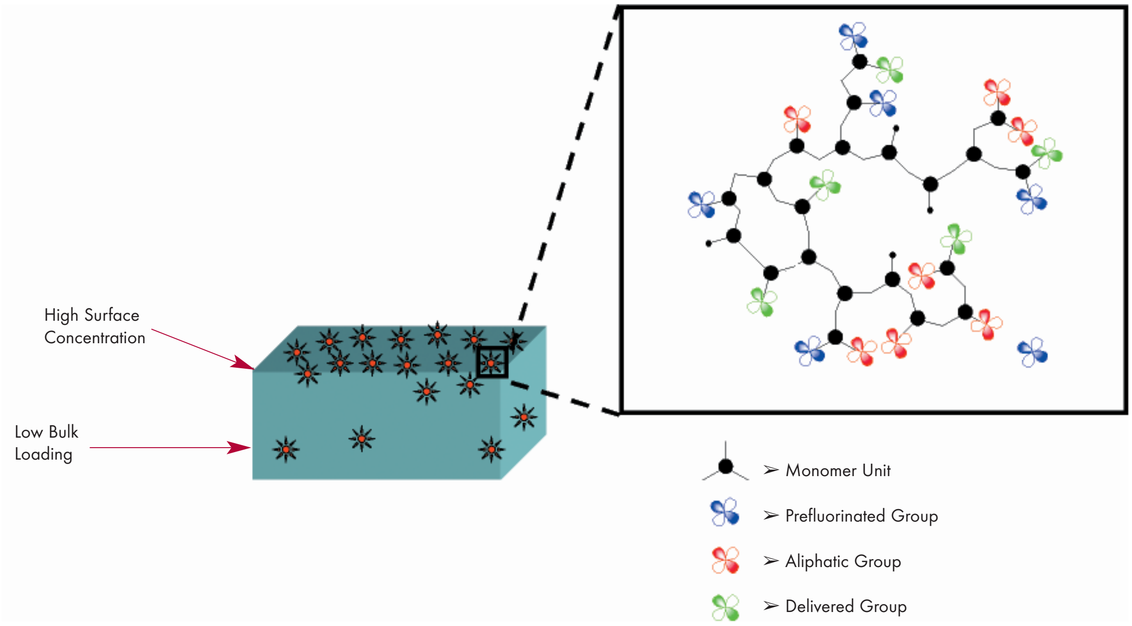

Figure 5. **Pictorial Representation of Self-Segregating Macromolecule in a Bulk Sample.**

at the surface of a polyurethane film in a quantity approximately ten times greater than its loading in the bulk. These results suggest that small amounts of additive could be used to provide truly functional materials, with active sites embedded or reacted into the polymer. Such an approach has the potential to be more robust than secondary coating treatments such as spray-on applications.

Dendrimer Enhanced Immunoassays

Rapid and reliable detection of biothreat agents is of paramount importance to a variety of defined operational requirements in the biodefense, counterproliferation, and domestic preparedness programs. Current point detection capabilities require expensive equipment and extensively trained personnel to perform their tasks. While many research teams focus their efforts on a "top-down" approach by shrinking existing bulky detectors using a "lab-on-a-chip" strategy, other teams are effectively using a "bottom-up" strategy whereby nanoscale manipulations improve device performance. Dendrimers are ideal nanoscale building blocks for nanomanipulation. [5]

Nanoengineered dendrimer-antibody conjugates can be appropriately designed to possess both antibody (protein that binds with high specificity with an antigen, which is a substance that can initiate an immune response) and dendrimer properties because they are about the same size (i.e. 5-10 nm in diameter). [6] The antibody maintains its primary antigen recognition capability, while the dendrimer strongly adsorbs on a substrate through dendrimer terminal unit surface interactions. The adsorbed conjugate will tend to self-orient the antibody binding domains, known as Fabs (areas on the antibody protein that bind to the antigen), for greater availability in the immunoassay (a technique or system used to detect and possibly identify biological substances, such as biothreat agents, through a binding event with antibodies).

Receptor antibody materials (bot-Fab) are currently used on gold substrates for the detection of biowarfare agents. Because of weak interaction with the gold particles used for the substrate, the gold particles within these bot-Fab/gold complexes tend to aggregate and form clusters. This can obstruct some of the antibody receptor sites from the surrounding environment, reducing their efficiency in detecting biowarfare agents. Research on combining antibody receptor materials into the structure of a dendrimer molecule has shown promise in reducing this problem. The functional groups terminating the branches of dendrimer molecules can be selected so as to enhance surface interaction with the gold nanoparticles (20-70 nm in size). Furthermore, the structure of the dendrimer/bot-Fab complex can be designed such that

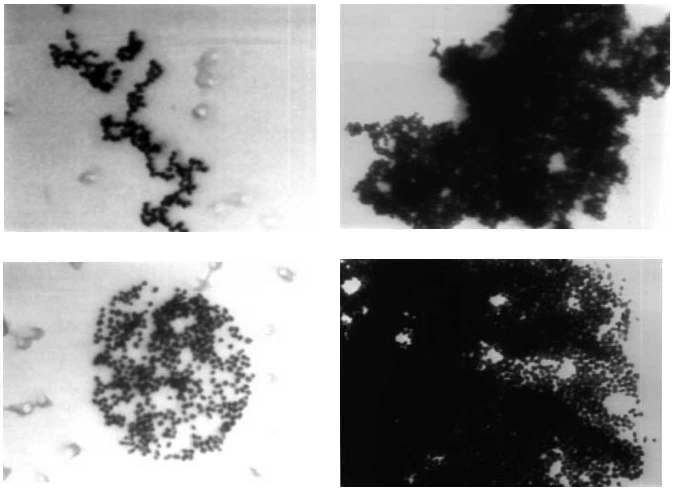

Figure 6. **The Effect of Dendrimers on the Aggregation Behavior of Colloidal Gold Conjugates.**

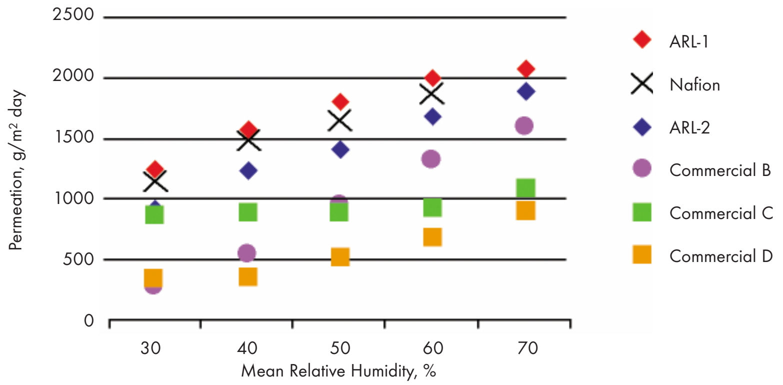

Figure 7. Water Vapor Permeation of ARL Membranes Compared to Commercial Materials.

the dendrimer strongly adheres to the gold surface while simultaneously forcing orientation of the bot-Fab materials outward so as to maximize their interaction with the environment. Testing of these dendrimer/bot-Fab complexes showed a marked reduction in the aggregation of the gold particles, improving their interaction with and detection of biowarfare agents. This is shown in the electron micrographs in Figure 6.

A new immunoassay formulation was created using this technology. Testing of the device showed that at least a 20 fold sensitivity enhancement was achieved with the dendrimer-anti bot Fab conjugates vs. the anti bot Fab alone. Similarly, production costs might be reduced by as much as 10-fold.

Other Self-Assembled Nanostructured Polymer Materials

This research focuses on the creation of nanostructured polymer and organic-inorganic hybrid materials in order to achieve unusual mechanical, transport, or electro-optical properties. One of the most promising routes to these materials is through the exploitation of the self-assembling characteristics of carefully chosen block copolymer** templates.

In utilizing these templates it may be important to have control of the orientation (parallel or perpendicular to a substrate) and long range order of the block copolymer morphologies. Innovative techniques, such as the application of electric field or the modification of substrate surface energies, to control orientation and long range order in block copolymer thin films are being explored. These efforts are being performed both internally and through collaborative research with the Army's Polymer Center of Excellence at the University of Massachusetts.

Permselective Membranes for Protective Clothing

The Army has a need for materials that exhibit selective permeability and favor water transport (for breathability) while inhibiting transport of larger organic molecules such as chemical agents. One approach to achieving this behavior is through the use of self-assembled block-copolymers. Through appropriate processing and suitable chemical modification, a tri-block copolymer with tailored chemistry and structure has been developed to create a material with nanoscale water transport channels embedded in a barrier matrix of polyisobutylene. [7]

The parent tri-block copolymer is based on a poly(styrene-isobutylene-styrene) that is chemically modified by sulfonation of the styrene domains (blocks). Using this sulfonation process on the styrene domains of a lamellar structure, hydrophyllic nanoscale channels embedded in the polymer material are formed that preferentially favor water transport, while acting as a barrier to other permeants. Because of this attribute, these polymers are being studied for use in protective clothing, serving as a barrier to hazardous materials, while still allowing moisture to escape. These polymers, therefore, have the potential to be used in protective suits that may breathe better than current designs.

Water vapor transport data of the modified membranes and other commercial materials are shown in Figure 7. Initial studies with live chemical agents indicate that the sulfonated elastomer exhibits excellent barrier potential. Further live agent evaluations are in progress on optimized formulations. Textile design and engineering efforts using the novel membranes as a component in protective clothing are currently underway.

SUMMARY

Nanomaterials technology holds tremendous promise for creating the next generation of materials for Army applications. Ongoing research has been developing the building blocks and tools necessary to create and control materials at the nanoscale. Applications that utilize the unique properties of nanomaterials are emerging and increasing in complexity. As these technologies continue to mature, the basic building blocks and tools that are being presently researched will continue to find widespread application.

ACKNOWLEDGEMENTS

This article represents the work of the authors and has reviewed the work of several researchers who have made formal and informal contributions to the efforts that have been described. Dr. Gary Hagnauer, (recently retired as ARL Senior Scientist for Polymer Materials) was instrumental in establishing the nanomaterials initiatives that have developed into significant research efforts. The dendritic polymer initiatives were developed under his leadership. Dr. Hagnauer and Dr. Donald Tomalia (Central Michigan University) are acknowledged for their numerous contributions to the Army's

collaborative dendritic polymer research programs that have led to the successful utilization of dendritic polymers for a number of applications.

The dendrimer enhanced bioassay work that was described here resulted from the extensive efforts of a research team led by former ARL scientist Dr. Ray Yin, who has since founded and led the nanotechnology firm ANP Technologies, Inc. The research on dendritic fiber coatings was conducted by ARL in collaboration with Professor Giuseppe Palmese from Drexel University. ARL scientists Dawn Crawford, Jim Sloan, and Gene Napadensky are acknowledged for their contributions on permselective membranes based on modified block-copolymer materials.

NOTES & REFERENCES

* Interphase is the boundary region between two phases, in this case a fiber and a matrix, containing elements of each phase.

† Perfluorinated groups are organic groups that have had all the hydrogen atoms replaced by fluorine.

‡ Aliphatic groups are typically defined as non-aromatic organic groups. These groups are composed of chains, such as alkanes, alkenes, alkynes or other groups that do not have the stability of aromatic compounds.

§ Delivered groups are the groups that are oriented in such a way that they can provide a specific functionality to the area of the bulk material where they are transported to.

** Block copolymers are polymers assembled from segments of different polymers whose ends have been terminated with select functional groups. These functional groups are designed to react favorably, upon polymerization, only with those groups of another select polymer segment. Carrying out polymerization in this fashion allows one to control the structure and hence the properties of a polymer chain. Through careful control of the chemistry during polymerization these polymer segments self-assemble into a large polymer with a well-defined structure. Using this technique, polymers having repeating units of three segments of polymer material within the backbone (tri-block copolymers) have been designed.

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Small Features Enable Big Results:

Nanotechnology Research Uncovers New Multifunctional Materials for Future Army Systems

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INTRODUCTION

The US Army Research Laboratory is pursuing research efforts that apply advances in materials engineered and designed at the nanoscale to enable enhancements of military capabilities. These projects include transparent armor materials and coatings, carbon nanotube composites, and metal/polymer composites.

Nanostructured transparent armor materials and coatings have the ability to provide increased protection beyond currently used polymeric systems. They may be applicable to both personnel armor in the form of visors and for windshield/canopies. Carbon nanotubes offer potential use in several areas due to their excellent mechanical, electrical, and thermal properties. Current research revolves around dispersing the nanotubes into a polymer matrix, creating materials applicable for future military systems. Metal/polymer composites are also being evaluated for multiple applications. These include optical displays, data storage, and actuation devices. This research along with additional ARL projects concerning nanotechnology (see "Small Features Enable Big Results: The Army's Latest Developments in Polymer Nanotechnology" in this edition of the *AMPTIAC Quarterly*) will provide the foundation for performance enhancements to Army systems and capabilities.

TRANSPARENT NANOCOMPOSITES

Nanostructured materials have the ability to transcend material limitations previously met in the development of high performance transparent armor. Polycarbonate and acrylic polymeric materials have been the standard for decades providing protection against small arms projectiles. The need for increased performance brought about the use of ceramic materials, usually laminated between layers of polycarbonate or acrylic materials. This layered approach improved ballistic performance, but at a substantial cost. Nanocomposite transparent armors have the potential to increase ballistic performance at a cost amenable to wide scale usage.

The use of high-performance polymer nanofibers and/or elastomeric nanofibers as reinforcements has received much recent attention. The advantages of using nanofibers for reinforcement in transparent nanocomposites are twofold. First, the small diameter of the fibers (about 100 nm) is well below the diffraction limit of visible light (wavelength = 400-700 nm), therefore nanofibers dispersed in a transparent medium should not scatter light in the visible spectrum. Second, nanofiber textiles have fiber surface areas that are orders of magnitude greater than conventional fabrics due to the small fiber diameter. The greater surface area will provide more interaction between the resin and reinforcing fiber, improving mechanical properties and potentially increasing the amount of energy dissipated during an impact event due to sliding friction associated with fiber pullout. Finally, as has been demonstrated in the case of inter-penetrating network (IPN) resins, the incorporation of a continuous elastomeric phase into a rigid thermoset can enhance the fracture toughness of the matrix.

Nanofibers are easily produced using electrospinning methods and a variety of polymers have been spun into fiber mats including structural materials such as nylon and more compliant materials including polyurethane elastomers. Recent results achieved through collaborative research with the Army's Composite Materials Center of Excellence at the University of

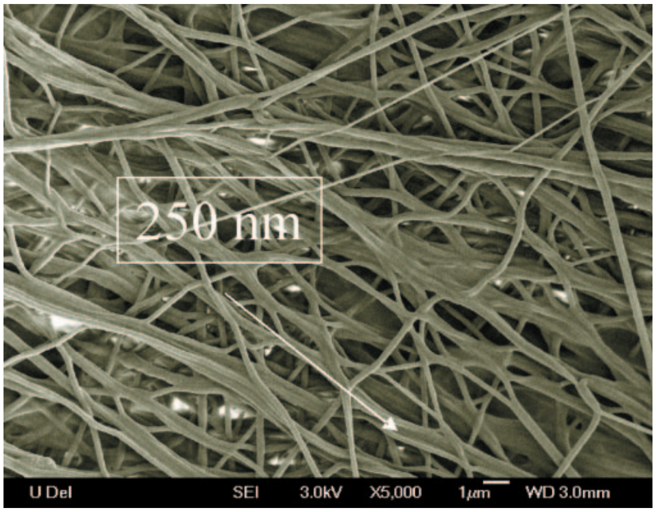

Figure 1. Electrospun TPU Fibers Used for Transparent Nanocomposites.

(a) Pure PMMA (b) 4% TPU Nanofibers/PMMA (c) 15% TPU Nanofibers/PMMA

Figure 2. Transparency of Pure PMMA Versus TPU/PMMA Composites.

Delaware Center for Composite Materials have shown that transparent composites can be made by using nanofiber mats that are impregnated with various thermoplastic and thermoset polymers. Figure 1 shows thermoplastic urethane (TPU) electrospun fibers while Figure 2 shows TPU/polymethylmethacrylate (PMMA) composites that possess high transparency and optical clarity (95 and 85% respectively) when compared to neat resin properties. In this case, a catalyst was added, followed by curing to produce a thermoset PMMA resin (PMMA is typically a thermoplastic polymer). Thermoplastic resins, including PMMA, have also been used to produce transparent nanocomposites. Mechanical properties of these materials show that incorporation of polyurethane nanofibers into PMMA resin increases the elongation at break by as much as 700% in comparison to pure PMMA. Ongoing research is assessing the impact performance of these systems and developing design rules for these new materials.

Transparent nanocomposite hard coatings represent a successful example of hybrid hard/ductile nanomaterials that may have use for soldier systems, including the next generation Joint Services Military Eye Protection Systems (MEPS) and headgear displays/visors for the Future Force Warrior. Figure 3 shows the optical clarity of silica (SiO_2)/PMMA nanocomposites for various silica content, prepared by sol-gel synthesis. Incorporation of silica increases the modulus and hardness of polymer matrix composites. The hardness of silica/PMMA nanocomposites were tested to reveal an increase from 0.21 GPa for 0 vol% silica content up to 0.34 GPa for a 30 vol% silica content composite.

Figure 3. Transparent Nanocomposite Materials That Have Demonstrated Increased Hardness Suitable for Scratch Resistant Coatings.

POLYMER-MODIFIED CARBON NANOTUBES

While carbon nanotubes have received an enormous amount of publicity, several hurdles need to be overcome to fully exploit their properties. Carbon nanotubes (CNTs) have unique properties that provide the potential to advance material systems in several areas. CNTs have a high Young's Modulus, high electrical conductivity, high thermal conductivity, and excellent chemical resilience. One specific hurdle to overcome is to effectively disperse CNTs into a polymer matrix, producing a composite with enhanced properties.

In order to facilitate favorable energetic interactions (which can lead to good dispersion of CNTs in a polymer matrix), the Army has investigated new methods to modify the multiwall CNT surface by attaching polymer chains at the surfaces of functionalized CNTs. Working with researchers at the University of Tennessee, the ability to grow polybutadiene (PBD), polyisoprene (PIP), polystyrene (PS), PMMA, and polyethyleneoxide (PEO) on CNT surfaces and directly control the solubility and dispersion of CNT materials has been developed. Using these methods, CNT modification can produce materials with different solubilities tailored for specific applications. Figure 4 shows various modified multi-wall nanotubes (MWNTs) dispersed in solvents. The polymer modification has a tremendous effect on the quality and stability of the dispersion.

SILVER PARTICLE/POLYMER FILMS

Many visual display devices make use of liquid crystalline polymers. These polymers change optical properties upon exposure to an electrical current. Therefore, light radiated through these displays is altered by the optical absorption and diffraction properties of the liquid crystal polymers. These changes in light transmission allow us to see images such as text or pictures. Currently the Army is looking at the use of silver nanoparticles for use in possible visual displays and/or optical data storage applications.

The in-situ formation of metal clusters in polymers is an attractive synthetic route for producing these materials [1-3]. The introduction of peroxide into a polyvinyl alcohol system facilitates the oxidation of the photoreduced metal particles, silver particles in this case. In short, the polymer films are doped with silver ions in a low concentration of peroxide. The films are subsequently dried and irradiated with photons of sufficient intensity and wavelength. The photoinduced formation of silver particles shows a strong dependence upon the induced wavelength and intensity.

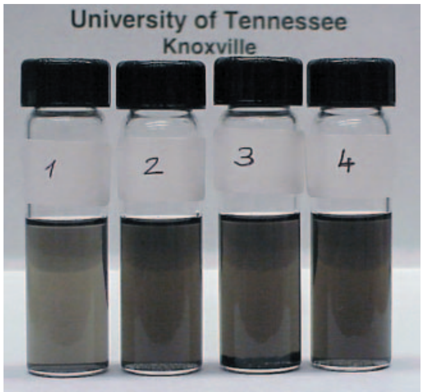

Figure 4. **Various Polymer-MWNT Composite (1%wt MWNTs) Solutions in Dichloromethane Photographed after 3 Days. Sample 1) PBD, 2) PIP, and 3) PS, All with Initial Composite Solution Concentration, [composite]$_0$ = 0.2 mg/mL, [MWNTs] = 0.02 mg/mL, 4) PMMA, [composite]$_0$ = 0.2 mg/mL, [MWNTs] = 0.014 mg/mL.**

After the formation of particles is achieved, the samples are protected from all sources of light, and a dark oxidation reaction is observed. Ideally, materials for these applications should possess both quick and good reversibility (the ability to lose their optical signal completely). Although the tested films do not exhibit good reversibility as shown in Figure 5, this research demonstrates the possibility of using metal particles in polymer films for Army display and information storage applications. This system is robust and was demonstrated in ambient atmosphere without the need for additional packaging. Efforts are underway to improve the kinetics and thereby optimize reversibility and speed.

PALLADIUM/POLYMER NANOCOMPOSITE ACTUATORS

Formation of palladium interlayers in polymer films for use as actuators is another area of research for organic/metal nanocomposites. Typically, thin metal layers on polymer films must be created using physical vapor deposition (PVD) under high vacuum. In PVD, the metal is resistance heated under a high vacuum which effectively reduces its melting and boiling point. The polymer film is placed in front of the flux of molten metal particles, and the polymer film is soon coated with a thin metallic film.

ARL is currently optimizing a non-vacuum process to produce polymer films with surface and embedded continuous metal layers. This process uses ultraviolet light to initiate photosensitive components within the polymer chain. The depth of the photoinduced chemistry is both wavelength and intensity-dependent. The metal-doped polymer films are heat treated at temperatures less than 325°C, and films with four distinct regions are produced, see Figure 6. The films are comprised of: 1) a resistive metal surface layer, 2) metal particle layer where the particle size is less than 10 nm, 3) a semi-continuous inter layer, and 4) a bulk region of metal particles where the particle size is greater than 10 nm. The films show an ability to actuate (bend) when exposed to white light and elevated temperatures. The radius of curvature in the bend is linearly dependent on the intensity of the light source and temperature.

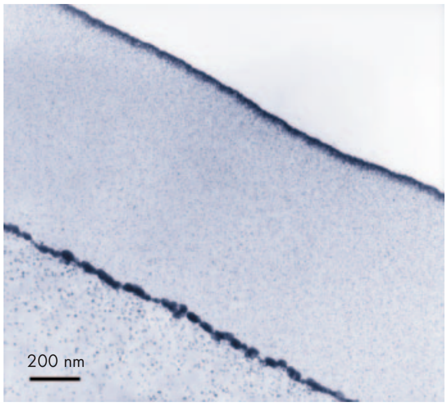

Figure 6. **Transmission Electron Microscope Image of Metal Interlayer Polymer Film.**

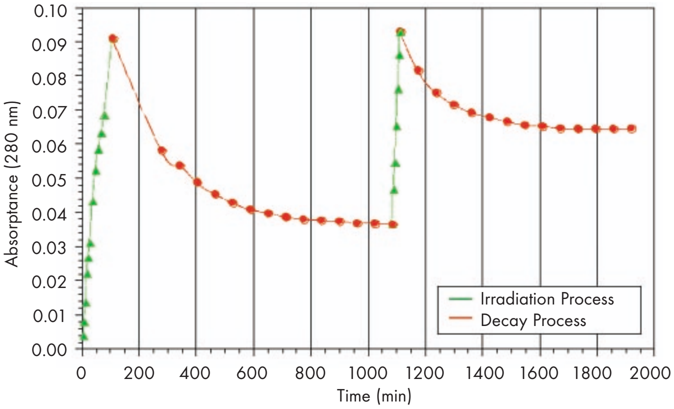

Figure 5. **Absorptance at 280 nm (Absorption Band for Silver Clusters) as a Function of Time during Irradiation and Decay Cycles.**

GLASS/METALLIC NANOCOMPOSITES

Much like the two previous nanocomposite systems, the photoreduction of silver and gold ions to form metallic nanoparticles within porous glass can create interesting composite materials. These systems are simple to produce and data indicates that the extent of metal particle formation is dependent on the wavelength and intensity of the impinging photons during the photoreduction process. This process can be used to control the color and reflectance of the glass. Some resulting irradiated samples are depicted in Figure 7.

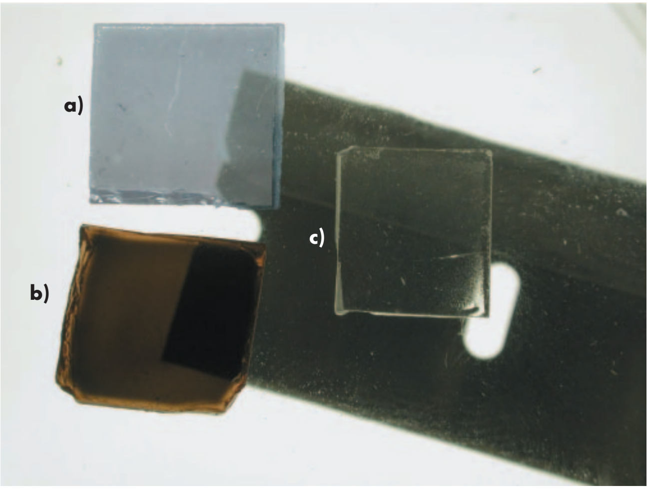

Figure 7. **Representative Depiction of Color Variance and Transparencies of Porous Glass Containing a) Gold Particles, b) Silver Particles, and c) No Particles.**

ARL is currently developing metal particle-based systems that would allow for a palette of colors that could then be selectively activated by careful selection of impinging wavelength and intensity of light. Efforts are underway to render the system reversible, where the photoreduced particles would undergo an oxidation reaction. During the oxidation of the photoinduced particles, the color of the systems will become less intense as the optical properties of metal nanoparticles are size dependent.

SUMMARY

Research into nanostructured materials and nanocomposites are of utmost importance for the improvement of Army systems. The Army is actively researching new materials and processing methods for the advancement of current systems. This research will provide insight to the development of enhanced systems in the fields of transparent armor, structural and functional carbon nanotube based materials, and metal/polymer composites for optical applications and actuation devices. Nanostructured materials bestow the potential for vast improvements across the board for military systems. The Army will continue its research into nanostructured materials that will provide benefit to future systems.

ACKNOWLEDGEMENTS

This article represents the work of the authors as well as many additional researchers who have made formal and informal contributions to these efforts. Alex Hsieh has worked with Professor Wei from Drexel University to develop the sol-gel transparent nanocomposite materials. Some of the research described was the result of collaborative research performed under two Materials Centers of Excellence programs for Polymers and Composite Materials. Professor Jimmy Mays from the University of Tennessee has worked with ARL researchers to produce the modified carbon nanotubes with controlled dispersion. Prof G. Mills and his group at Auburn University have contributed to the development of hybrid materials using photoreduction methods.

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Dr. Carl Krauthauser was an Associate Research Scientist at the Center for Composite Materials at the University of Delaware for 3 years (2001-2004), and is now a Research Physicist with the Armor Mechanics Branch of the US Army Research Laboratory. Dr. Krauthauser has 12 years experience working in the field of Atomic and Molecular Physics, with current interest in long chain high performance rigid-rod polymers. He received a BS in Physics and a BS in Mathematics from Villanova University in 1987, and his PhD in Atomic and Molecular Physics from the University of Delaware in 1994. His research interests include: polymer nanofibers, high performance polymer fibers, polymer surfaces and interfaces and phase behavior of complex polymer systems.

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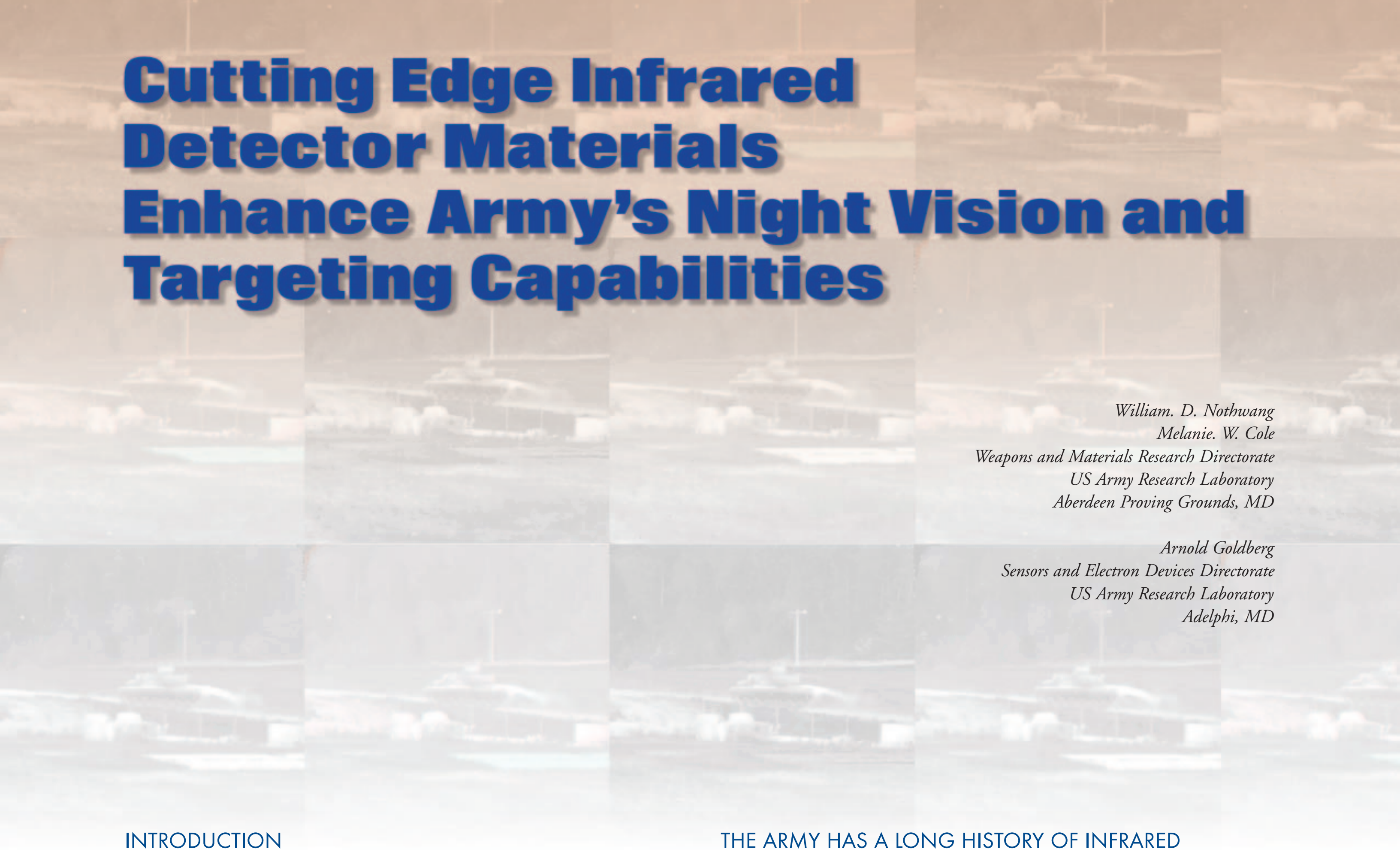
Dr. Joseph M. Deitzel is an Associate Research Scientist with the Center for Composite Materials, at the University of Delaware. Dr. Deitzel has 12 years experience working in the field of polymer science. He received his BS in Physics from the University of Akron and his PhD in Polymer Science from the University of Akron. Dr. Deitzel was a Research Fellow in the Polymers Research branch at the US Army Research Laboratory, where he contributed to research projects dealing with materials issues related to soldier protective clothing. His research interests include: polymer nanofibers, high performance polymer fibers, polymer surfaces and interfaces and phase behavior of complex polymer systems. Dr. Deitzel has authored numerous publications and presently holds one patent.



Cutting Edge Infrared Detector Materials Enhance Army's Night Vision and Targeting Capabilities

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INTRODUCTION

Advanced electronic materials supply the cutting edge that the Army is relying on to deliver the next generation of sensing devices and provide the foundation that will allow a new era of sensors for applications only previously imagined. Electronics now dominate nearly every aspect of the military with applications in the mess hall to the battlefield. The Army is currently developing these new applications, and researching dozens more that have yet to be realized. With so many demands, the field of electronic materials is vast. This paper will focus on one specific sensing application, infrared (IR) detectors, and the work that Army researchers and developers have done to transition this technology to soldiers in the field. Infrared detector materials, while only one example, represent a bell weather technology for electronic materials as a whole. As such, one needs to understand their importance to the Army, before examining recent advances in the field.

It should be noted that there is not one solution to the Army's needs for infrared technology. There are applications that require an extremely high sensitivity and refresh rate (the time between distinguishable signals), and there are applications with less stringent requirements that must be less expensive. There is a whole family of technologies that have been developed to meet these needs, and the three areas, pyroelectric thin film detectors, quantum well infrared detectors, and mercury-cadmium-telluride based detectors, discussed here are representative but by no means all encompassing of infrared detector technologies and materials being researched in the Army today.

THE ARMY HAS A LONG HISTORY OF INFRARED DETECTOR USE

Infrared detectors have been an increasingly important part of the Army's arsenal since the early 1960's, when a cooled forward-looking infrared (FLIR) detector was the first night vision system developed. The Army adapted this system in 1972 into a common module FLIR system. In 1978, uncooled thermal imaging was demonstrated to the Army, and 1985 welcomed the first battery operated night vision system. Shortly thereafter, in 1988, the first commercial IR cameras became available. The focal plane size, and the resolution, was increased to 256x256 pixels in 1990, and 512x512 in 1992. Presently, IR imaging systems, cameras, and detectors can be found commercially in everything from medical devices, fire control, surveillance, and even driver vision enhancement in some automobiles [1]. Military use includes night vision, rifle sights, surveillance, missile guidance, tracking, and interceptor applications[2]. Uncooled detectors, which typically require long exposure times and large lenses are unsuitable for the latter applications, while the cooled systems, which are somewhat bulky and expensive, are unsuitable for some of the former applications.

The Army is the largest consumer of infrared detectors in the DOD with most every component and system being slated for upgrade to an infrared capable environment. There are more than 500,000 vehicles Army wide, and they are each scheduled for an upgrade to a Drivers Vision Enhancement system to incorporate nighttime imaging[3]. Man-portable thermal weapons sights and vehicle mounted heavy weapons'

Figure 1. LWIR and MWIR Images[4].

currently account for 800,000 and 180,000 units respectively[3]. This brings the current Army investment in IR imaging to just over $6.5 billion.

TYPES OF INFRARED DETECTORS

The situational awareness provided by infrared detectors allows for advanced lethality and survivability across the full spectrum of military operations. Infrared sensors are used to detect energy emitted from targets, and their surroundings for a wide range of defense applications. The spectrum for IR detection and the associated thermal imaging equipment has been in the Short Wavelength InfraRed (SWIR) at 1-3 µm, the Medium Wavelength InfraRed (MWIR) at 3-5 µm, the Long Wavelength InfraRed (LWIR) at 8-12 µm and the Very Long Wavelength InfraRed (VLWIR) at >12 µm wavebands, corresponding to regions of atmospheric transparency (i.e. low absorption) and also to thermal blackbody maxima at around room temperature[2]. A combined image using multiple wavelengths within the IR spectrum increases the ability to discern between a variety of potential threats as seen in the fused image of Figure 1. Enhanced weapon system performance may be achieved in several complimentary ways including the use of integrated sensors and munitions which are lightweight, have low power consumption, are producible at high rates, and reliable.

In general, the IR detectors can be classified as either photon detectors or thermal detectors. In the first category, photons interact directly with the charge carriers in a semiconductor or metal to generate a photocurrent. Two families within photon detectors are those made using quantum confinement in the compound semiconductors GaAs and AlGaAs called Quantum Well Infrared Photodetectors (QWIPs), and those fabricated using an alloy of the semimetal Mercury Telluride and the semiconductor Cadmium Telluride (HgCdTe) generally called “MerCad” or MCT. Thermal detector materials, on the other hand, are characterized by the modification in properties due to the change of temperature, arising from absorption of the IR radiation. Photodiodes such as the InSb family deployed on the F-23 JSF, while not being directly addressed here, are important DOD technologies.

MCT and QWIP photodetectors require a specific cooling system to operate at a temperature where they exhibit maximum detection, offer extremely fast refresh rates, much smaller focusing optics, and can have a much higher resolution in a smaller detector size, see Figure 2. Thermal detectors, however, can operate at or near room temperature, but they require larger focusing optics and longer exposure times[2]. Most legacy photon detectors utilize photoconductive HgCdTe as a detector material; though, QWIPs composed of III-V (compounds from the third and fifth columns of the periodic table) semiconductor super-lattices (GaAs/AlGaAs) are also being actively developed for these same applications.

Although the fabrication costs for QWIP detectors is on par or less than the cost for thermal detectors, the necessary requirement of cooling brings factors of size, weight, volume, operating life, maintenance, cost, and reliability into the detector design. As a result, for many applications where high sensitivities are not necessary, lower cost, lighter weight thin film pyroelectric detector systems are finding relevance. The development of uncooled thermal detectors, particularly those based on the use of pyroelectric ceramic materials, currently offer advantages for certain applications in comparison with the cooled photon detector technology; though, as cooling technology continues to improve, this may not hold true for much longer. There is a constant drive within the DOD to improve sensitivity, reliability and energy consumption and lower cost, weight and size.

PYROELECTRIC BASED INFRARED DETECTORS

According to the September and October 2001 issue of the *Army AL&T*, the development of uncooled thermal detectors has been designated an important technology breakthrough[5]. The article, written by Douglas K. Wiltsie (Technical Director for Project Manager Night Vision/ Reconnaissance, Surveillance, and Target Acquisition, PM NV/ RSTA) states that small uncooled thermal sensors offer the Army medium-performance alternatives that are cost effective, light weight, and low powered (uncooled FLIRs are specifically either pyroelectric or microbolometer devices). These sensors are currently applied in rifle sights and driver viewers, and according to Wiltsie, futuristic applications include the Enhanced Night Vision Goggle and families of unattended ground imaging sensors.

Applying new technologies to multiple products will reduce costs and capitalize on economies of scale in manufacturing. Wiltsie further states that a major attractive characteristic of the uncooled technology is the elimination of the need for a mechanical scanner and cryogenic cooler, and hence the uncooled devices will draw significantly less power [5,6].

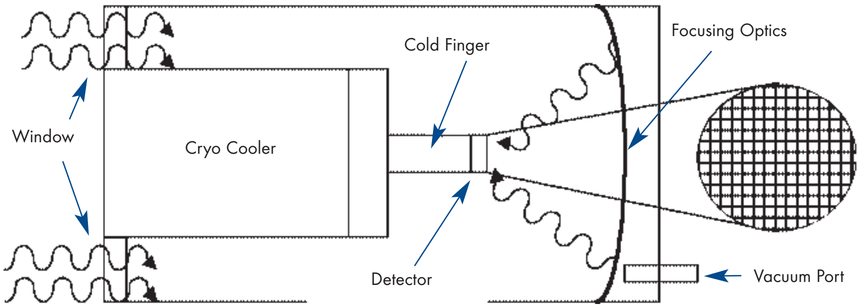

Figure 2. Cross-Section of a Dewar Containing a Cryogenically Cooled (<77K) QWIP/MCT Photodetector.

The primary consequence of this technological advancement has not been the replacement of the expensive, high performance, cooled detectors with pyroelectric detector materials, though this has happened to a certain extent; rather, it has been the proliferation of inexpensive, mid-performance detector materials allowing night vision equipment to become standard issue [6].

The Army continues to investigate a variety of alternative materials in addition to QWIPs, MCT, and bulk barium strontium titanate (BST) infrared sensors and bolometers. Pyroelectric detectors offer the advantage of room temperature operation and thus do not require costly, heavy, bulky cooling systems. To further investigate their application to Army systems, the Army Research Laboratory (ARL) recently completed a collaborative Director Research Initiative involving the Weapons and Materials Research Directorate (WMRD) and the Sensors and Electron Devices Directorate (SEDD). The materials investigated are suitable for small, light-weight infrared detection systems that are reliable and require minimal power. While there are ongoing efforts to examine thermal detector materials like bulk BST, thin film vanadium oxide, amorphous silicon, and yttrium barium copper oxide, ARL-SEDD and WMRD have focused much effort on developing thin film pyroelectric materials for IR sensors. All of these materials are being evaluated for room temperature/uncooled applications.

For a given material and area of the detector, the sensitivity can be increased by decreasing the thickness of the detector. Hence, thin film pyroelectric materials for IR detectors are expected to be better than bulk ceramic materials that are currently used in many applications. In one example of recent research at ARL, BST based thin films were investigated for use as phase transition pyroelectric thin film materials. Undoped and doped (Mg, Al, Ta, or La) BST thin films were fabricated via the metal-organic solution deposition (MOSD) technique. The metrics of success for all of these materials include low volume specific heat, a moderate dielectric constant, low loss tangent, a large pyroelectric coefficient, and the system must be single phase, dense, have minimal defects, a smooth surface and a high film resistivity. As shown in Figure 3, the absolute metric values were based on achieving a detectivity material figure of merit value, *D**, which is competitive or better than that of the industry standard lead titanate ($PbTiO_3$) based thin films [3].

A comparison of recent joint ARL-WMRD and SEDD research shows that the MOSD fabricated BST films designed, characterized, and optimized in this investigation possessed low dissipation factors, reasonable permittivities, excellent insulating properties and a high pyroelectric constant yielding a high calculated value of D*, competitive with that of Pb based thin films for IR pyroelectric detector applications. The MOSD fabricated, undoped BST thin films were determined to be an excellent candidate material for IR pyroelectric detector applications. Preliminary results also suggest that the 5 mol% Mg doped BST and 1 mol% La doped BST thin films are strong candidates for utilization as IR pyroelectric materials [3].

The accomplishments of this research endeavor were due to the combined efforts and expertise of the joint ARL WMRD-SEDD research team. This study examined fundamental research issues while at the same time addressed a current Army problem in advanced sensor technology.

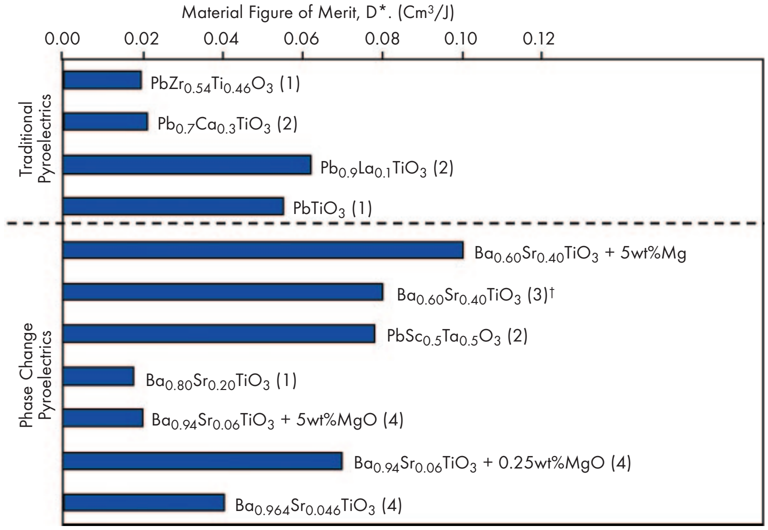

Figure 3. Comparison of *D** for Conventional and Phase Transition Pyroelectric Thin Films. The Materials were Deposited by: 1) Sol-gel, 2) Sputtering, 3) MOSD, and 4) PLD.
(†) indicates the results obtained recently by Army researchers [3]

QUANTUM WELL INFRARED PHOTODETECTORS

In the most general sense, QWIPs work by absorbing individual rays of light. In QWIPs, two very similar but slightly different materials are placed next to each other. Where the two materials touch, a "quantum well" is created and this quantum well can trap electrons. Due to the discrete energy levels in a quantum well, electrons in the well absorb very specific wavelengths.

In most QWIPs, the well material is Gallium Arsenide (GaAs) while the barriers are made of Aluminum Gallium Arsenide ($Al_xGa1\text{-}_xAs$, where x is the Aluminum mole fraction). Extremely thin layers (nano-scale) make up the structure. The absorbed light energy (or photon) causes an electron to become excited to a higher state, where it produces a photocurrent before it falls back to the ground state. By very carefully engineering the bandgap of a material, it is possible to tune the sensitivity of a detector to a very specific wavelength.

Typically, the bandgap tuning is done by changing the quantum well parameters such as the well thickness and the barrier height. III–V materials with relatively large bandgaps (1.43 eV for GaAs, greater than 1.7 eV for AlGaAs) are commonly used for QWIP fabrication. The InGaAs/AlGaAs materials can detect photons between 4 and 20 µm wavelengths, or within the MWIR to VLWIR spectrum. To optimize performance, the interface must be very flat, and the materials must be exceedingly uniform [2,7].

Thin film detector materials are typically deposited via molecular beam epitaxy, MBE, which is a very precise method of putting down one atomic layer at a time in a controlled manner. MBE has been shown to be a very effective process for QWIPs fabrication. Using MBE grown films on high quality substrates allows for the fabrication of an extremely high performance thin film, but it incurs a relatively high cost. Recent advances have succeeded in lowering this cost by increasing the throughput and the substrate size. However, QWIPs must still be cooled to a very low temperature (<77K) to achieve optimum performance, and this further increases the cost.

The GaAs/AlGaAs material system has numerous advantages, including: high bond strength, good thermal stability, ease of doping, and no need to passivate the surface due to materials stability, making it ideal for radiation hard (i.e. space) and harsh environment applications. There is a commercially viable GaAs industry, which significantly lowers the cost of device fabrication with these materials. After years of research, GaAs based QWIPs with all of these advantages have been successfully fabricated and tested. The challenges today facing QWIP researchers lay not in the fabrication of the base GaAs system, but rather in modifying it to improve its properties and lower its cost [7].

One such modification attempted by researchers at ARL-SEDD, is the design of multi-chromatic detectors [7]. These detectors would be able to detect and distinguish between light of differing wavelengths. Most display technologies (and the human eye) are tri-chromatic. Traditional infrared detectors, however, are mono-chromatic. The depth of view humans see is due to the eyes' ability to detect the different wavelengths of red, green and blue light. Multi-chromatic IR detectors, shown in Figure 4, would allow the simultaneous detection of multiple different wavelengths within the IR spectrum. As different materials emit light at different wavelengths, using a multi-chromatic detector allows for an increased ability to discern between varieties of threats and collect a wealth of new information. These include identifying buried objects, improved temperature sensing, decoy detection, and material identification [7].

Current methods for fabricating dichromatic detectors include using a mechanical filter wheel that "chops" the signal, a dithering system with a striped filter, or using two separate focal plane arrays (FPAs). None of these methods are efficient or entirely effective. To overcome this, researchers at ARL-SEDD have designed a linear array of quantum grid infrared photodetectors (QGIPs). The detector material, based on a binary super-lattice, has a spectral window between 8-14 µm, where it absorbs photons. The geometrical shape of the grid

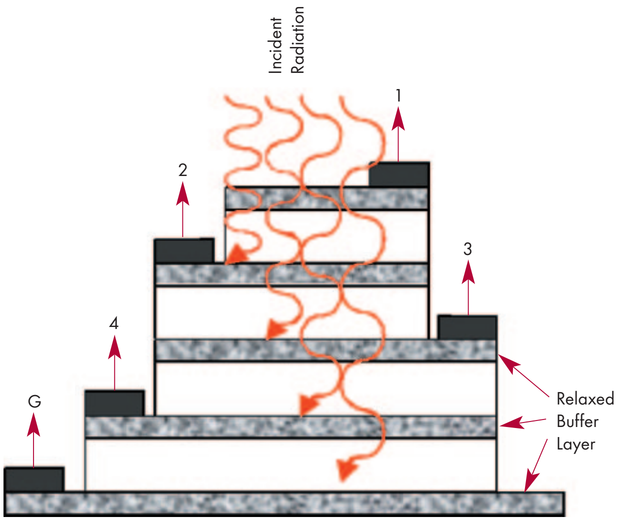

Figure 4. Multi-Chromatic QWIP Structure (1-4, G Represents the Electrical Signals from Each Layer[8]).

then selects specific wavelengths for each photodetector element, allowing multiple wavelengths to be detected from the same incident light, simultaneously. This makes it ideal for stand-off spectral analysis for chemical detection. By fabricating the QGIPs into an array, it will be possible to see infrared images in multiple colors. One such example is a new QGIP being developed with two QWIPs that allow detection into the LWIR and VLWIR, where there is a significant amount of information that was not previously visible. These detectors have been found to have very uniform stable sensitivities across the range of operating biases and temperatures [9].

In a parallel effort, based on previous work, researchers at ARL-SEDD have been working to improve the detection limit within photodetector materials [10]. In present detectors, there is a threshold bias voltage, below which no signal is detected. The threshold is due to the lack of photocurrent generated at the contact layer, which induces a large contact resistance. This decreased efficiency is attributed to the presence of a large number of defects that exist in the material at the interface between the doped contact layers and the doped quantum well. To overcome this, a compositionally graded contact layer has been fabricated. The composition within the new contact changes atomic layer by atomic layer, from the quantum well concentration at one end to the contact concentration at the other end. By grading the composition in this manner, the ARL-SEDD researchers have been able to completely eliminate the threshold voltage and enhance the low-bias performance of the detectors. This will significantly reduce the power needed to run these devices, making them smaller and less expensive [11].

MERCURY-CADMIUM TELLURIDE BASED PHOTODETECTORS

The MCT based detector systems are the first photodetector systems that were widely used and represent a mature thermal imaging technology being deployed within numerous Army and DOD systems. They have found applications in many detectors that require an extremely fast refresh rate, such as missile seekers. In order to achieve this high refresh rate, MCT detectors have to be cooled to low temperatures, frequently below liquid nitrogen temperature (77 K), and often as low as 30 K. At these temperatures the films are able to achieve refresh rates less than a millisecond, and in some cases less than a microsecond. The currently-deployed MCT based systems employ HgCdTe films grown by liquid phase epitaxy (LPE) on a semiconductor substrate. Most of the substrates currently in use are quite expensive, such as sapphire or CdZnTe. As the technology is more mature than QWIPs or pyroelectric thin films, the research effort within the Army has focused on trying to improve the resolution of the system, increase the operating temperature, and lowering the cost.

There are two important elements of any detector unit: the array of photodetector elements and the array of silicon readout integrated circuitry (ROIC). Traditionally, HgCdTe detector elements are grown epitaxially on lattice-matched and optically transparent cadmium-zinc-telluride ($Cd_{0.96}Zn_{0.04}Te$) substrates, and a complimentary metal-oxide-semiconductor (CMOS) process is used to produce ROICs. The detector elements are bonded to the ROICs with an indium bond layer to form high performance infrared focal plane arrays (IRFPAs). The CdZnTe substrates are very expensive and contribute to the poor reliability of large IRFPAs. Currently, the size of IRFPAs is limited because the indium bond breaks with repeated cycling of temperature between room temperature and operating temperature (77 K). Recent research at ARL-SEDD and the Communications and Electronic Research, Development and Engineering Center's Night Vision and Electronic Sensors Directorate (CERDEC-NVESD) has indicated that this is caused by the difference in thermal expansion coefficient between the ROIC-Indium-CdZnTe [12].

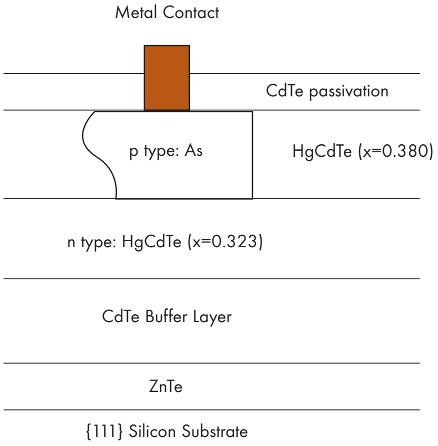

Figure 5. $Hg_{1-x}Cd_xTe$ P-N Double Layer Heterojunction Photovoltaic Diode Structure for MWIR[15].

To fabricate larger, more reliable IRFPAs two different solutions have been investigated within the Army: (1) growing the detector material on a silicon substrate that is then indium bonded to the ROIC, and (2) integrating the HgCdTe detector material directly onto the ROIC without an indium bond. Both solutions require a significant redesign of the material's microstructure at the atomic level, and for this MBE is ideally suited. Buffer layers and doping must be used to minimize defects that will inhibit the device's performance and lifetime.

Army researchers have recently designed a successful MWIR photovoltaic test structure on a silicon substrate, as shown in Figure 5 [13]. One of the major innovations that has allowed this advance to take place is the growth of a CdTe buffer layer on the silicon substrate. The proper orientation of the crystallized CdTe allows for the minimum Hg to be used during MBE growth of the HgCdTe. It has proven very challenging to grow properly oriented CdTe, but with a thin ZnTe layer on {111} (crystallographic plane) silicon, it has been achieved. When scaled to full production levels, this structure will enable much larger IRFPAs (i.e. greater resolution) at a lower cost [14].

This work has been accomplished with a collaborative effort between ARL-SEDD and CERDEC-NVESD. While examining some of the fundamental science questions behind the performance of the MCT systems, the collaborative research effort was able to significantly improve the quality, performance, and reliability of the systems being delivered to the soldiers in the field, and should significantly reduce the cost.

CONCLUSIONS

The advances in infrared materials technologies described here characterize the effort being put towards developing the next generation of Army technologies across the entire spectrum of electronic materials research. While these efforts and many more have been underway to develop the next generation of electronic materials based systems, there have also been parallel endeavors where Army researchers are producing advancements in electronic materials for the generation after next. Some of the recent successes in this area include:

- There has been significant work at ARO, focusing on improving the efficiency and effectiveness of Light Emitting Diodes from spin-loss effects, white light emitters, nitrogen defect structure, InGaN/GaN quantum well emitters, and doping of erbium and europium into nitrides. This work will have future applications in a wide variety of amplifiers, focused light, lasers, and illumination technologies [16,17].
- There have been some significant advances at ARL-SEDD and CERDEC-NVESD on Schottky Diodes from AlGaN and Cd/CdTe materials. Electron transport measurements have been made and surface treatments were examined to help design better diodes on silicon substrates [18].
- Some of the most promising work occurs where multiple disciplines overlap. The Army Research and Development Command has recently assisted in developing an extremely small ultraviolet (UV) source for detection of biological particles. By decreasing the size of the UV source, the entire detector becomes small enough, inexpensive enough, and light enough to be easily and rapidly deployed for a variety of applications [19].
- Once IR detector materials are developed there is still a significant amount of materials research that needs to be done before a device can be fielded. Recent work at the Army NVESD has focused on exactly this obstacle. They have made recent advances adapting devices and materials for multiple roles to both simplify the devices and reduce their cost, while also improving the overall performance [20].
- Extremely exciting are the potential discoveries being examined in molecular electronics within an ARL-WMRD and ARL-SEDD collaboration. This technology promises construction of electrical circuits out of individual molecules. Individual circuit elements have been demonstrated, and current research is focusing on methods for engineering molecules so that they self-assemble into device structures [21].

These are but a few of the examples of research being undertaken at the Army research facilities focusing on electronic materials for potential applications in the Future Force.

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Clearing the Air:

Army Composites Research Reduces Harmful Emissions

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Figure 1. Current and Future Uses of Composite Materials in the Army Include Component Replacements in the HMMWV and the Apache Longbow.

INTRODUCTION

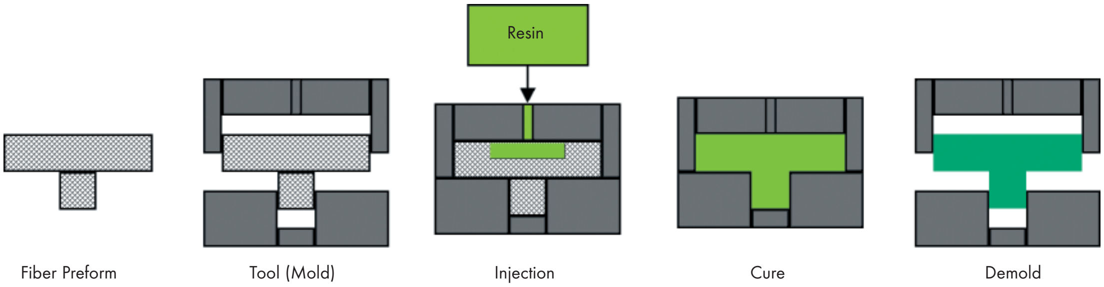
The Army and the DOD have been moving towards using polymer matrix composites (PMCs) in their current set of vehicles, ships, and equipment because of their combination of light weight and good mechanical properties. Programs have been initiated to replace steel components with composite parts on the high mobility multipurpose wheeled vehicle (HMMWV), the Apache Longbow helicopter, (Figure 1), as well as many other army vehicles. For instance, composite rotor blades have already replaced metal blades in the Apache Longbow. Furthermore, future classes of vehicles and ships will use significantly higher amounts of composite materials, making these vehicles lighter, faster and more maneuverable.

Fabrication of composite materials can, however, produce large amounts of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs). VOCs are materials that readily vaporize under ambient conditions while HAPs are defined by the 1990 Clean Air Act Amendments (Section 112) as chemicals that require emissions limits. Sources of pollution from PMCs include disposal of hazardous polymer ingredients, solvents used for viscosity reduction, gases evolved during and after processing, and disposal of contaminated scrap materials. Through implementation of the Clean Air Act and Clean Water Act, the Environmental Protection Agency (EPA) has established regulations limiting the amount of VOCs, HAPs, and heavy metals that can be used in the fabrication of composite materials.

The Army has developed a number of potential solutions to these problems that may impact the Department of Defense (DOD) and commercial composite manufacturers. High VOC containing solvents such as styrene and methyl methacrylate have been partially replaced with low VOC plant-derived fatty acids. Modified resins are used which allow curing methods other than autoclave curing which produces nitrous oxide (NO_x) HAPs. The result is environmentally friendly PMCs with properties comparable to current commercially manufactured PMCs.

FABRICATION PROCESSES

Liquid molding, depicted in Figure 2, is used to manufacture many thermoset PMC parts, such as automobile components and furniture. Vacuum Assisted Resin Transfer Molding (VARTM) is among the most common manufacturing processes to produce composites. In all of these processes, a liquid resin is injected into a mold containing fibers, such as glass or carbon fibers. It is important that the resin have a low viscosity (resistance to flow) so that the resin fills the gaps between fibers. Otherwise, defects will be present, significantly reducing the mechanical properties of the part. The high viscosity of thermoplastic polymers, like polycarbonates, is



The fiber preform is placed into the mold. The resin is injected into the mold.
The resin is then cured, after which the composite part is demolded.

Figure 2. **General Resin Transfer Molding Process.**

why these materials cannot be used to a large extent in composite manufacture. Once injected into the mold, the thermoset resin is then cured (i.e. reacted to form a solid) at room temperature or at elevated temperatures. Unlike thermoplastics, thermoset resins cannot be melted and reprocessed once cured.

The most commonly used thermoset resins for making composite materials are epoxy resins, unsaturated polyesters (UPE), and vinyl esters (VE). Reactive diluents in UPE and VE resins, such as styrene and methyl methacrylate, are used to reduce the resin viscosity to enable liquid molding. However, these diluents are VOCs and HAPs that can produce adverse health effects including headache, fatigue, depression, irritation, and cancer and are damaging to the environment.

VOCs evaporate at substantial rates at room temperature and could potentially produce smog-promoting ozone as well as long-term and acute health effects. VOC/HAPS are emitted during all of the phases of composite fabrication and even after fabrication (Figure 3). Emissions occur during the mixing of diluents, catalysts, and initiators into the system. Composite parts typically have very large surface to volume ratios, which allows up to 20% loss of diluent content during the molding stage. The elevated temperatures increase the vapor pressure of styrene and thus increase the rate of VOC emission. Unfortunately, even after cure during the lifetime of the part, VOC emissions can be substantial.

Studies have shown that up to 50% of the styrene in vinyl ester resins is unreacted after cure [1]. These unreacted monomers (simple compounds which react to form a part of a thermoset polymer) evaporate as VOCs, giving the composite an unpleasant odor and possibly leaching out into the water supply during the lifetime of the part. Studies have shown that although the composites industry only consumes 9% of the styrene, it produces 79% of the styrene emissions [2]. For these reasons, by means of the Clean Air Act, the EPA has enacted the Reinforced Plastic Composites National Emissions Standards for Hazardous Air Pollutants (NESHAP) to limit styrene emissions from composite manufacturing[3]. This legislation could have a significant impact on the use of composite materials in military as well as commercial applications unless methods for mitigating VOC emissions during composite processing, curing, and fielding of the composite part are developed. Current resins typically contain approximately 40-50% VOC content. The new regulations require the VOC content to be effectively about 30%, resulting in emissions reduction of approximately 8000 tons per year. Although some commercial resins have as little as 30% VOC content, these resins suffer from inferior properties.

Autoclave processes are used to cure PMCs and adhesives at elevated temperatures and high pressure. Global heating in an autoclave requires the application of pressure on the entire part. Nitrogen is used to provide the pressure and leads to the generation of high amounts of NO_x emissions, which is also regulated as a HAP under the Clean Air Act. NO_x emission is

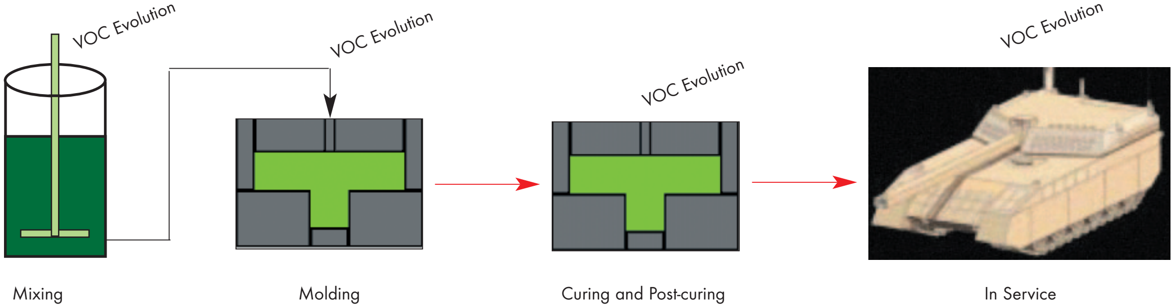


Figure 3. **VOC Emissions are Liberated During All Stages of Composite Production.**

conservatively estimated at 2% of the resin or adhesive mass [4]. The DOD produces approximately 30 million pounds of composites per year, of which half is processed in an autoclave resulting in about 150,000 pounds of HAP emissions per year. NO_x emissions generated from adhesives amount to approximately 90,000 lbs/year. As a result, there is a large push in the DOD and composites industry for "moving out of the autoclave."

Resins used for repair of PMC components for DOD applications produce significant amounts of hazardous emissions [4]. In addition, spoilage of these resins results in large amounts of hazardous waste a year. Estimates show that resin spoilage amounts to 20% of composites resulting in roughly 5 million pounds of hazardous waste per year, and 40% of adhesives materials resulting in 22 million pounds per year. Furthermore, many PMC components have been designed using existing technologies that fail to provide for practical and affordable component repair. These systems will generate large amounts of waste; and therefore, it is important to develop affordable and environmentally friendly PMC repair technologies, resins, and adhesives with longer shelf-lives.

UNSUCCESSFUL ENVIRONMENTAL SOLUTIONS

An obvious solution to reducing diluent emissions is simply to reduce the reactive diluent content in resins. There are a number of problems with this approach. First, the resin viscosity increases exponentially as the diluent content is decreased, making it impossible to use liquid molding techniques to produce composite parts. In addition, properties such as the strength and toughness decrease significantly as the diluent content is reduced. Lastly, reducing the styrene content increases the resin cost because vinyl ester/unsaturated polyester monomers typically cost double that of inexpensive diluents like styrene.

Various petroleum-based monomers, such as vinyl toluene with VOCs lower than that of styrene, have been used as styrene replacements [5]. However, these styrene replacements still produce significant VOC emissions, and are regulated by the EPA [3]. In addition, few monomers yield resins with performance comparable to styrene-based resins, and even fewer can match the low cost of styrene.

Vapor suppressants have been used to reduce emissions from vinyl ester resins. These suppressants are typically a surfactant or paraffin wax that segregates to the air interface and reduces the styrene evaporation rate [2]. Unfortunately, these suppressants also tend to segregate to the resin-fiber interface, which decreases fiber-matrix adhesion and the mechanical properties of the composite.

Another possible solution is to trap the VOC emissions during resin processing, composite production, and painting applications. These trapping devices need to absorb most of the VOC emissions and then efficiently remove the emissions from the air before exhausting to the atmosphere. Trapping devices fail in two major aspects. First, their use is not feasible in the production of large scale structures. Large scale structures are typically fabricated outside or in covered shelters, and building a device to trap a significant portion of the emissions is cost prohibitive. Secondly, although such devices would remove the VOCs from the atmosphere, the workers, due to their proximity to the structure being fabricated, would still be subjected to emissions and the associated health risks.

NO_x emissions can be eliminated by using an inert gas, such as argon, to generate the pressure required for autoclave processes. However, the cost of switching to argon is not economically feasible. Electron beams have been used as a mechanism to cure thermoset polymers. E-beams are a source of ionizing radiation that can generate ionic species, free-radicals, and molecules in excited states capable of initiating and sustaining polymerization. They can be used to reduce VOCs and NO_x emissions by cationic polymerization of epoxy monomers. Yet, the photoinitiators (compounds which cause polymerization upon the absorption of light) designed for E-beams are very expensive, and the initiator is easily poisoned by nitrogen and alcohols. Furthermore, cationically cured epoxies suffer from poor interfacial strength.

Resin suppliers have been trying to improve the shelf-life of resins and adhesives through the use of new inhibitor packages. The shelf-life has been improved but is still less than one year for most resin systems, and large amounts of spoiled resins are still produced annually.

SUCCESSFUL ENVIRONMENTAL SOLUTIONS

We have developed three solutions to reducing the VOC emissions from UPE and VE based composite resins. These solutions involve replacing conventional reactive diluents with plant oil derived monomers, altering the molecular structure of the cross-linking agent and reducing the styrene content in these resins. This also allows the use of environmentally friendly repair techniques, such as E-beam curing (Figure 4) which decreases cure time and temperature and reduces hazardous waste generation and NO_x emissions. These methods are currently in the process of being patented [6].

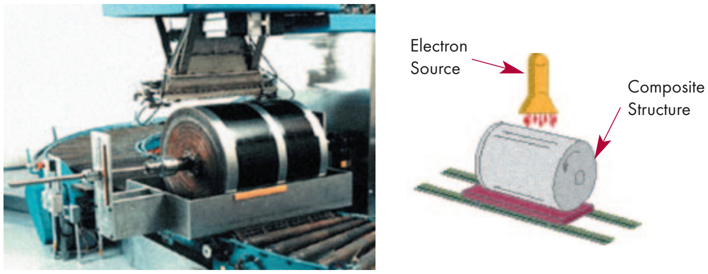


Figure 4. **Photograph and Schematic of E-beam Curing Equipment [7].**

Fatty Acid Monomers

Triglycerides are the main component of oils derived from plant and animal sources. Triglycerides are three fatty acids connected by a glycerol center (Figure 5). Triglycerides are simply broken down into fatty acids using industrial processes, such as acidolysis and saponification. A number of synthetic routes have been established for making fatty acid-based monomers. These synthetic routes can either use the acid group of the fatty acid or the functionality along the fatty acid backbone to attach

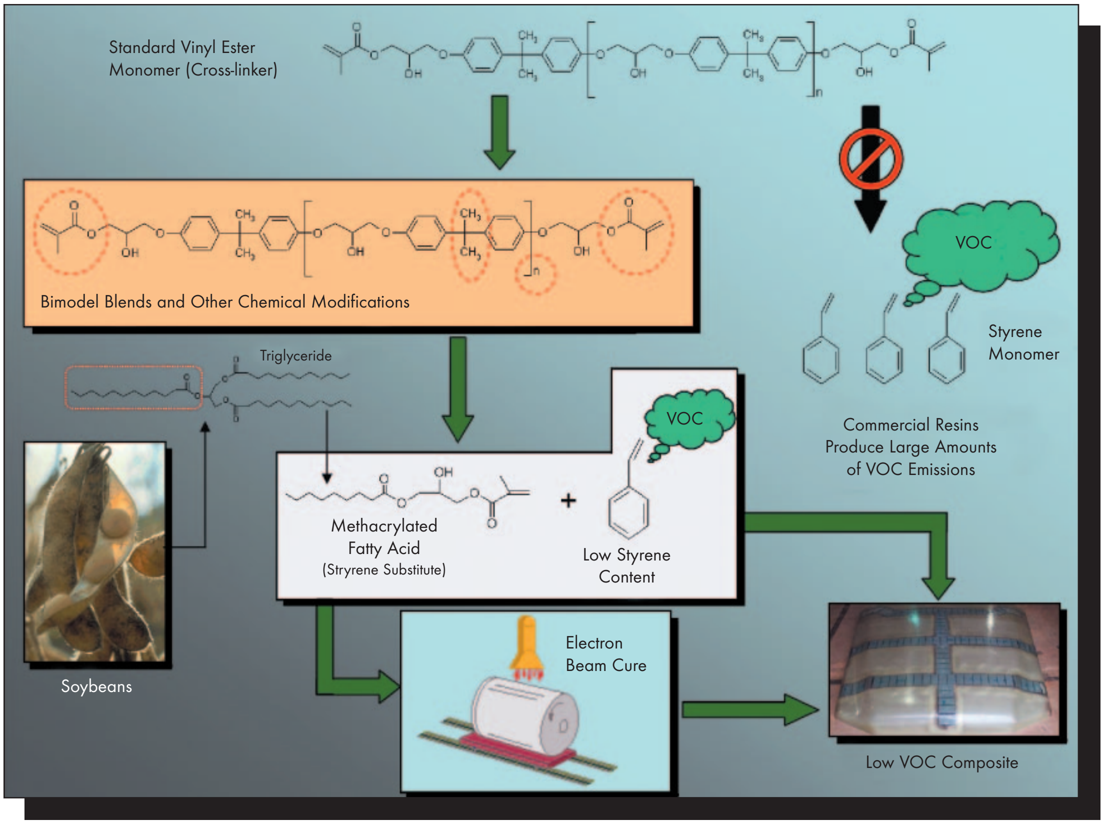


Figure 5. Methods to Reduce VOC Emissions in Thermoset Resins.

functional groups that can polymerize. The resulting monomers have fairly high molecular weight and are non-volatile, making them excellent alternatives to styrene in liquid molding resins. Due to the low cost of fatty acids and the simple modifications to produce fatty acid monomers, these monomers are inexpensive, with an estimated cost only slightly above that of styrene. Although plant oils have been used to make polymers for years, the use of fatty acid monomers as reactive diluents is a novel concept [6].

Ideally, all of the styrene in UPE and VE resins could be replaced with fatty acid-based monomers; however, the resulting resin and polymer properties are poor relative to commercial resins. Good performance can be realized by partially replacing styrene with fatty acid monomers. Styrene contents ranging from 10 wt% to 20 wt% (55-78% reduction in VOC content relative to commercial resins) were used resulting in good resin and polymer properties. The resin viscosities were far below the threshold for liquid molding processes and have been successfully used to produce defect free composite parts at high production rates. The glass transition temperature (T_g), the temperature at which a material transitions from hard and rigid to soft and rubbery, was similar to commercial resins, and the toughness was twice that of commercial resins. On the other hand, the stiffness and strength were a bit lower than that of commercial resins. Fortunately, we have found a number of methods for improving the stiffness of fatty acid-based polymers. The first involved using fatty acid monomers with shorter chain lengths. Experiments have shown that the resin viscosity decreases while the stiffness and T_g increase as the fatty acid chain length decreases. In addition, slightly modifying the VE chemical structure offers promise for improving the strength and stiffness by altering the polymer morphology.

A number of composite materials were made using VE resins with both styrene and fatty acid monomers as the reactive diluents. To prove that these resins can be used to produce large scale structures, a composite hood for an M35-A3 truck (Figure 6) was fabricated using a low VOC resin containing 15% fatty acid monomers and only 20% styrene. The resin infused very quickly for such a large structure (7 ft x 7 ft) and cured well to produce a fine composite structure. Therefore, successful low VOC resins are not merely a concept, but instead are reality.

Bimodal Blends of Vinyl Ester Monomers

The molecular structure of VE monomers can be used to alter the polymer properties and reduce the styrene content in these resins. Simply reducing or increasing the molecular weight of vinyl ester monomers does not provide a means for both decreasing styrene emissions and maintaining resin and polymer properties. Low molecular weight VE monomers have poor fracture properties because of their high cross-link densities. High molecular weight VE monomers yield resins with high fracture properties because of reduced cross-link density (i.e. matrix toughening). A mixture of low and high molecular weight VE monomers (i.e. bimodal blend) could be used to maintain low resin viscosities and low styrene contents while achieving high fracture toughness [6].

Continued on Page 124

Army Develops New Environmentally Compliant Coating Technologies

Coatings are used to prevent corrosion and damage to vehicles and structures, while also providing camouflage. Prior to the application of coatings, the metal surfaces are usually cleaned with solvents and treated with chemicals, such as lead and hexavalent chromium, to promote adhesion and corrosion resistance of the coating. Chemical agent resistant coatings (CARCs) contain polymer binders that provide the required performance level of the product, pigments that provide the desired color and gloss, and solvents/additives that control the viscosity and aid in film formation [1]. An aliphatic polyurethane binder provides the chemical agent resistance while the camouflage properties are provided by an appropriate selection of tinting pigments for visual color and near-infrared reflectance, plus extender pigments for gloss control.

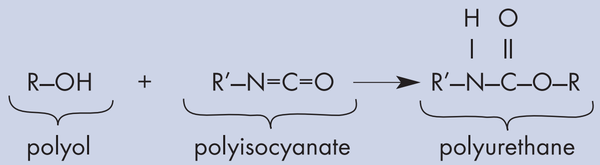
In a typical solvent-based urethane system, polyol reacts with polyisocyanate to form polyurethane, see Figure 1. If designed properly, crosslinking (bonds between polymer chains) in this system provides high-performance coatings. CARCs must display resistance to alkali, hydrocarbons, and acids. The coating must also exhibit high flexibility and mar resistance (i.e. high ability to resist damage). Lastly, the coating must have a very low gloss for camouflage requirements. This usually requires high pigment contents, which tend to have an adverse effect on the coating's performance.

The use of organic solvents to clean surfaces prior to coating has been affected by the Environmental Protection Agency mandated Reinforced Plastic Composites National Emissions Standards for Hazardous Air Pollutants and harsher regulations imposed by local governments. Typical cleaners, such as isopropanol and tetrachlorethylene, are volatile organic compounds (VOCs), materials that readily vaporize under ambient conditions, and/or hazardous air pollutants (HAPs) as defined by the 1990 Clean Air Act. The use of lead or chromium pre-treatments are regulated under the Clean Water Act because heavy metals accumulate in organisms and can cause blindness, auto-immune disorders, and cancer among other health problems. CARCs require a solvent to reduce the viscosity for painting and film formation. Previous CARCs use organic solvents that produce large amounts of VOCs and HAPs during application and drying. The Clean Air Act and its amendments has set the VOC limit for the CARC topcoat at 3.5 lbs/gal, but local governments have set this limit as low as 1.8 lbs/gal. Therefore, new environmentally friendly CARC systems, cleaning solvents, and primers are necessary.

The Army has developed a number of solutions to reduce the overall environmental impacts of surface preparation and coating processes (Figure 2). Low VOC solvents for cleaning, dry (no water) metal coating processes, and low VOC CARCs are all excellent methods leading to cost efficient, good performance coatings. The systematic approach to developing alternative processes and materials has resulted in methods that have a very beneficial cumulative impact.

A few low vapor pressure solvents were identified that can be used to effectively clean composites prior to repair [2]. Exxsol D60 and Isopar G, both developed by Exxon Chemical, clean surfaces as well or more effectively than conventional solvents, such as isopropanol and acetone. Furthermore, these solvents are similar in cost. Because these alternative solvents have substantially lower vapor pressure, they produce less VOC/HAP emissions and are less flammable.

Different materials and approaches can be used to increase the part-life rather than using a high VOC/HAP chemical treatment. Tantalum coated gun barrels that protect the bore surface from the hot propellant gases were developed to eliminate the need for hexavalent chromium processing [3]. Furthermore, the tantalum coating was deposited using an environmentally friendly method called



$$\underbrace{R\text{–}OH}_{\text{polyol}} + \underbrace{R'\text{–}N{=}C{=}O}_{\text{polyisocyanate}} \longrightarrow \underbrace{R'\text{–}\overset{H}{\overset{|}{N}}\text{–}\overset{O}{\overset{\|}{C}}\text{–}O\text{–}R}_{\text{polyurethane}}$$

Figure 1. Chemical Reaction to Produce Polyurethane.

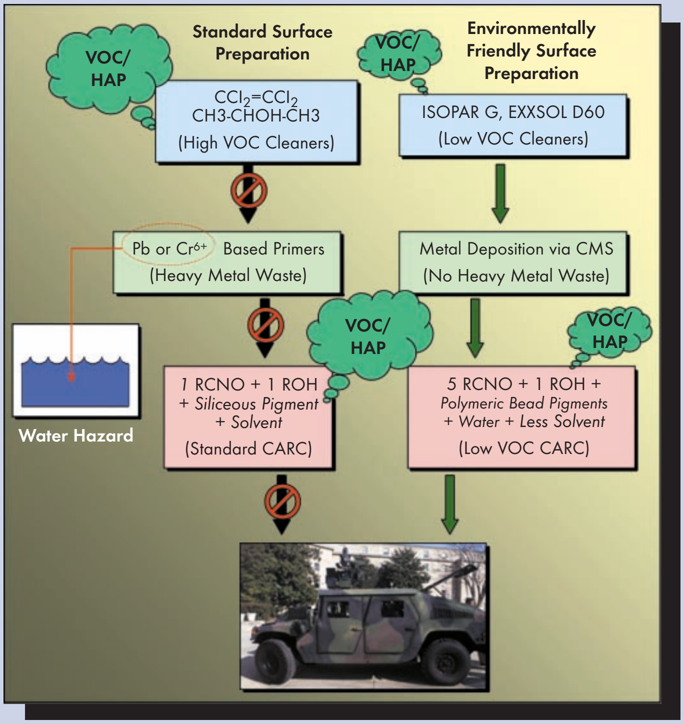


Figure 2. **Methods for Reducing VOC/HAP Emissions and Heavy Metals in Surface Preparation and Coating Processes Include Low VOC Solvents for Cleaning, Dry Metal Coating Processes, and Low VOC CARCs.**

Cylindrical Magnetron Sputtering (CMS) that does not generate heavy metal-based hazardous wastes. CMS is a magnetically enhanced sputtering system that is capable of providing high deposition rates over large areas while maintaining low substrate heating levels. In fact, the resulting gun barrels exhibit superior corrosion and wear resistance relative to chromate treated barrels. In cases where CMS cannot be used, the Army has also developed lead-free and acid-free solid rocket motor propellants reducing the need for lead and chromium treatments [4].

ARL developed a water dispersible CARC as a “drop in” replacement for the previous solvent-based CARC that can be applied and stripped using existing equipment [5]. The patented (US patent #5,691,410) water-based system eliminates HAPs and ozone depleting chemicals entirely, along with 4 millions lbs/year of VOC emissions, a 50% reduction, thereby meeting the new emissions requirements. The binder is still a mixture of polyisocyanates and polyols that cross-link to form polyurethane. While there is still competing reaction occurring with water, the chemical kinetics, raw materials, and a large excess of isocyantes to hydroxyl groups (5:1) were used to ensure good coating performance. Polymeric beads were used rather than siliceous-based pigments. This allowed for lower pigment contents to produce the same low gloss coating, while further improving the coating’s performance.

The water-based system was found to be a better CARC than the solvent-based system because of its superior flexibility and durability, and it requires one-third less paint [5]. This improved performance increases the time between finishing and reduces damage to the structure resulting in less coating maintenance. Furthermore, the cost per square foot per year of service for the environmentally friendly CARC is actually less than that of the previously used solvent-based system even though the water dispersible CARC costs more per gallon. In addition, dry abrasive blasting was successful in removing the environmentally friendly CARC, rather than using solvent-based paint removers. For these reasons, the Army has switched almost completely to the environmentally friendly CARC. More recently, the Army has conducted an extensive investigation of coatings and their degradation mechanisms, thereby improving coating durability even further and generating less VOC emissions [6].

The Army recently developed a universal ammunition coating (UAC) for munitions systems [7]. To improve the overall coating performance for munitions, a new class of corrosion-inhibiting pigments was incorporated into a durable fast-drying alkyd (drying oil modified polyester) polymer system. In addition to meeting the requirements for emissions, substrate adhesion, and long-term storage with energetic materials, the UAC provides improved corrosion resistance, eliminates the primer coats on certain munitions, and is a drop in replacement for existing coatings. After extensive evaluations, the UAC was qualified for Army use.

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Figure 6. Photographs of a) the Unpainted Composite Hood and b) the Hood Affixed on an M35-A3 Truck. The Blue Stripes are PVC Foam Stiffeners that are Fabricated into the Part.

Experimental results showed that the styrene content of these bimodal blends can be reduced while still maintaining low enough viscosity for composite liquid molding processes. The viscosity was found to be dependent on the number average molecular weight of the bimodal blends of VE monomers. As a result, the styrene content can be decreased to as low as 30-37 wt% while maintaining good resin processability. Although not a severe reduction in styrene content, this does amount to ~20% reduction in VOC emissions relative to commercial resins. The modulus and strength were also comparable to commercial resins. But most importantly, bimodal blends substantially improved the toughness relative to commercial resins. Therefore, the concept of bimodal blends of VE monomers can be used not only to reduce VOC emissions, but also improve the composite properties.

Composite Repair

E-beam curable resins were developed that can be used in VARTM applications [4]. These resins consists of di-epoxy, tetrafunctional amines, di-vinyl monomers, and monomers with both epoxy and vinyl functionality. The liquid monomeric resin has a low enough viscosity for VARTM, whereby it can be injected into a mold containing glass or carbon fibers and properly wet the fibers. When the resin mixture is cured at room temperature, the epoxy-amine forms a network, while the vinyl functionality remains unreacted inside the network. This gelled mixture is then irradiated with an E-beam to form a second network by cross-linking the vinyl groups, which are subsequently linked to the epoxy network. The T_g of the resulting polymers are high (250-350°F) with fracture toughness values above that of other E-beam resins. Furthermore, the shelf-life of the resin was found to be nearly infinite, with no chemical change occurring as a function of time until the two-part system is mixed together. This resin has been commercialized as Prepreg T-17 by YLA, Inc. in Benicia, CA for E-beam/VARTM applications.

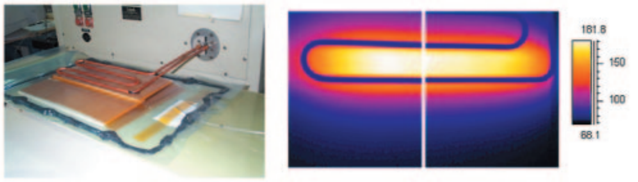

Figure 7. The Coils Magnetically Induce the Resin Cure by Heating the Composite Material.

Environmentally friendly E-beam adhesives were formulated in a similar fashion [4]. However, blends of mono- and multi-functional amines and epoxies were used to prevent gelation of the epoxy-amine network. Instead, when these components completely react, the resin viscosity increases to that of a paste. The paste can be applied to join sections of a composite, fill in holes, etc. and then be completely cured via E-beam. These resins were toughened through the addition of a functionalized rubber that phase separates into rubbery domains during cure. The resulting polymers have high T_g and excellent adhesion strength that far exceeds previously developed commercial E-beam resin systems.

The most common bonding methods for repairing composites are the use of convection ovens, thermal blankets, and radiant heaters. All of these processes heat the entire part and do not target just the repair zone. This requires long process times and exposes large areas of the composite structure to excessive heating, which could have detrimental effects on the composite's performance. Induction heating occurs when magnetic or conductive materials, like carbon-fiber composites, are subjected to a high frequency electromagnetic field (Figure 7). For parts not using carbon-fibers, metal wire meshes are impregnated with resin/adhesive at the point of repair or the repair resins are formulated with 20-30% magnetic particles by volume [8]. Induction heating can achieve thermal powers necessary for high temperature and rapid heating. This achievement is not trivial and has been made possible only though the development of high frequency (>10 MHz) self-tuning induction power supplies. Furthermore, induction heating can be used with both thermoset and thermoplastic resins.

Both E-beam and induction heating processes eliminate the need for autoclave processing, which completely eliminates

NO_x emissions. In the cases where thermoplastic resins can be used to replace thermoset resins for repair, VOC/HAP emissions can also be eliminated using the induction heating technology. Even for thermoset systems, emissions are reduced by 50% through the use of E-beam cure because of the rapid cure associated with E-beam. In addition, the E-beam curable resins were designed to have nearly unlimited shelf-life, thereby reducing the amount of hazardous waste produced by DOD and industry in terms of spoiled resins. Overall, a conservative estimate of the annual savings for the DOD is a substantial $220 million on top of the large environmental benefit associated with these technologies.

CONCLUSIONS

The military and commercial industry has a large need for high performance composite resins with reduced VOC emissions. Previously developed solutions to the emissions problem are not acceptable because the resins still produce large amounts of VOCs or performance is severely reduced. The Army's solutions to these problems involve modifying the molecular structure of the cross-linker molecules, using plant derived fatty acid monomers as styrene substitutes, using epoxy/amine/vinyl E-beam curable resins, and induction curing techniques. These solutions allow for severe reduction in VOC and NO_x emissions and reduction in hazardous waste, while producing resins and coatings that have comparable, and in some cases, superior properties to commercial polymers. Therefore, these solutions will help enable the Army and the entire DOD to produce the next generation of lighter, more efficient, and environmentally compliant vehicles, ships, and structures.

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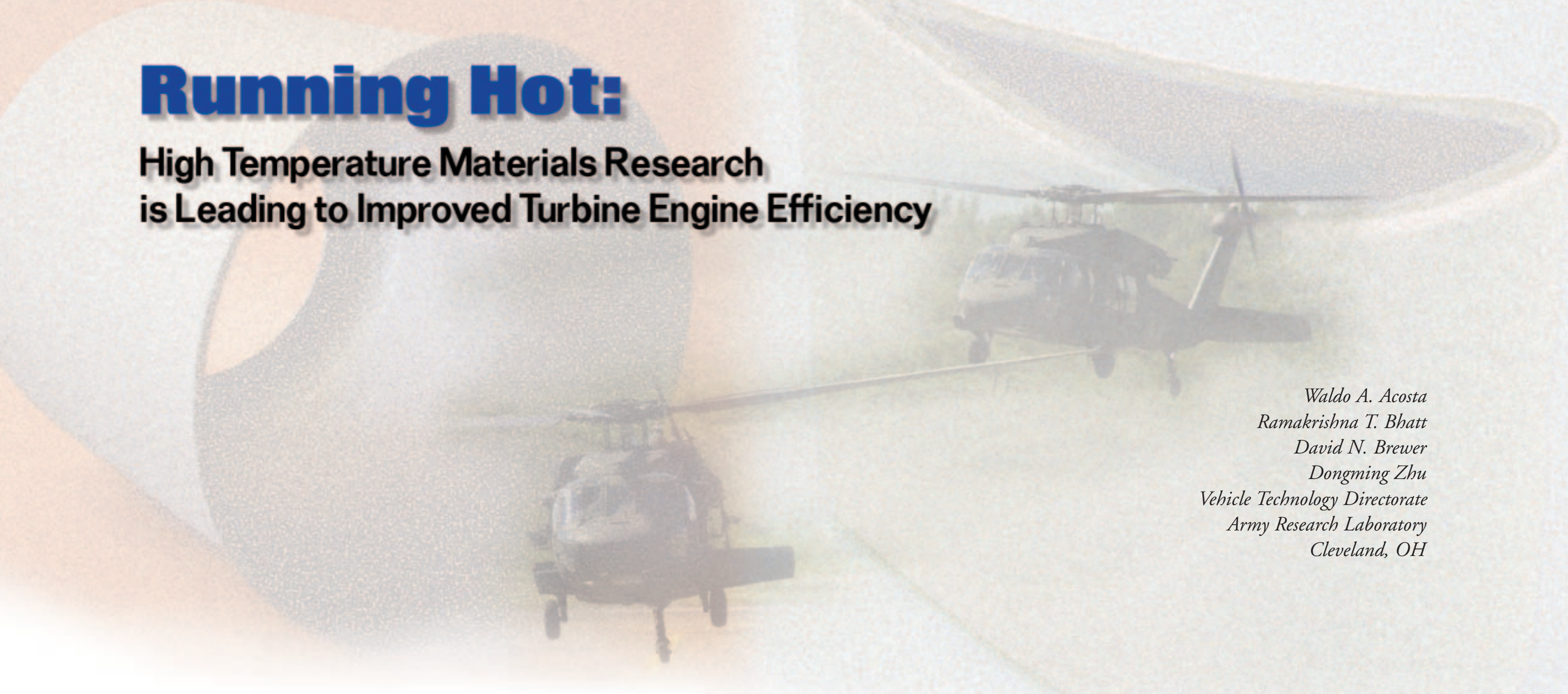

Running Hot:

High Temperature Materials Research is Leading to Improved Turbine Engine Efficiency

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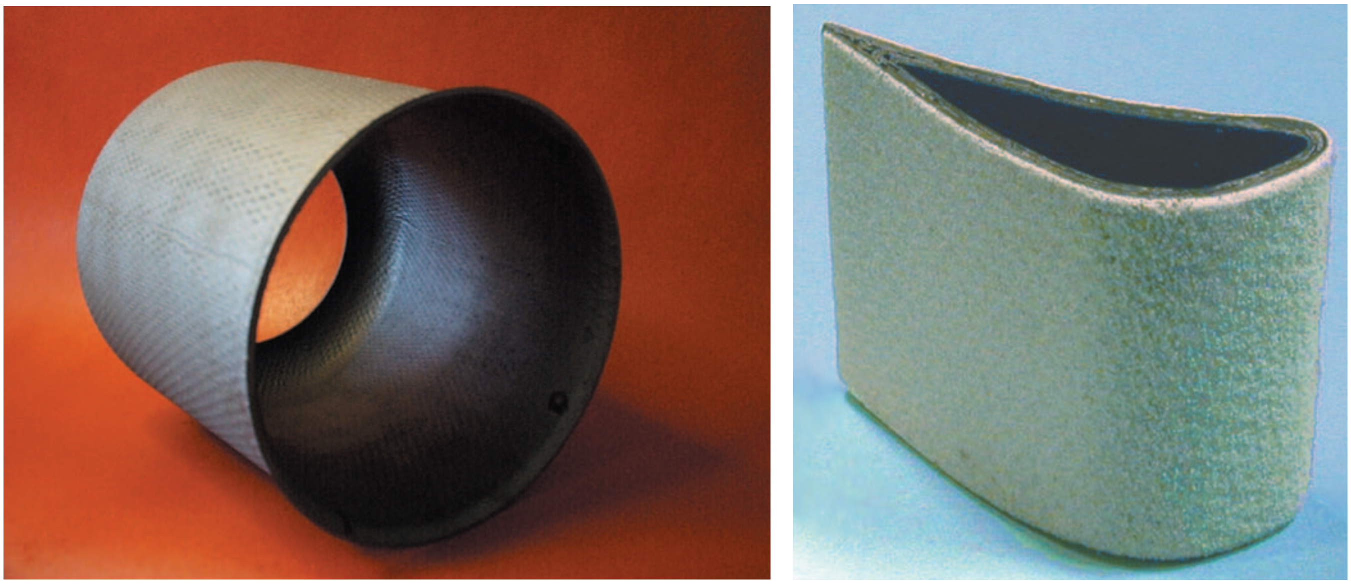
INTRODUCTION

Future Army helicopters will be able to fly farther and carry more payload thanks to the advanced material systems being developed by scientists and engineers at the Army Research Laboratory (ARL). Current gas turbine engine components, mainly the combustor and turbine, are made of heavy metal alloys that depend on significant amounts of air to cool and maintain them at or below their maximum use temperature of about 1100°C. Major efficiency gains can be made if the cooling air is dramatically reduced, completely eliminated, or the operating temperatures of components can be increased. The cooling system does not produce the primary work function, propulsion; therefore it is viewed as a penalty or inefficiency to the operation of a gas turbine engine. Turbine engine operational efficiencies can be increased through the use of ceramic matrix composites and ceramic thermal barrier coatings.

TURBINE ENGINE MATERIALS DEVELOPMENT

During the evolution of gas turbine engines, there have been great improvements made to the design of the combustor liners, turbine vanes, and blades (Figure 1). Those improvements have made more efficient use of the cooling air, resulting in significant cooling system reductions and efficiency improvements. However, the material operational temperatures have not been increased and are preventing further improvements in fuel efficiency (Figure 2).

Ceramic materials have the potential of operating at temperatures greater than 1100°C with minimal or no cooling, which will produce a variety of performance advantages. ARL, in collaboration with NASA, has been working on the development of fiber-reinforced ceramic matrix composites (CMCs) for potential use in combustor and turbine vanes and blades. CMCs are capable of higher operating temperatures, are about



a) CMC Combustor Can

b) CMC Turbine Vane Coated with a Thermal Barrier Coating

Figure 1. **Gas Turbine Engine Components.**

Figure 2. Present and Future Army Helicopter Systems will Benefit from Advances in Gas Turbine Engine Technology.

30 to 50% lighter than the metallic alloys currently in use, exhibit the necessary toughness needed to operate in the turbine engine environment, and provide at least the same level of safety and operability. There are several key factors that need to be met to apply CMCs with success. Achieving a CMC system with the required thermal and structural properties will depend on the ability to design and process the CMC so that it achieves the proper microstructural features.

Our efforts have been centered on the development of a silicon carbide (SiC) fiber-reinforced SiC matrix composite system (SiC/SiC), which was initially developed under NASA's Enabling Propulsion Materials (EPM) Program [1]. The goal of the EPM Program was to develop a SiC/SiC system capable of operating for many hundreds of hours at temperatures up to 1200°C. The current goal is to develop a SiC/SiC system capable of operating at 1427°C for hundreds of hours and at the same time retaining the thermal and structural properties required by the particular component. This

Table 1. Key Constituent Material and Process Data For NASA/ARL-Developed CMC Systems.

CMC System	N22	N24-A	N24-B	N24-C	N26-A
Upper Use Temperature	2200°F (1204°C)	2400°F (1315°C)	2400°F (1315°C))	2400°F (1315°C)	2600°F (1427°C)
Fiber Type	Sylramic (*Dow Corning*)	Sylramic-iBN (*Dow Corning + N*)			
Interphase Coating	CVI Si-doped BN (*GEPSC*)		CVI Si-doped BN outside debond (*GEPSC + N*)		
Matrix	CVI SiC – low content (*GEPSC*)			CVI SiC – medium content (*GEPSC + N*)	CVI SiC – medium content (*GEPSC*)
	SiC slurry infiltration (*GEPSC*)				PIP SiC (Polymer Infiltrate and Pyrolysis) (*Starfire + N*)
	Silicon melt infiltration (*GEPSC*)			Silicon melt infiltration (*N*)	

N = NASA/ARL Processing
GEPSC = GE Power Systems Composites

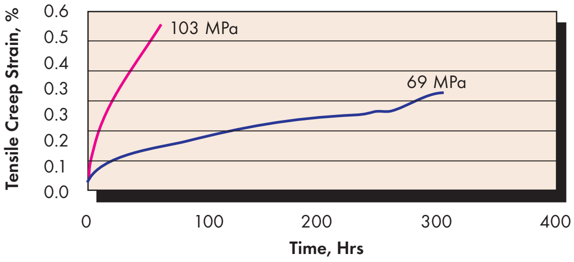


Figure 3. **Effect of Stress on Creep Behavior at Constant Temperature (1500°C) for Sylramic-iBN Hybrid SiC/SiC Composites Fabricated by CVI and PIP.**

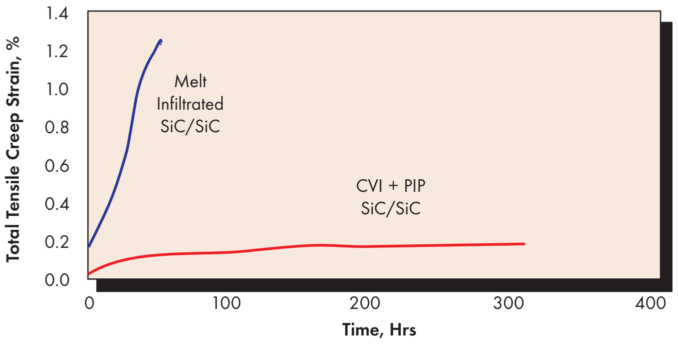


Figure 4. **Creep Behavior of Melt Infiltrated SiC/SiC (With Silicon) and Hybrid (Medium CVI +PIP) SiC/SiC Composites (Without Silicon) at 69 MPa, 1450°C in Air.**

requires the optimization of many factors within the SiC/SiC microstructure, including the fiber type, fiber coating material, fiber architecture, and matrix structure. The selection of a few first-order property goals facilitated this task including a high tensile proportional limit stress after processing, high ultimate tensile strength (UTS) and strain after processing, high UTS retention after interphase (region between the fiber and matrix) exposure at intermediate temperatures in wet oxygen, high creep resistance at upper use temperature under high tensile stress, long rupture life (greater than 500 hours) at upper use temperature under high tensile stress, and high thermal conductivity at all service temperatures [2].

Various CMCs developed by NASA/ARL are shown in Table 1 [2]. In addition to the organizations listed, these CMCs have been processed at other organizations resulting in material systems with similar properties. Recently, two types of hybrid SiC/SiC composites with no residual silicon were fabricated: the first using a combination of polymer infiltration and pyrolysis (PIP) and chemical vapor reactive (CVR) process; the second using a combination of chemical vapor infiltration and PIP. Preliminary results indicate both types of hybrid SiC/SiC composites are very promising for high temperature applications, up to 1450°C. However, additional studies are needed to optimize processing and properties of these composites. Figure 1 indicates that at a stress level of 69 MPa, Sylramic-iBN hybrid SiC/SiC composites fabricated by a combination of CVI and PIP methods show a creep rupture life greater than 300 hours at 1500°C in air. At 103 MPa, the same composite fails at about 60 hours (Figure 3).

Residual silicon in a SiC matrix has significant influences on the upper temperature capability of SiC/SiC composites. The SiC/SiC composites without any residual silicon show creep rupture lives greater than 300 hours, whereas those containing residual silicon rupture in less than 100 hours (Figure 4).

THERMAL AND ENVIRONMENTAL BARRIER COATINGS

Ceramic thermal and environmental barrier coatings (TEBCs) have the potential to increase further the efficiency of gas turbine engines by providing them with the ability to operate at higher gas temperatures while reducing cooling requirements. Figure 5 shows that the development of revolutionary ceramic coatings results in a step increase in combustor and turbine vane and blade temperature capability. As shown in the figure, advanced TEBC systems will withstand higher surface temperatures and larger thermal gradients than current coating systems. This will require the development of advanced ceramic coatings with lower thermal conductivity to allow the use of a thin layer coating while achieving a larger temperature gradient across the coating, thereby enabling reductions in cooling requirements since a lower substrate temperature will be maintained.

ARL researchers, in collaboration with NASA, have been developing advanced thermal barrier coatings (TBCs) for metallic turbine airfoils and TEBCs for thermal barrier coatings SiC/SiC combustor applications. The incorporation of multi-component, paired-cluster rare-earth oxide dopants into conventional zirconia-yttria (ZrO_2-Y_2O_3), and hafnia-yttria (HfO_2-Y_2O_3) oxide systems to develop the advanced oxide coatings has been shown to achieve low conductivity, high temperature stability, and improved durability [3]. We synthesized TBC systems containing ZrO_2-Y_2O_3-Nd_2O_3(Gd_2O_3, Sm_2O_3)-Yb_2O_3(Sc_2O_3) oxide clusters and investigated their

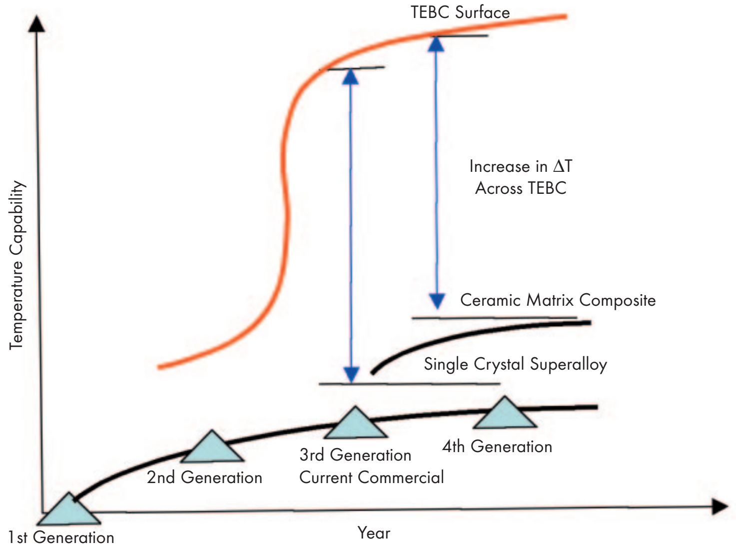


Figure 5. **Potential Benefits from the Development of Advanced Barrier Coatings.**

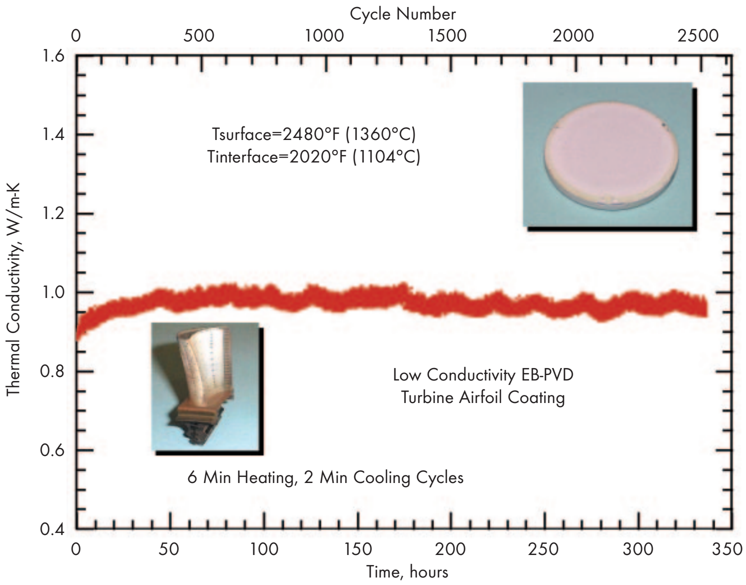


Figure 6. **Advanced Low Conductivity EB-PVD Thermal Barrier Coating Demonstrated Cyclic Durability.**

thermal conductivity, sintering behavior, and cyclic durability at high temperatures. Figure 6 shows the advanced low conductivity electron beam - physical vapor deposited (EB-PVD) turbine airfoil thermal barrier coating demonstrated more than 200 hot-hour high-heat-flux, high-thermal gradient cyclic durability at 1360°C (2480°F).

Under the wet oxidizing conditions encountered in the combustion gases, silica (SiO_2) formation on the surface of unprotected SiC/SiC reacts with water to form volatile species, giving rise to paralinear oxidation kinetics and a gas velocity-dependent degradation of the Si-based materials [4]. Advanced thermal and environmental barrier coatings for SiC/SiC combustor liner and turbine vane applications will extend operating temperatures up to 1650°C while protecting the SiC/SiC substrate from the wet oxidizing combustion environment.

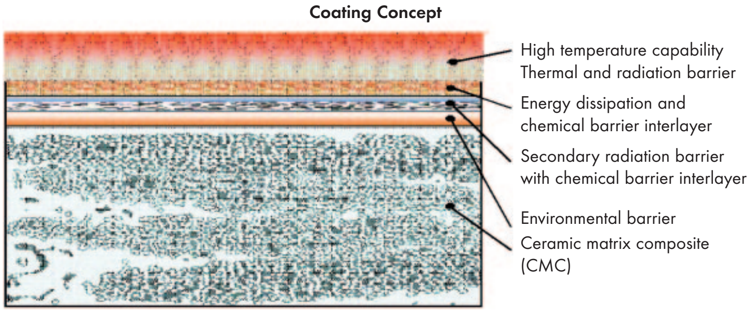


Figure 7. **Advanced Coating Design Concept for 1650°C CMC Combustor.**

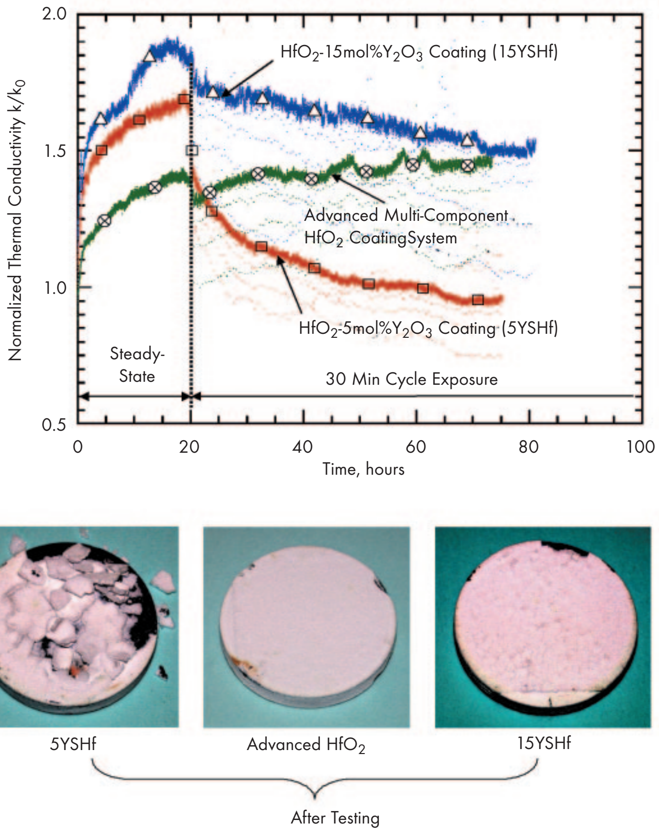


Figure 8. **Sintering and Cyclic Behavior of a Multi-Component HfO_2-Y_2O_3-Gd_2O_3-Yb_2O_3 Coating.**

Figure 7 shows an advanced coating design concept for the 1650°C TEBC system for CMC combustor applications. The top layer is a high-temperature capability ceramic thermal barrier coating, designed to provide the major thermal protection for the sub-coating systems and CMC substrate. It also acts as the first-stage radiation barrier by reducing the transmission of infrared thermal radiation from the combustion gas environment. The energy dissipation, secondary radiation barrier and environmental barrier layers will also be incorporated into the coating system to provide strain tolerance, further reduce radiation energy penetration, and ensure environmental protection functions.

HfO_2-based oxides have been developed as a potential candidate for a 1650°C coating material for advanced thermal/environmental barrier top coating applications. Figure 8 shows the 1650°C sintering and cyclic behavior of a multi-component HfO_2-Y_2O_3-Gd_2O_3-Yb_2O_3 coating that was deposited on a mullite ($3Al_2O_3$-$2SiO_2$) based environmental barrier coating, Si buffer layer, SiC substrate. The advanced multi-component HfO_2 coating had a relatively low conductivity increase during the first 20 hour steady-state testing, and also showed essentially no cracking and delamination during the subsequent 100 cycles where the specimens were subjected to 30 minute exposure to 1650°C, indicating its excellent sintering resistance and cyclic durability as compared to the baseline coatings. This coating system recently demonstrated 300 hour long-term 1650°C sintering and cyclic durability on SiC/SiC under thermal gradient cyclic testing, far beyond the current state of the art baseline ZrO_2-Y_2O_3 coating capabilities.

LIFE ANALYSIS

The structural integrity of any material system, whether metal or ceramic-based, cannot be guaranteed to be 100 percent safe. Many factors come into play that can introduce uncertainty. Among them are the uncertainties of the properties of the in-situ material, limitations in the analysis, both human and analytical; and last but not least the actual load conditions under which the structure will ultimately be placed. Safety factors are used during the design process to account for those uncertainties; nevertheless it is a requirement that the probability of failure be within an acceptable range for each particular application.

A turbine vane made of SiC/SiC was designed, fabricated, tested, and analyzed to demonstrate the performance increases that result from these new advanced composite materials. Because of scatter in material property data and uncertain load conditions, a formal probabilistic analysis and reliability assessment of the vane was conducted in order to calculate the probability of failure to meet design requirements [5]. Two cases were studied. The first had four random variables that were material property related. The second case added two random variables that were load related. The study found that there was a 1.6% probability that the material system would not meet the requirements for which it was designed. The importance of this methodology is, in addition to providing a quantifiable risk assessment; it also provides a tool that would allow specific tailoring of the structure's design for a specific reliability.

CONCLUSIONS

The research and development of ceramic matrix composites and ceramic-based coatings for use in turbine engines components has the potential to achieve increased levels of efficiency and push the performance of Army vehicles to new heights. The use of ceramics as opposed to metals allows higher operating temperatures and little to no cooling requirements. These material technology improvements can transition the Army into becoming a more mobile and effective force.

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In Memoriam: Bruce K. Fink

It is with great sadness and a heavy heart that we announce the recent passing of one of this issue's principal sponsors, Dr. Bruce K. Fink of the Army Research Laboratory (ARL). This issue of the AMPTIAC Quarterly *was already on press when we received word of his tragic death. The cover of the quarterly had not yet gone to print, which presented the opportunity to insert this announcement and tribute.*

Bruce was a highly accomplished man – whether as an engineer, scholar, manager, or soldier; he served his country, his profession, his peers, and his community with distinction; having risen rapidly in each forum, with the trust and respect of those around him. His entire adult life was a testament of his drive to excel. A complete listing of his achievements would require many more pages than are available here. At best, we can provide the reader with a brief portrait of the man.

Upon his graduation from college Bruce was commissioned into the US Army as a regular officer. While on active duty, he served 10 years as a Combat Engineer Officer, and also earned both his MS and PhD degrees. He eventually left active service after attaining the rank of Major, and having won many awards and commendations.

Bruce's civilian career at ARL spanned over 10 years, where he conducted research in numerous fields, such as the processing and modeling of composites, lightweight structures, armor, and the integration of materials and structural design. He was instrumental in establishing a new way of approaching materials research so that it was more focused on the soldier; a necessary part of meeting the goals of the Current and Future Force. He rose through the ranks quickly. In his capacity as Chief of the Materials Division of ARL's Weapons and Materials Research Directorate, he was responsible for reorganizing the Materials Division along functional rather than discipline lines. This remains the Division's current structure, leaving his signature on the organization. He earned more than 30 different technical awards; including the Paul Siple Award for the best paper at the Army Science Conference, and the US Army Research and Development Achievement Award. He was a prolific author and speaker, and was the originator of several patents. During his career, he also served as an adjunct professor at the University of Delaware and Tuskegee University.

Bruce was a very important member of the greater technical community, having served leadership and advisory roles in such organizations as the National Science Foundation, the Military Handbook 17 Committee, and the National Materials Advisory Board.

Bruce was an energetic and vital individual who was an integral part of the DOD materials community. Bruce was not only a dynamic and creative leader, but also an empathetic and thoughtful man who easily and almost invariably crossed the boundary between colleague and friend. He will be missed not just within the Aberdeen and Army Research communities, but throughout the DOD and the national and international materials and defense research and engineering arenas.

Beyond the professional man was one who was deeply committed to a greater sense of community. He was highly active in his church, directing and supporting a number of his congregation's efforts. Always eager to pitch in, he also served the greater community in a variety of roles, large and small. Such consummate gentlemen are rare in this world. His loss will be felt by us all. - Editor

2005 Army Materials Summit

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