AMPTIAC

QUARTERLY
Volume 8, Number 2
2004

Reducing Acquisition Risk

Better Military Systems through Smart Materials Selection Practices

MaterialEASE:

Elastomers are far more important than you might think!

Nanotechnology Update:

AFRL/ML's R&D Progress

AMPTIAC is a DOD Information Analysis Center Administered by the Defense Technical Information Center

Editorial: It's not easy being a "Materials Guy"

As we have written numerous times within the pages of the Quarterly, materials are the enablers of all technology: manned space flight, supercomputers, automobiles, cellular phones, life-saving medical equipment, and even food storage and preservation are all possible because of the development of one or more new material technologies.

One of the most frustrating things about being a material professional is constantly listening to engineers and managers repeat the same old mantra, "we don't have any materials problems." Presuming they don't run away immediately after this admission, they eventually tell us about their problems in design, manufacturing, quality, reliability, and maintenance. What they fail to recognize is that a lot of these *are* materials problems. In fact, many of the problems inherent in the various stages of the product development cycle (the acquisition cycle in the DOD) are material-originated in nature.

More to the point, the vast majority of these assorted 'problems' are the direct result of design teams making poor material choices during the pre-production phases of the product life cycle. Are these poor choices the results of incompetence, negligence, or even malice? Not at all – they are examples of the growing 'understanding gap' that has developed between the materials community (those with a firm understanding of how materials work) and those who actually make the decisions on what materials to use in applications. In short, materials selection is an endangered practice: part art, part science; it has traditionally represented a synergy of materials science and sound design principles, drawing on an appreciation of the projected operating environment and a cognizance of how material choices impact performance. When materials selection is performed properly, its results are invisible to users. It's only when some type of problem arises (such as unexpected maintenance) do materials and their selection rationales get any attention (and unwelcome at that).

Both our lead article and the MaterialEASE feature discuss different aspects of materials selection, and the pitfalls of what happens when improperly implemented. Whether the issue is corrosion, hydraulic seals, or even thermal shielding, the problem is the same. It seems that the emphasis placed on materials selection in the design process is waning with each passing year.

This diminishing experience base is the result of several trends: the military downsizing precipitated by the end of the Cold War and its resultant "brain drain"; acquisition reform (relegating basic material decisions to contractors, while concurrently eliminating a large percentage of military specifications and standards), and a steady decline in engineering enrollment at America's universities. What's more, few engineering schools teach more than the rudiments of material selection (i.e. strength, stiffness, weight) in their curricula, thus new engineers are ill-equipped to address the multitude of requirements incumbent in any design activity. Engineers must discard the mindset of designing systems to perform the day they leave the factory. Accounting for the time-dependent nature of materials during design will do more to extend system service life than any other post-production effort.

As our military systems are pressed into increasingly longer periods of service, the limitations of those materials selected decades ago are becoming increasingly evident. They manifest themselves in terms of maintenance, repairs, spare parts, and other types of rework. A more disturbing thought yet: If current systems (designed in the pre-reform era) are having problems attributable to materials selection, what about future systems not yet designed or fielded?

However, the outlook is not all gloomy. Recent DOD initiatives are reexamining the department's role in providing guidance and encouragement to contractors in critical enabling technologies, materials among them. Simultaneously, there are task groups working to revive selected military specifications and standards; which would provide program offices and contractors with needed guidance to make better design decisions. Lastly, there is a growing assemblage of material principals (including AMPTIAC) calling for accredited universities to revise their engineering curricula to make the fundamentals of materials selection a required subject area in applicable undergraduate degree programs. The objective is not to make designers material experts; but rather to instill a basic competence, allowing them to recognize and "flag" materials issues for further scrutiny by specialists. If we as a technical specialty can incorporate that principle into the engineering paradigm, then the battle will be more than half-won.

Ultimately, it will not be any sweeping reform or government initiative that will win the day: it will be the numerous individual efforts made by each of us at opportune moments to "nudge" the system. If in our own arenas, we can get designers to look beyond basic requirements and their standard menu of 'tried and true' materials, then we will have done a great service for our profession, our colleagues, and our nation.

Christian E. Grethlein
Editor-in-Chief

Editor-in-Chief
Christian E. Grethlein, P.E.

Creative Director
Cynthia Long

Information Processing
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The AMPTIAC Quarterly *is published by the Advanced Materials and Processes Technology Information Analysis Center (AMPTIAC). AMPTIAC is a DOD-sponsored Information Analysis Center, administratively managed by the Defense Technical Information Center (DTIC). Policy oversight is provided by the Office of the Secretary of Defense, Director of Defense Research and Engineering (DDR&E). The* AMPTIAC Quarterly *is distributed to more than 15,000 materials professionals around the world.*

Inquiries about AMPTIAC capabilities, products and services may be addressed to

David H. Rose
Director, AMPTIAC
315-339-7023
email: amptiac@alionscience.com
url: http://amptiac.alionscience.com

We welcome your input! To submit your related articles, photos, notices, or ideas for future issues, please contact:

AMPTIAC
ATTN: CHRISTIAN E. GRETHLEIN
201 Mill Street
Rome, New York 13440

phone: 315.339.7009
fax: 315.339.7107
email: amptiac_news@alionscience.com

Reducing Acquisition Risk by "Designing in" Corrosion Resistance

David H. Rose
AMPTIAC Director
Rome, New York

Addressing the problem of corrosion in weapons systems, support systems, and military infrastructure has historically been an ambitious undertaking. While most would agree that it is one of the more serious problems plaguing military systems, the unanimity of opinion generally stops there. To various principals within the DOD, there are tremendously disparate perspectives on what corrosion even represents. To some, it is strictly a maintenance problem – an inevitable part of doing business. To others, corrosion is a chemical phenomenon that occurs in most metals, but no connection is made to real-world impacts. In most cases, these views are highly compartmentalized, lacking the 'big picture' of how corrosion affects the entire life cycle of DOD assets, from design through retirement and disposal. Fortunately, the new DOD Corrosion Policy, recently instituted by Undersecretary Wynne has already started to provide DOD personnel with a more global view of the subject. While much has already been written about what this policy means for reducing costs, and who is doing what to reduce corrosion (see Vol. 7, No. 4 of the AMPTIAC Quarterly*), little has been mentioned about how one goes about actually reducing corrosion in military systems. In response to this call, AMPTIAC is preparing to publish a major, first-of-its-kind corrosion resource:* A Program Management Guide for Selecting Materials. *It will provide program managers and design engineers with guidance on how to actually select materials in the design process which will enhance corrosion prevention and control. As publication of this handbook may still be several months away, we offer the following teaser in the interim to whet your appetite. We hope you find it useful!* - Editor

INTRODUCTION

Corrosion is a process that occurs when a material electrochemically reacts with compounds in its surrounding environment, in which the original material is chemically "consumed." As a material corrosively deteriorates, its material properties likewise degrade. The results of corrosion manifest themselves as weapon system or component failures in the worst cases, or as unsightly blemishes in the best (Figure 1). It's important to realize that corrosion afflicts nearly all systems in all operating environments. Moreover, it can significantly impact readiness of DOD systems if excessive maintenance is required to ensure continued safe operation. Corrosion costs can be extensive, and for complex systems, combating its effects can take a great deal of time and expertise to correct. Overall, the costs of combating corrosion are very high. A recent, federally funded study has estimated the cost to the DOD at over $20B per year [1].

All too often, it is the case that corrosion begins on the drawing board, where critical design decisions will determine much of a system's future. In general, systems are designed to meet performance goals where strength, weight, thermal, and electrical requirements are primary technical considerations. Other important attributes, such as corrosion resistance and environmental compatibility, typically receive far less attention. Without an upfront analysis to assess and address potential corrosion issues, problems often occur once the system has been put into service. Correcting unanticipated corrosion problems during the operational phase of an asset's lifecycle can be very costly. In some cases it may be impossible to restore a system to its original state without replacing problematic components or structures at great expense.

Developing new systems that are inherently corrosion resistant – either through selecting and using corrosion resistant materials, or if appropriate, by employing corrosion preventative compounds and coatings – is one sure way to reduce total ownership costs. To be effective though, these considerations must be made early in the acquisition cycle. Design and acquisition principals must recognize corrosion as a risk factor to be managed.

When DOD and contractor personnel come to recognize that corrosion is one acquisition risk factor among many

Figure 1. Corrosion of a Military Ground Vehicle.

requiring active management, then the question will become: *what design practices are used to minimize the effects of corrosion?* The process by which designers choose materials to meet system performance requirements (typically defined by system design specifications) is known in engineering circles as *Materials Selection*. Sound material selection decisions can greatly minimize the incidence and severity of corrosion, but usually cannot eliminate it entirely. This is where maintenance strategies should be formulated. However, systems with 'corrosion-smart' designs are far more maintainable, as corrosion problems are more predictable and less frequent.

Due to various factors, including available time and training deficiencies, designers often overlook steps needed to ensure adequate corrosion resistance in their designs. To be totally effective, designers must consider the inherent corrosion behavior of candidate materials in the prospective environment of an application, as well as any potential interaction these materials might have with adjacent materials, design details that could exacerbate corrosion problems, and corrosion prevention technologies such as coatings and other compounds needed to minimize maintenance requirements. In addition, designers must also consider other factors such as cost and appearance. If little thought is given up-front to select the best combination of structural materials and corrosion prevention technologies, then a maintenance nightmare could be in the making!

Ensuring that a system will age gracefully is the responsibility of all stakeholders in the development process including the design activity, as well as DOD program managers and their staff. Corrosion is a risk factor that, if mismanaged, can result in systems far more expensive to maintain than planned or desired. Mitigating corrosion-originated reliability and maintenance problems certainly will affect readiness and operations and maintenance (O&M) budgets. If the DOD acquisition program office and the prime contractor work together and consider corrosion prevention and control early in the development cycle, then total ownership costs can be reduced from the onset. These principles apply equally well to weapon systems (aircraft, land systems, ships, munitions, etc.), support systems (trucks, cargo planes, supply ships, stationery and mobile equipment, etc.) and infrastructure (buildings, storage tanks, piping, water treatment plants, piers, etc.).

REDUCING ACQUISITION RISK AND TOTAL OWNERSHIP COST

As stated previously, the best way to prevent or minimize corrosion throughout a system's lifecycle is to select corrosion-resistant materials during the design process, followed by employing an array of innovative corrosion prevention and control (CPC) technologies to augment that protection. These steps are essential to preserving systems in their original, corrosion-free state after entering service. Enhancing the materials selection process to better highlight CPC issues offers numerous benefits; among them are improved reliability, reduced maintenance, increased availability, improved performance and efficiency, improved safety, increased service life, and reduced life-cycle cost. Extending the service life of a fielded system is far easier and less costly to realize if excessive corrosion is prevented from occurring in the first place. While this undertaking may seem challenging (and more costly up-front), the long-term benefits more than justify the investment.

System Life Cycle

Figure 2 illustrates the life cycle of a system as it relates to component failure. Known as the 'bath tub curve', the figure demonstrates the various rates at which components may fail during their service life. Generally, this figure addresses the sum total of all failures, including those induced by corrosion. However, it's reasonable to assume that a similar curve would result from failures due to corrosion alone.

As illustrated on the curve, the three phases of a system life cycle consist of 1) introduction of the system into service, 2) normal operational use, and 3) wear-out. During the introductory phase the manufacturing defects are identified and corrected, which results in a higher number of failures initially, followed by a steady decline. For systems designed with insufficient attention to corrosion, this initial phase corresponds to the identification and mitigation of unexpected corrosion. The bulk of the life cycle is spent as the system operates normally (the second phase) with only routine maintenance and repairs. It is very important to properly maintain the system during this phase by employing corrosion preventative measures. If steps are not taken, the system will corrode, thus accelerating the initiation of the third phase, where the number of failures and associated maintenance actions, including component replacement, begin to increase steadily as the system reaches its maximum operational life. Proper materials selection during the design phase, followed by the use of appropriate CPC practices during service, will delay the onset of wear-out and enable the affordable extension of a system's life.

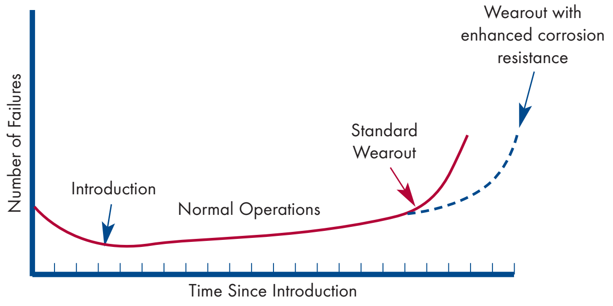


Figure 2. **Classic System Life Cycle.**

There is a direct correlation between the number of failures shown in Figure 2 and total ownership cost. As the amount of failures (and resultant extraordinary corrosion preventative measures) rise, so does the total cost. In systems designed without inherent corrosion resistance, it can be expected that the wear-out phase will be reached in a shorter period of time. Consequently, an entirely new system would have to be purchased earlier than scheduled or alternatively, extensive maintenance would be necessary to keep the existing system in operation; both of which would carry significant costs.

While it's difficult to project a definitive return on investment resulting from increased attention to CPC issues during system design, it is quite easy to understand intuitively that a system designed with inherent corrosion resistance will last

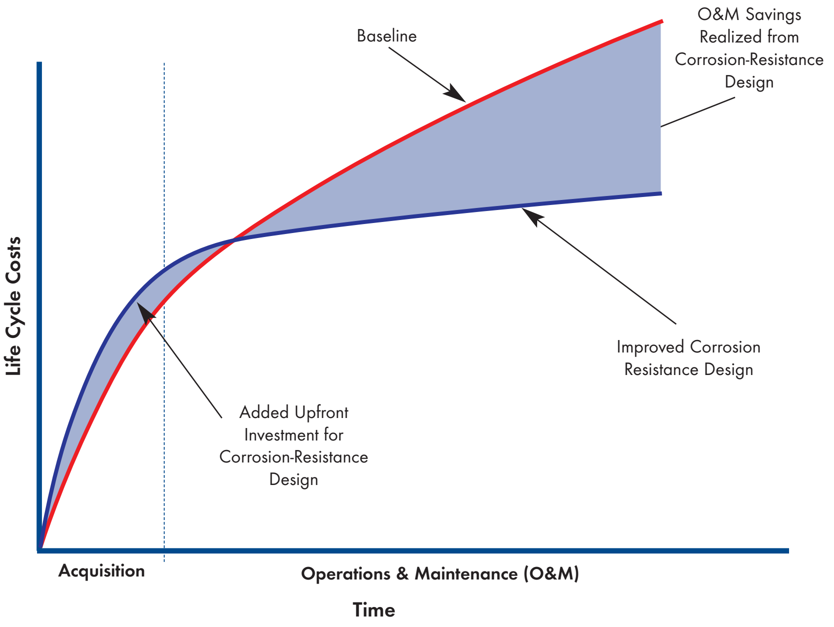


Figure 3. Total Ownership Cost Comparison.

longer than one without. Figure 2 addresses both situations, with the dashed lines indicating a longer service life for the system designed with corrosion resistance in mind. Take for example a hypothetical weapon system that, due to its inherent corrosion resistance, has a life span that is two years longer than a similar (baseline) system. If the baseline life was ten years and the total acquisition cost were $1B, the return on investment due to delayed acquisition of a follow-on system would be $200M. In reality, the cost savings would be even higher than this projection, because this example totally ignores O&M savings.

Mitigating unexpected corrosion can be very expensive, both in terms of direct cost and its impacts on readiness. If a system were designed with corrosion resistance built-in, less maintenance would be required, thus reducing O&M expenditures while increasing system availability at the same time. It easily can be seen that extending the service life of a system before it reaches the wear-out phase is extremely beneficial in terms of cost avoidance and that the savings can be substantial, especially if the acquisition of a new system is delayed.

Another way of considering the influence of CPC on total ownership costs is displayed in Figure 3. It depicts acquisition costs versus time for two hypothetical systems; one designed with inherent corrosion resistance and the other without. As shown in the figure, the acquisition costs for the system designed with enhanced corrosion resistance will be higher (due to increased engineering time and potentially more expensive materials). However, over the system's life these costs will be more than recovered in O&M cost savings, such that the total ownership costs of the corrosion resistant system will be lower than the baseline system.

Managing the Risk Factor

If one accepts the premise that corrosion is a risk factor – that if poorly managed it will increase total ownership costs – then one might ask: *how do you manage the risk?* Developing a new system with the lowest total ownership cost can only be achieved if proper oversight and attention are paid to material selection during the design process. Currently, there are no available management tools that can calculate the return on investment that would result from increased attention to CPC issues during the design phase. As previously stated, it is intuitively obvious that controlling corrosion will increase readiness through greater availability and reliability coupled with less maintenance. The challenge for program managers (and their contractors) is accounting for the risk of corrosion so that these benefits can be realized while minimizing total ownership costs.

Management tools (software) which can quantify the total ownership cost savings due to improved CPC strategies are not presently available, nor are there any formal procurement processes accounting for CPC efforts. Prior to the implementation of the Acquisition Reform Initiative, military specifications and standards codified the lessons learned from observations of failures and correctable problems on legacy systems. These documents included substantial CPC information. When the majority of these documents were rescinded in the early 1990's, the increased risk of corrosion, and the associated impact on readiness and total ownership cost, was not considered. Similar to other risk-related activities such as survivability, manufacturing, and reliability; CPC awareness and planning would tremendously benefit if risk analyses were conducted during the system engineering process. Accounting for and managing the risk associated with corrosion prevention and control will undoubtedly reduce ownership costs.

PROPER MATERIALS SELECTION ENSURES CORROSION RESISTANCE

A thorough and realistic consideration of corrosion prevention and control during the materials selection phase of the design process is key to developing systems that will age in a predictable and affordable fashion. The process of materials selection is not used solely to choose the material to build a structure or component. Rather, it is used to select a system of materials that together provide the necessary properties to meet performance requirements. Furthermore, a successful material selection effort will help to ensure that a system will continue to perform to specification over time, demonstrating its robustness against aging phenomena, such as wear, fatigue, and especially corrosion.

While materials selection is a crucial part of the design process, it can lead to future problems, especially if the designer focuses upon meeting performance requirements with little regard to maintenance needs. The use of CPC methods must be planned, and not left as an afterthought, or else it is highly likely that maintenance problems will plague the system throughout its service life. CPC methods include an array of technologies; such as chemical treatments, paints, platings, and cathodic protection.

Figure 4. Various Army Systems Exposed to the Marine Environment During Transportation.

Figure 5. Munitions Are Frequently Stored in High Humidity Environments.

Impact of the Corrosive Environment

Planning for the graceful aging of a structure or system during materials selection requires a firm understanding of its operating environment. The word environment as used here describes the conditions a system may be exposed to while in service. For example, a ship floating in the ocean is considered to be in a *marine environment*, while turbine blades experience *a high temperature environment* inside a jet engine during operation. In reality though, things are not quite that simple, because systems experience a variety of simultaneous environmental conditions. Systems often contain many fluids and chemicals that are necessary for its components to operate, but some of these can be very corrosive and cause a material to degrade. For instance, designers must consider cleaning chemicals and hydraulic fluids as sources of contamination that can cause a material to corrode. There are many other materials and contaminants that exist within the operational environment that can influence the rate at which a structure or component corrodes. Designers must take a step back and gain a firm understanding of all environmental factors that can influence corrosion before selecting the construction materials. Again, it's important to note that an environment isn't a single condition, but rather is a combination of factors which work in concert, such as operating temperature and humidity, salinity, and mechanical loading. Other contributing influences include chemicals, fuel, pollutants, solar radiation and biological organisms.

Having a firm understanding of the operational environment is crucial to designing a corrosion resistant system. However there are other environmental conditions that occur during storage or transportation that must also be considered. As Figure 4 attests, systems can experience corrosive environments during transportation that are far more severe than their operational conditions, yet designers can easily overlook the threat of transportation-induced corrosion, since systems experience only brief periods being transported from one part of the globe to another. Storage conditions must also be analyzed to determine whether they may damage or degrade a system. Some weapons, like air-launched missiles, are stored in controlled-humidity containers, which help keep these systems in their pristine, uncorroded state. Other weapons, like the gravity bombs shown in Figure 5, may be exposed to extremely high humidity levels while in their protective shelters. As shown in this figure, these weapons can experience severe corrosion, so much so that they may become useless and have to be replaced at a significant cost.

The Importance of Corrosion Testing and Information Resources

One of the reasons why selecting corrosion-resistant materials is a challenging process is that corrosion data aren't usually available in forms that are immediately and directly related to the respective environment of the system or structure. Because of the extremely large number of available materials, (including variants subjected to different fabrication processes, and environmental conditions), it is too costly and nearly impossible to test all the combinations of materials and environments. The result is that it can be very difficult to find completely relevant data to substantiate decisions.

Materials scientists over the years have devoted significant resources to corrosion testing and analysis. Accelerated testing using salt spray or controlled humidity and temperature chambers are often used to investigate a material's potential to corrode or how well a CPC technology will function. Unfortunately, these tests don't replicate true operational conditions, nor do they account for the synergistic effects of other contributing factors such as atmospheric pollutants or chemical exposure. This is what makes conducting realistic corrosion analyses so challenging.

Perhaps the best source of information to address both the expected operational environment and the potential for corrosion problems is to consult the existing literature. Such a review can determine whether there is documented field service experience on a legacy system similar to the one being designed. Natural aging information for a system or structure operated within the same (or similar) environment to one being designed can provide some excellent insight as to what to expect. In addition, if materials used on the older system have shown the potential to corrode, then there are some lessons learned that can be used to preclude incorporation of problematic materials in new systems.

It can be tempting to minimize predicted corrosion problems by relying solely upon legacy technology. It is common practice in industry to build new systems from the same materials as their predecessors. In some situations, this may be an entirely acceptable approach, but it is fraught with the risk of overlooking new materials and technologies, thus representing a lost opportunity. New materials are often innovative in nature, allowing a designer to exploit their improved properties to provide performance advantages over a legacy or competing system. For situations where no laboratory or in-service data are available, designers shouldn't be deterred from the use of new materials. The known environmental conditions within an existing system of similar nature can be used as a guide to project whether future corrosion problems can be expected for new materials. Such an assessment can lead engineers to develop test protocols which will quantify the degree of corrosion resistance inherent in the new material. Additionally, it may be possible to employ effective CPC strategies with a new material to provide the necessary corrosion protection.

DESIGN APPROACHES TO ENSURE CORROSION RESISTANCE

There are other considerations in the design process beyond selecting corrosion resistant materials and associated CPC technologies. Even with proper materials selection, designers can unintentionally exacerbate the likelihood of corrosion by creating conditions that favor its occurrence. For example, by not including drainage holes in a structure subjected to rain or wash water, liquid can become trapped and accelerate the corrosion process in an entirely unanticipated location and fashion. Other considerations include using materials that won't wick moisture. It's important to avoid, if at all possible, the use of wood, paper, cardboard, open cell foams, and sponge rubbers in systems that operate in wet environments, or in environments that have a high humidity. These materials tend to retain water and consequently function as a reservoir for adjacent materials that may be susceptible to corrosion.

Another significant design consideration involves junctions where two adjacent components come together. Known as *faying surfaces*, these areas can see sufficient relative movement between each other so that protective surface layers at the joint may wear away, exposing the underlying material directly to a corrosive environment. To protect faying surfaces, proper sealing materials (tapes, films, sealing compounds) and primers must be employed.

The intimate contact of two adjacent materials can be the causative factor for another corrosion mechanism, *galvanic corrosion*. One of the eight main forms of corrosion, it results when dissimilar metals come in contact with each other and are exposed to corrosive conditions. One of the best ways to prevent these materials from corroding further is to electrically insulate them through the use of coatings at the interface between them. A nonconductive coating will prohibit electrons from moving between the two materials, thus stopping the oxidation process.

Another important aspect is to design the system or structure for maintenance access. It is vitally important that inaccessible areas be minimized so that maintenance personnel can both inspect the areas for corrosion and reapply CPC compounds or replace components if necessary. For those situations where inaccessible areas are unavoidable, then it is even more important that an upfront analysis be conducted to ensure that proper corrosion resistance can be sustained to preclude unanticipated and extremely costly damage after the system is fielded. When analyzing maintenance access requirements, designers should consider that nondestructive evaluation techniques will be needed to detect hidden corrosion at some point during the operational use of the system. The structure must be designed to accommodate the necessary testing apparatus to preclude hidden corrosion from creating an unsafe or unreliable system.

DESIGN PITFALLS

As it relates to corrosion prevention and control, there are several pitfalls that can and do occur periodically. Unfortunately, designers seldom have a strong background or understanding of corrosion. Most view corrosion as a single process; and thus are unaware that highly accelerated, localized corrosion mechanisms even exist. It is also a mistake to assume that two seemingly identical materials that may have the same composition (relative amounts of elemental constituents) but have been processed differently (different heat treatments for example), would exhibit the same corrosion rates. The potential for a material to corrode is often strongly influenced by the processes used to create it.

Another pitfall is that characteristic relationships used to predict corrosion rates are inappropriately applied. A designer who lacks the necessary understanding of corrosion may consider all corrosion phenomena a single process, and thus may be prone to misapplying an equation developed for a different corrosion form. For example, a well-understood and predictable process such as *uniform corrosion* has been characterized by several constitutive equations which predict degradation rates. Unfortunately, unsuspecting engineers could mistakenly apply such equations to a highly accelerated localized form of corrosion like *pitting*. Localized forms of corrosion, like *pitting* or *crevice* corrosion, experience extremely high corrosion rates in very small and often hidden locations. The rates of corrosion for these mechanisms vary widely from one case to another; hence they don't lend themselves at all to predictive methodologies. Engineers not understanding the differences in corrosion mechanisms can and often do misapply equations which results in a strong potential for unexpected failures.

Although experimental data concerning corrosion abounds, it is often in inconsistent formats. Combined with the fact that corrosion rates are highly dependent upon usage environments, material composition, and processing history, a common mistake is to utilize data inappropriately or incompletely. A designer with the right intentions can easily misuse data to substantiate a design decision that may lead to entirely wrong conclusions. Another contributing factor is that corrosion data, especially that relating to natural aging, is scattered and available from many different sources. This type of data is seldom consulted, and consequently design decisions don't fully benefit from the lesson's learned. The net result in both cases is that a system, structure or component will possess far worse corrosion characteristics than initially believed or desired.

FINDING THE RIGHT BALANCE

For the uninitiated, this discussion might give the impression that corrosion cannot be prevented without conducting painstaking and extraordinary measures. It is important to point out that the goal of materials selection isn't to eliminate corrosion in all circumstances, but to manage and minimize it. The challenge to effective corrosion prevention and control is to strike a balance to ensure adequate inherent corrosion resistance and ease of maintenance while at the same time balancing cost. Cost includes not only the design time required to analyze and select the most appropriate material, but also the material cost itself. In general, materials that are inherently corrosion-resistant are typically more expensive than those that are not. During the design process, engineers must choose materials that provide the best combination of performance, including corrosion resistance, that will ensure that systems will adequately perform their function over the intended lifespan within fiscal constraints.

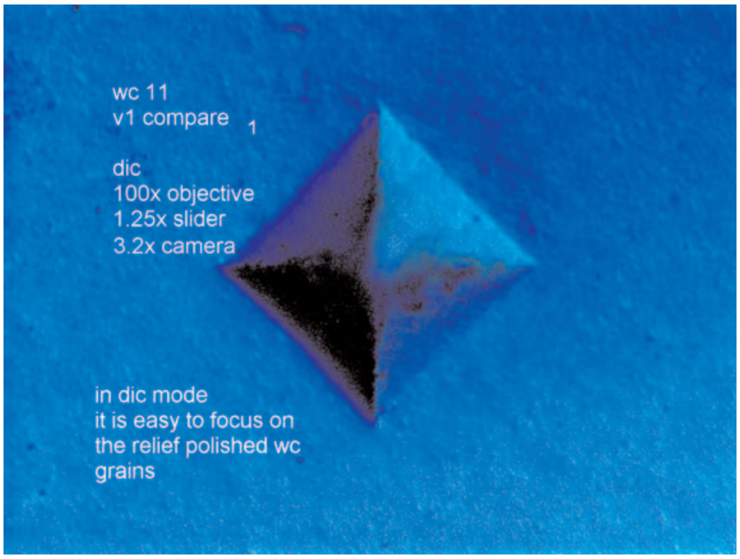
Reducing risk on new systems has to be an important concern for all stakeholders in the acquisition process. This risk can take several forms, all of which can seriously impact readiness, especially if unanticipated (but completely avoidable) corrosion problems occur during service. Some of the biggest problems experienced by Program Offices are unexpected maintenance, reliability problems, and premature wearout. Having to replace components or even entire systems because they experience unexpected corrosion is clearly an unaffordable prospect that significantly impacts total ownership costs as well as the ability of our troops to effectively accomplish their military objectives. Even more important is that hidden corrosion can and will cause unexpected failures that can be catastrophic in nature. Correcting these problems before they occur, by way of the materials selection process, is the best strategy for the long run.

REFERENCE

[1] G. Koch, M. Broyers, N. Thompson, Y.P. Virmani, J. Payer, *Corrosion Costs and Preventative Strategies in the United States* (FHWA-RD-01-156)

Standard Reference Material 2831: Vickers Hardness of Ceramics and Hard Metals

NIST recently announced the introduction of a new Standard Reference Material (SRM) for Vickers Hardness of Ceramics and Hard Metals: **SRM 2831**. Vickers hardness is an important property for ceramics, carbides, and hard metals. It is increasingly being incorporated into materials specifications for cutting tools, silicon nitride ball bearings, and ceramic implant materials. Although Vickers hardness reference blocks made of steels and softer metals have been readily available for many years, there have been none available for harder materials. The SRM is a disk of a commercial tungsten carbide with 12% cobalt binder phase. Each disk has five 9.8 N indentations made in the center of a polished face. The disks have highly polished surface and excellent hardness uniformity. Indentations are sharp and well-defined in this fine-grained material. The disks are individually certified for the average diagonal length (nominally 35.0 mm) and the average hardness (nominally 15.0 GPa or 1,530 N/mm^2). Two international round robin studies used prototype SRM 2831 disks to good advantage and verified the suitability of the tungsten carbide. SRM 2831 supports ASTM standards C 1327, E 384, and E 92, as well as ISO standards 14705 and 3878, CEN ENV 843-5, and JIS R 1610. For additional information, contact George Quinn, the technical point of contact at (301) 975- 5765 (george.quinn@nist.gov) or the NIST SRM Customer Service at (301) 975 6776 (srmorder@nist.gov), or visit the SRM Home page http://ts.nist.gov/ts/htdocs/230/232/232.htm and enter *2831*. The new SRM 2831 will complement the companion silicon nitride SRM 2830, Knoop Hardness of Ceramics, which is also available off the shelf.



SSPC – A Leader in the Fight against Corrosion

SSPC
the society for protective coatings

As a follow-up to our recent special issue on Corrosion (Vol. 7, No. 4), we wanted to bring to the attention of our readers another leader in the corrosion prevention and control field: SSPC – The Society for Protective Coatings. SSPC enjoys a long heritage of achievement and service in protecting the nation's durable assets from the effects of corrosion. - Editor

SSPC MISSION

Founded in 1950, SSPC is a non-profit association whose mission is to advance the technology and promote the use of protective coatings for the preservation of industrial, marine, and commercial structures, components, and substrates. SSPC strives to achieve its mission through various products, services, and information resources, including standards development, publications, training courses, certification programs, conferences, and an expanding range of online services.

SSPC STANDARDS

Since its inception, SSPC has been a leading source of standards, guides, specifications and other consensus documents on surface preparation, coating selection and performance, coating application, and other materials, technologies and practices. Foremost among these are:

SSPC-SP 5	Surface Preparation Standards For White-Metal
SSPC-SP 10	Surface Preparation Standards For Near-White Metal
SSPC-SP 7	Brush-Off Standard
SSPC-SP 6	Commercial Blast Cleaning Standard
SSPC-PA 2	Measurement Of Dry Coating Thickness With Magnetic Gages
SSPC-Guide 6	Guide For Containing Debris Generated During Paint Removal Operations
SSPC-SP 12	Surface Preparation And Cleaning Of Metals By Waterjetting Prior To Recoating (also NACE No. 5)

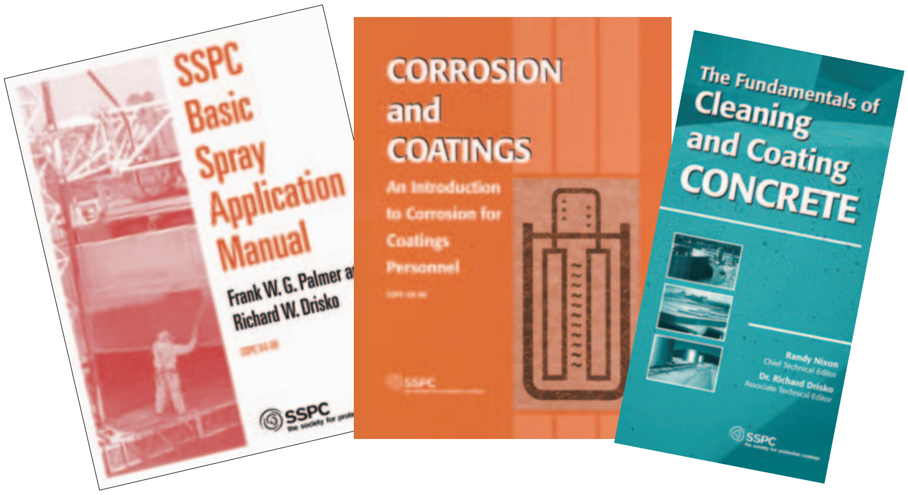
SSPC PUBLICATIONS

SSPC's offers a wide variety of publications, many of which are now industry standards. Most notably, SSPC's two-volume painting manual has become one of the protective coatings industry's most well know and most widely used reference books. SSPC publications address a panorama of topics – painting procedures, materials, and equipment; surface preparation and coating work on steel and concrete; corrosion basics for coatings personnel, cleaning and coating concrete, and spray application standards and practices.

SSPC VISUAL STANDARDS AND REFERENCE PHOTOGRAPHS

In addition to the written surface preparation standards, SSPC has also developed a series of supplemental visual standards and reference photographs. Examples include:

SSPC-VIS 1	Dry Abrasive Blast Cleaned Steel
SSPC-VIS 2	Visual Rust Standard
SSPC-VIS 3	Power- And Hand-Tool Cleaned Steel



SSPC-VIS 4/ NACE VIS 7	Steel Surfaces Cleaned By Waterjetting
SSPC-VIS 5/ NACE VIS 9	Steel Surfaces Cleaned By Wet Abrasive Blast Cleaning

Each of these contains a set of bound full-color reference photographs of painted and/or unpainted rusted steel before and after cleaning in accordance with certain SSPC surface preparation specification.

SSPC TRAINING COURSES

SSPC offers a wide variety of training courses ranging from comprehensive overviews to in-depth technical training. Some examples are:

SSPC-C1	Fundamentals of Protective Coatings for Industrial Structures (in-class or online e-course)
SSPC-C2	Specifying and Managing Protective Coatings Projects
SSPC-C7	Fundamentals of Dry Abrasive Blast Cleaning

SSPC CERTIFICATION PROGRAMS

SSPC offers several nationally recognized independent painting contractor certification programs. Each program is based on consensus standards developed by a diverse committee of industry professionals.

SSPC-QP 1	Certifies contractors who perform surface preparation and industrial coating application on steel structures in the field
SSPC-QP 3	Certifies a contracting company's ability to perform surface preparation and protective coating application in a fixed shop facility

SSPC CONFERENCES

SSPC's next major conference will be The Paint and Coatings Exposition 2005 (PACE 2005) will be held in January 2005 at the MGM Grand Hotel and Conference Center in Las Vegas, Nevada; featuring a series of technical events, committee meetings, seminars, and workshops, as well as a trade show of over 300 exhibits.

SSPC ONLINE

Since 1997, SSPC Online has provided information on SSPC products and services to SSPC's internet users. The site features a wide variety of coatings-related information resources, useful tools, an archive of papers and technical presentations, an interactive members' directory, an e-commerce site, online registration and enrollment forms, regulatory and coatings industry news, and more. For more information, visit SSPC online at http://www.sspc.org.

Material EASE

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AMPTIAC

Christian E. Grethlein, P.E.
Benjamin D. Craig
Richard A. Lane
AMPTIAC
Rome, New York

ELASTOMERIC SEALS 101 – A BRIEF TUTORIAL

This underrated group of materials is far more important than you might think

In material circles, it doesn't take much prodding to get a vigorous discussion going about high-performance materials, or one of the many emerging material technologies. However, bring up the subject of 'rubber', and it tends to produce more eye-rolling than genuine interest. Elastomers *(as they're more properly known) are one of the most critical non-structural material in vehicles, systems, and some structures, yet are also one of the least considered during design. Unfortunately, such oversights can have catastrophic or even fatal consequences when elastomeric seals fail in service; bringing unwanted levels of attention to previously ignored problems. This issue of MaterialEASE provides an overview of elastomer basics, and will give the reader a better appreciation of the importance of these materials. For readers who would like to learn more about elastomers,* AMPTIAC *has published a State of the Art Report,* Elastomeric Materials for Static and Dynamic Seal Applications *(AMPT-30), which is available for sale by phone or through our website, http://amptiac.alionscience.com.* - Editor

THE BASICS

Elastomers vs. Rubbers

Elastomers are a class of materials with properties quite distinct from all other solid materials. They are highly elastic; capable of being stretched many times their original length, and upon release, quickly revert to their original state. Their ability to deform significantly, and hence conform to the geometries of adjacent surfaces, makes them ideal for use in seals, sealants, gaskets, and shock absorbing applications. As the roots of the word imply, the term *elastomer*, a contraction of *elastic polymer*, refers to any polymeric material exhibiting highly elastic behavior. International industry usually regards *elastomer* as an American term, but even in the US, *rubber* remains the predominant lay term both in standards and in factory practice[1].

Elastomers may be obtained from nature or via synthesis. *Natural rubber* is any elastomeric material formed from a natural source of latex†. The most common source is the Hevea tree (*Hevea Brasiliensis*), found primarily in tropical regions[2]. Once the latex is extracted from the "rubber tree," it is coagulated and further processed to fabricate the desired rubber product. Synthetic elastomers may be formulated from either organic or inorganic sources. The organic elastomers, generally referred to as *synthetic rubbers*, are typically derived from petroleum by-products. The inorganic synthetics are based on silicone chemistry.

Elastomer Chemistry

Polymers and Elastomers The term *polymer* is Greek in origin, meaning "many units." Elastomers are a subclass of polymers – their main distinction from other polymers is their remarkable elasticity and deformability; upwards of 400 to 600%, as opposed to 2-5% for other polymers. Polymers (and elastomers) may either be thermoplastic or thermosetting in nature. Thermoplastic polymers are composed of serpentine, high-molecular-weight strands, with individual units linked by covalent bonds (Figure 1). Consequently, thermoplastics tend to be soft and ductile, and with sufficient heat, they will become softer

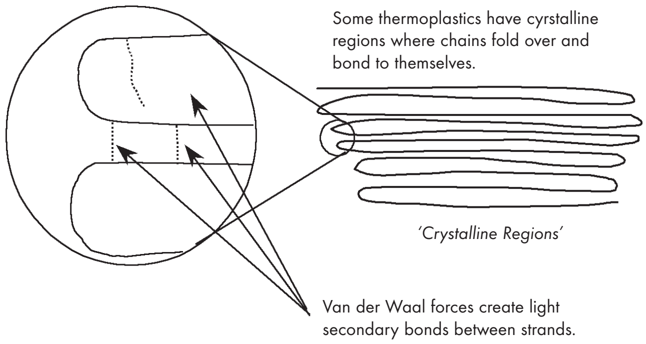


Figure 1. **Morphology of a Thermoplastic Polymer.**

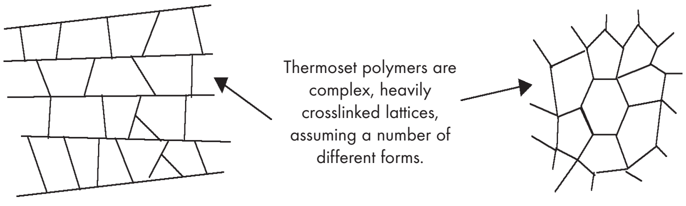


Figure 2. **Morphology of a Thermosetting Polymer.**

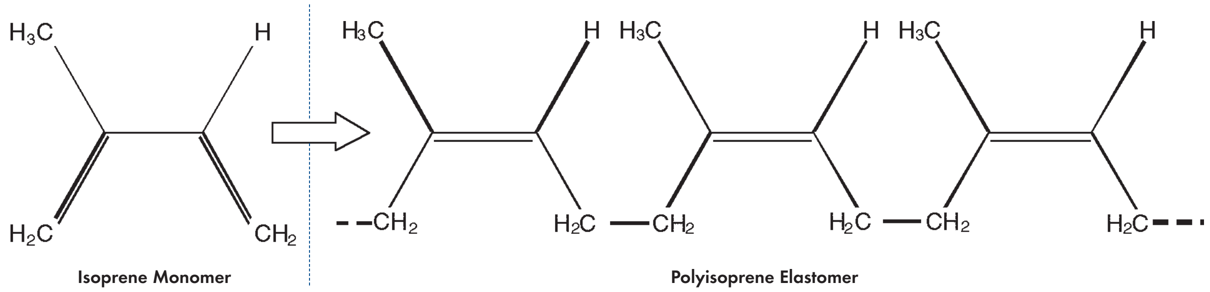


Figure 3. **Polymerization of Polyisoprene (Natural Rubber).**

and may be processed more than once. Most physical, mechanical, and electrical properties of a polymer are highly dependent on its average molecular weight.

Thermosetting monomers are typically multibranched molecules, meaning that when the polymerization reaction begins, the individual monomers (low weight molecules) link together, but not in a 1-dimensional manner like thermoplastic strands, but in a 2- or 3-dimensional manner, forming a lattice of covalently bonded chains. Each lattice is a molecule unto itself and adjacent lattices may crosslink to form an even larger molecule (Figure 2). Long-term exposure to high temperatures will continue the polymerization reaction, making the polymer denser, tougher, and stronger. Thermosets do not melt, but if heated to a sufficiently high temperature, they will start to decompose.

Chemistry of Natural Rubber The extracted latex product from Hevea rubber plants is 2-methyl-1,4-butadiene, more commonly known as *Isoprene* (Figure 3). The elastomer is formed when isoprene polymerizes into a chain molecule. The most common configuration of isoprene elastomer is *cis*-isoprene, and is the one referred to as *natural rubber*.

Effects of Vulcanization Charles Goodyear's inadvertent discovery of the vulcanization process changed the future of rubber overnight. Heating raw isoprene with trace amounts of sulfur (plus an accelerator) causes the sulfur to form short linear sulfide chains, which in turn bond to various sites along the polyisoprene chains. The sulfur crosslinks are primarily responsible for the highly elastic nature of refined natural rubber. Thus, vulcanization converts it from a dimensionally unstable, viscoelastic material to an extremely stable elastic material.

Synthetic Rubbers Global conflicts and periodic supply shortages catalyzed the development of the first synthetic analogs to natural rubber. Since the 1920s, a number of "synthetic rubbers" have been introduced, each a variant of the basic isoprene elastomer. Beyond establishing more reliable supplies, many of the synthetics were developed to enhance one or more elastomer properties – usually expanding operating temperature range, or improving chemical resistance. Carbon-based synthetics differ from isoprene by the addition or substitution of different atoms or functional groups along the polymer chain's backbone. Table 1 provides definitions of the various types of synthetic elastomers. The first inorganic elastomers were synthesized near the start of World War II. These organo-silicon compounds, or *Silicones*, represent a whole new branch of synthetics, and feature several qualities that make them superior to their organic counterparts.

Chemistry of Silicones Silicone polymers are fundamentally structured the same as organic polymers but employ silicon (Si) instead of carbon as the backbone of the chain. More precisely, silicone's backbone is comprised of alternating Si and O atoms (polysiloxane). The oxygen bonds between the Si atoms provide molecular stability by spacing the Si atoms (which are much larger than C atoms) beyond the range of their mutual repulsion. Polydimethylsiloxane is the most common silicone monomer used to create silicone elastomers (Figure 4).

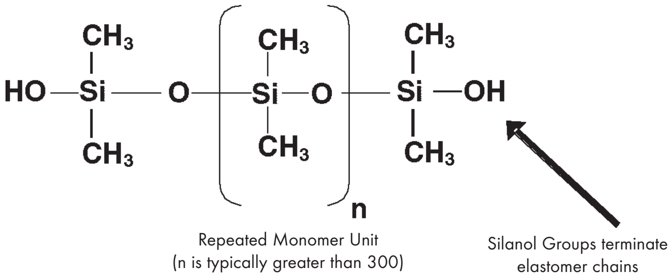
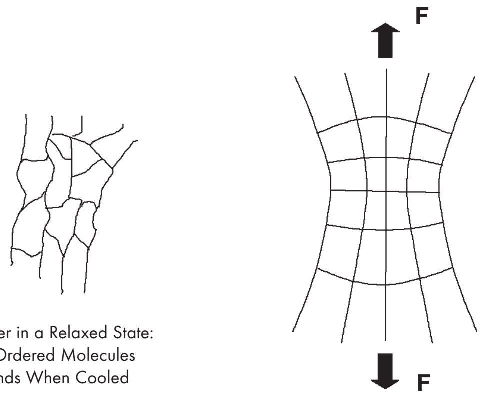


Figure 4. **Polydimethylsiloxane (Silicone) Elastomer.**

Elastomer Thermodynamics

The thermodynamics of elastomers are rather unique compared to other solid materials. Typically, most solids expand when heated, but elastomers under tension actually contract when heated. This behavior is known as the *Gough-Joule effect*, and is due to their internal structure. In a relaxed state, the molecules of an elastomer are 'tangled' around themselves and adjacent molecules. When stretched, they untangle, becoming more ordered[3]. In effect, their relative state of entropy decreases as they are extended (Figure 5). The thermodynamic



Elastomer in a Relaxed State:
- Less Ordered Molecules
- Expands When Cooled

Elastomer in an Expanded State:
- More Ordered Molecules
- Shrinks When Heated

Figure 5. Typical Structure of an Elastomer.

behavior of all materials dictates that the relative state of entropy increases upon heating and decreases upon cooling. Therefore, when an already-extended elastomer (in a low entropy state) is heated, it must contract in response to the relative increase in entropy. Similarly, an elastomer in a relaxed state (high state of entropy) will expand when cooled.

ELASTOMERS FOR SEAL APPLICATIONS

Elastomers are available in both natural, and synthetic forms; typically composed of polymers with a macromolecular structure. All elastomers are organic (carbon-based) polymers with the exception of silicones and fluorosilicones. Seal materials have been classified in ASTM Standard D1418 according to their chemical composition with letter designations[2], and are presented in Table 1.

Material Comparisons

The following tables summarize and compare the important properties of the various elastomers. Table 2 provides operating temperatures and recommended uses of the materials. Table 3 lists the relative costs of elastomeric materials. Table 4 contains relative performance in response to environmental factors.

For more information, AMPTIAC's State of the Art Report, *Elastomeric Materials for Static and Dynamic Seal Applications*, presents comprehensive tables of chemical resistance for all major elastomer classes evaluated for a variety of chemicals.

Table 1. Elastomer Seal Classifications[2].

M Class: Elastomers having a saturated chain of the polymethylene type

ACM	Copolymers of ethyl or other acrylate and a small amount of monomer which facilitates vulcanization.
EPDM	Terpolymer of ethylene, propylene, and a diene with the residual unsaturated portion of the diene in the side chain.
CFM	Polychloro-trifluoroethylene
FKM	Fluoro rubber of the polymethylene type having substituent fluoro and perfluoroalkyl or perfluoroalkoxy groups on the polymer chain.
FFKM	Perfluoro rubbers of the polymethylene type; having all substituent groups on the polymer chain - either fluoro, perfluoroalkyl, or perfluoroalkoxy groups.
FEPM	Copolymer of tetrafluoroethylene and propylene.

O Class: Elastomers having oxygen in the polymer chain

ECO	Ethylene oxide (oxirane) and chloromethyl oxirane (epichlorohydrin copolymer)

R Class: Elastomers having an unsaturated carbon chain

BIIR	Bromo-isobutene-isoprene rubbers
CIIR	Chloro-isobutene-isoprene rubbers
CR	Chloroprene rubbers
IIR	Isobutene-isoprene rubbers
NBR	Isoprene rubber, natural
SBR	Styrene-butadiene rubbers

Q Class: Elastomers having silicon in the polymer chain

FVMQ	Silicone elastomer having fluorine, vinyl, and methyl substituent groups.
PMQ	Silicone elastomers having methyl and phenyl substituent groups.
PVMQ	Silicone elastomers having methyl, phenyl, and vinyl substituent groups.
MQ	Silicone elastomers having only methyl substituent groups, such as dimethyl polysiloxane.

T Class: Elastomers having sulfur in the polymer chain

EOT	A rubber having either a $-CH_2-CH_2-O-CH_2-O-CH_2-CH_2-$ group or $-CH_2-CH_2-$ group or occasionally an -R- group, where R is an aliphatic hydrocarbon between the polysulfide linkages in the polymer chain.

U Class: Elastomers having carbon, oxygen, and nitrogen in the polymer chain

AU	Polyester urethane.
EU	Polyether urethane.

Not shown:

Z Class: Elastomers having phosphorous and nitrogen in the polymer chain.

N Class: Elastomers having nitrogen in the polymer chain.

Table 2. Common Trade Names and Uses for Basic Types of Elastomers[4].

Elastomer	Trade Names and Manufacturers*		Temperature Range	Compatible Fluids and Lubricants
Nitrile or Buna N (NBR)	Chemigum Paracril Hycar Krynac Ny Syn	Goodyear Tire & Rubber Uniroyal Chemical Co. Goodrich Chemical Co. Bayer Chemical Corp. DSM Copolymer, Inc.	-54 to 135°C (-65 to 275°F)	Synthetic hydrocarbons MIL-H-83282, MIL-H-46170 Petroleum oils MIL-H-5606, MIL-H-6083 Water Silicone greases and oils Di-ester-base lubricants (MIL-L-7808) Ethylene-glycol-base fluids
SBR (Buna S or GRS)	(Too numerous to list)		-54 to 107°C (-65 to 225°F)	Automotive brake fluid Alcohols (low molecular wt.) Water
Butyl Rubber (IIR)	Polysar Butyl Bucar Butyl Exxon Butyl	Bayer AG Chem/Rubber Columbia Carbon Co. Exxon Chemical Co. USA	-54 to 107°C (-65 to 225°F)	Phosphate-ester type hydraulic fluids (Skydrol, Fyrquel [Cellulube], Pydraul) Ketones (MEK, acetone) Silicone fluids and greases
Chloroprene Rubber (Neoprene, CR)	Neoprene Butaclor PeroTex-neoprene	E. I. duPont de Nemours Enichem/Petrochem. Petro-Tex Chemical Co.	-54 to 149°C (-65 to 300°F)	Refrigerants (Freon, NH_3) High-aniline-point petroleum oils Mild acid resistance Silicate ester lubricants
Ethylene Propylene Rubber (EPM) and Ethylene Propylene Diene Rubber (EPDM)	Nordel Royalene Vistalon Epcar Epsyn	E. I. duPont de Nemours Uniroyal Exxon Chemical Co. USA B. F. Goodrich Co. Copolymer Rubber & Chemical Corp.	-54 to 149°C (-65 to 300°F)	Phosphate-ester-base hydraulic fluids (Skydrol, Fyrquel [Cellulube], Pydraul) Ketones (MEK, acetone) Alcohols Automotive brake fluids
Fluorocarbon Rubber (FKM) and Perfluorocarbon Rubber	Viton Fluorel Kalrez Kel-F	E. I. duPont de Nemours Minnesota Mining & Mfg. Co. (3M)	29 to 204°C (-20 to 400°F)	Synthetic hydrocarbons MIL-H-83282, MIL-H-46170 Petroleum oils MIL-H-5606, MIL-H-6083 Di-ester-base lubricants MLO 8200, MLO 8515, OS-45 Silicone fluids and greases Halogenated hydrocarbons (carbon tetrachloride, trichloroethylene) Selected phosphate ester fluids Acids Chlorotrifluoroethylene (CTFE)
Polyacrylate Rubber (ACM)	Cyanoacryl Hycar Krynac Thiacril	American Cyanamid Co. B. F. Goodrich Co. Polysar Ltd. Thiokol Chemical Corp.	-18 to 177°C (0 to 350°F)	Polyol ester-type hydraulic fluids Sulfur-bearing chemicals Hypoid gear lubricants
Polyurethane Rubber (AU, EU)	Adiprene Cyanaprene Disogrin Elastothan Formez Pallathane Vibrathane	Uniroyal Chemical American Cyanamid Co. Freudenberg-NOK E. I. duPont de Nemours Uniroyal Thiokol Chemical Corp. Uniroyal	-54 to 93°C (-65 to 200°F)	Aliphatic solvents Mineral oils
Silicone (SI)	Silastic (various) (various)	Dow Corning Corp. General Electric Union Carbide & Carbon	-115 to 121°C (-175 to 250°F)	High-aniline-point oils Dry heat Chlorinated diphenyls Military aircraft fuels JP-4, JP-5, JP-8
Fluorosilicone (FSI)	Silastic L.S. Sylon	Dow Corning Corp. 3M	-62 to 177°C (-80 to 350°F)	Military aircraft fuels JP-4, JP-5, JP-8
Epichlorohydrin Rubber (CO, ECO)	Herclor Hydrin	Hercules, Inc. B. F. Goodrich	-54 to 135°C (-65 to 275°F)	Aliphatic solvents Aromatic fuels Motor oils

* Many of these trade names are registered trademarks of their manufacturer

Table 3. Relative Costs of Elastomers[5].

Elastomer	Relative Cost
Styrene butadiene	1.00
Natural rubber	1.14
Butyl rubber	1.25
Ethylene propylene diene	1.00
Neoprene	1.25
Acrylonitrile butadiene	1.40
Polyacrylate	3.50
Polysulfide	2.50
Fluorocarbon	45.00
Fluorosilicone	50.00
Silicone	12.00
Polyester urethane, polyether urethane	4.00 - 10.00
Epichlorohydrin	3.00

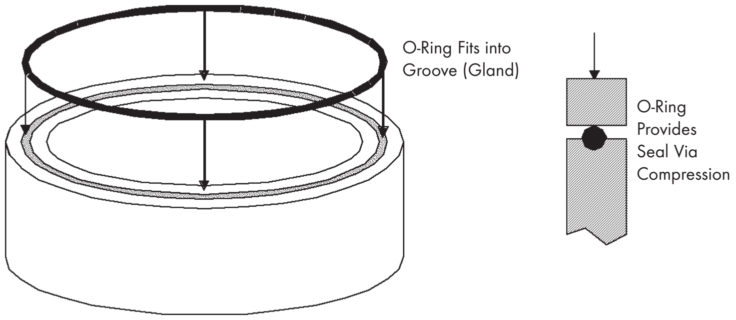


Figure 6. Example of a Static Seal (O-Ring).

Table 4. Relative Property Comparisons of Commonly Used Elastomers[4].

	Nitrile	SBR	Butyl	Neoprene	Ethylene Propylene	Fluorocarbon	Fluorosilicone	Polyacrylate	Polyurethane	Silicone	Epichlorohydrin
Ozone resistance	P	P	GE	GE	E	E	E	E	E	E	E
Weather resistance	F	F	GE	E	E	E	E	E	E	E	E
Heat resistance	G	FG	GE	G	E	E	E	E	F	E	FG
Chemical resistance	FG	FG	E	FG	E	E	E	P	F	GE	G
Oil resistance	E	P	P	FG	P	E	G	E	G	FG	E
Impermeability	G	F	E	G	G	G	P	E	G	P	GE
Cold resistance	G	G	G	FG	GE	FP	GE	P	G	E	GE
Tear resistance	FG	FG	G	FG	GE	F	P	FG	GE	P	G
Abrasion resistance	G	G	FG	G	GE	G	P	G	E	P	G
Compression set resistance	GE	F	FG	G	GE	G	P	G	E	P	GE
Dynamic properties	GE	G	F	F	GE	GE	P	F	E	P	G
Acid resistance	F	E	G	FG	G	E	FG	P	P	FG	FG
Tensile strength	GE	GE	G	G	GE	GE	F	F	E	P	G
Electrical properties	F	G	G	F	G	F	E	F	FG	E	F
Water/steam resistance	FG	FG	G	F	E	FG	F	P	P	F	F
Flame resistance	P	P	P	G	P	E	FP	P	P	F	FG

E = Excellent, G = Good, F = Fair, P = Poor.

SEAL TYPES

Seal Designs

Seals can be categorized into two groups, depending upon their application. *Static*, or gasket materials are in stationary systems; while *dynamic*, or packing seals are in moving systems, such as pistons. Systems are designed so that the seal material is put in compression when assembled (Figure 6). The stiffness of the seal in shear and the pressure applied on the adjacent walls, prevent fluids from leaking past the seal. The higher the compression, the higher fluid pressures that can be contained by the seal.

Static Seals Static seals can be produced in two different ways. They can be molded into specific shapes prior to assembling the system, or they can be formed in place. The formed-in-place seals have the advantage of filling in the total surface area of the surrounding walls. This reduces the number of small gaps between surfaces, limiting potential leakage. The disadvantage is that excessive motion in the system can break the seal, resulting in leakage. Gaskets manufactured into sheets and cut to size are the typical seals used in automotive applications. Pre-molded O-rings used in static applications are mounted in a groove called a "gland" and are placed in compression upon assembly.

Dynamic Seals A dynamic seal is always mounted in a gland. It may be in motion itself for "inside" packings, or may be stationary for "outside" packings, as seen in Figure 7. O-rings are the most widely used design, although additional seal geometries used include T, U, and V-shaped rings. The O-ring design is usually the first design considered due to a number of factors. Their advantages include[6]:

- Simplicity
- Low cost
- Ease of maintenance
- Low distortion of structure
- Small space requirement
- Ruggedness
- Ease of installation
- No adjustment required
- No critical torque in clamping
- Reliability
- Effectiveness over wide pressure and temperature ranges.

V-shaped rings are used in systems where any leakage is critical. They are also favored where the seal material is to be replaced without complete disassembly of the system[6]. A number of V-rings are normally used in a stacked configuration with an adaptor on both ends of the stack and possibly a spacer as seen in Figure 7. Adjustment of the stack, with the spacers, is required to obtain the proper compression on the seal material.

Material EASE

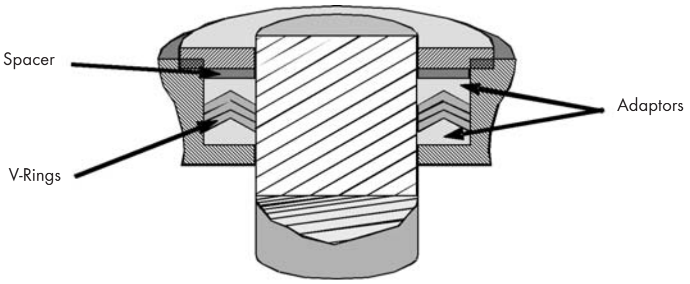


Figure 7. **Outside Packed V-Ring Installation[6].**

Hydraulic Seals

Selecting materials for any hydraulic seals is both critical and daunting. Seal materials must not only be able to function and endure in the extremes of the service environment, but must also be compatible with the selected hydraulic fluid. The combination of chemical resistance, high and/or low temperature performance, and wear resistance for packing seals can make the selection of seal materials for hydraulic systems a difficult choice. In an ideal concurrent engineering setting, all design factors – hydraulic fluid, service requirements, seal design/geometry, and seal materials – are considered together; resulting in the synthesis of a highly robust hydraulic system. More typically though, hydraulic systems are designed in advance, leaving it to the materials engineer to find a seal material which meets preset requirements.

Ground vehicles and equipment do not generally reach the elevated temperatures of military aircraft, so that more materials are available for consideration. An extensive chemical compatibility rating of elastomers with several hydraulic fluids is available in AMPTIAC's State of the Art Report (referenced on page 11).

Fuel Tank Seals

Several parameters are critical when selecting candidate elastomers for use in fuel tank applications; the most obvious being fuel compatibility. The seal must be capable of operating in the presence of fuel for extended periods of time without severe property degradation or complete failure. One example of fuel compatibility is shown in Table 5. It is also important to consider whether the elastomer could contaminate the fuel. Elastomeric seals that can function continuously under the normal conditions experienced in fuel tank operation have great value simply for maintenance reasons. Continuous operation with limited maintenance is very desirable, but must be balanced against the concerns of safety, since fuel leaks can cause serious functional problems, and are clearly dangerous.

HOW TO SELECT AN ELASTOMER

The Importance of Materials Selection

Historically, elastomeric seals are rarely given sufficient consideration in most material selection activities or system design efforts. Seals in general, elastomeric or otherwise, fail to garner the attention paid to the other "marquis" subsystems. Primary structural or mission-critical components, such as airframes, propulsion systems, drive trains, stealth, or electronic/avionic systems seemingly tend to receive top billing. Recent history is all-too-replete with reminders of the criticality of seal materials. Eighteen years after the Challenger disaster, most persons old enough to remember the event, technical and layperson

Table 5. **Fuel Compatibility of Elastomers for Seals and O-Rings at Low Temperatures[7].**

Material	Diesel Fuel	JP-8	JP-5	JP-4	Gasoline	Water	Low-temperature bound (°C)
Nitriles	✓	✓	✓	✓	✓	✓	-40 to -54
Fluorosilicones	✓	✓	✓	✗	✗	✓	-50 to -73
Fluorocarbons	✓	✓	✓	✓	✓	✗	-40 and below

✓- Compatible, ✗ - Not typically used

Elastomeric History: A Brief Timeline

Since the time of Columbus, the course of elastomers has been driven by geopolitics, war, and economics; with the occasional dash of chemistry and engineering sprinkled along the way.

Pre-1400s: Having learned to extract rubber from no less than eight different species of latex-yielding trees, the Indian tribes of Central and South America employ rubber for numerous uses.

1492: Columbus "discovers" rubber and brings samples back to Europe. The Spaniards named this substance *caucho*, a corruption of the Indian word for rubber, *cachuchu* (Inca for "weeping tree").

1766: English scientist Joseph Priestley noticed that this substance could be used to "rub" out, or erase the writing of pencils, thus coined the word rubber.

1800 (ca.): Industrialists in Scotland develop a solvent process to rubberize textiles, producing waterproof fabrics on an industrial scale.

1803: English scientist John Gough observes that rubber warms when stretched, contrary to the behavior of other solids.

1820: Thomas Hancock develops the process of mastication.

1826: Michael Faraday determines the hydrocarbon nature of rubber $(C_{10}H_{16})$.

1830s-1840s: Calendaring and extrusion processes are developed, allowing sheets of uniform thickness and parts of uniform cross-section to be manufactured.

1839: Charles Goodyear discovers the process of *vulcanization*, which produces stable forms of rubber. Demand rises rapidly, hailing the start of the modern rubber industry.

1845: Scottish engineer Robert W. Thomson patents the first air-filled rubber tire.

1857 While synthesizing molecules of oxygenated silicon, German Chemist Friedrich Wohler coins the term *Silicone* to label this new group of compounds.

1859: James Prescott Joule, one the fathers of modern thermodynamics, revisits Gough's earlier observations about rubber warming when stretched. Using thermodynamic principals, he explains the basis for this phenomenon, which is now called the *Gough-Joule Effect*.

1876: Hevea seeds collected by British industrial concerns in the Amazon Basin are sent back to Britain to be germinated. Successfully germinated plants are subsequently shipped to Ceylon (now Sri Lanka), Singapore, and Malaysia, where the first rubber plantations are established.

1888: Scotsman John Boyd Dunlop invents the first pneumatic bicycle tire, and with it, founds the Dunlop Tire Company, and a whole new industry.

1890s: Rubber plantations are prospering in Southeast Asia, as a result of the transplant of Amazon Hevea seeds. The timing was fortuitous, as blight wipes out most of the known reserves in the Amazon during this same time period.

1892: The United States Rubber Company (now part of Continental) is founded.

1895: The Michelin brothers begin producing pneumatic tires for early racing cars.

1896: B.F. Goodrich Tire Company is founded.

1898: Goodyear Tire & Rubber Company is founded.

1899: Firestone Tire & Rubber Company is founded.

1899-1937: English Chemist Frederick Kipping publishes 54 papers on the subject of *organo-silicon* compounds, the precursors to modern silicones. Purely interested in the science and chemistry of these compounds, Kipping fails to grasp their potential commercial value.

1908-1927: Ford's introduction of the Model T car made the automobile. affordable to average people, spurring rapid improvements in tire and rubber technology. By 1920, the cost of tires had come down from $100 to $30 and service life had been extended from 500 miles to over 12,000 miles.

1914-1918: The first push to develop synthetic rubbers begins in Germany (and other countries) to avert cutoff of rubber supply and to establish domestic sources during war.

1920s-1930s: American and British efforts to develop their own synthetics shift into high gear.

1929: Polysulfide rubber is invented.

1930 (ca.): I.G. Farbenindustrie introduces *Styrene Butadiene Rubber.* (SBR), the world's first mass-produced synthetic elastomer. Marketed under the name Buna-S, it remains in production to the present day.

1931: Polychloroprene is invented.

1936: Nitrile rubber is invented.

1938: J. Franklin Hyde (of Corning Glassworks) synthesizes ethyl phenyl silicone, the world's first true silicone elastomer.

1939: The term *elastomer* first appears in the technical literature. The term was invented as a way to distinguish synthetic rubbers from their natural counterparts. Its usage in this respect has diminished, but it has left a mild controversy over terminology as a lasting legacy.

1940: Corning Glassworks sets up first ethyl phenyl silicone pilot plant, with Dow Chemical Corporation as its major supplier.

1943: Corning and Dow both recognize tremendous commercial potential of silicone and form Dow-Corning, a separate but jointly-owned company.

1939: Eugene Rochow synthesizes methyl silicone for the Hotpoint Company (a subsidiary of General Electric). GE's management is slow to share Rochow's optimism about silicone's potential.

1941: Eugene Rochow is awarded a patent for his direct synthesis process in the manufacture of methyl silicones. This milestone leads to the founding of GE Silicones.

1950s: The first organic fluoroelastomers are introduced, with superior chemical properties.

1960s: The first fluorosilicones are introduced to the market.

1986: The explosion of the Space Shuttle *Challenger* brings dubious attention to o-rings and elastomers, and highlights the criticality of these under-recognized materials.

alike, can recall that failure of an o-ring on one of the solid rocket boosters started a chain reaction of catastrophic failures, culminating in the loss of the orbiter and its crew.

While not all seals are used in life-critical applications, they are nonetheless, critical to the full and nominal operation of the systems that they serve. They are used in a whole host of different applications, performing under a seemingly infinite number of operating and environmental conditions. Seals perform a function like no other component: they serve as protective barriers for critical components and subsystems – in essence, isolating them from surrounding hazards. Beyond serving as effective barriers, they are also excellent shock absorbers, acoustic barriers, vibration dampers; and are extremely capable of compensating for minor dimensional mismatches between mated surfaces. However, not every elastomer is suitable for every application.

As an integral part of any design activity, the material selection process is application-driven. That is, materials most likely to meet specified performance requirements are employed. Understanding the operating conditions within the seal environment, and consequently its performance requirements, will direct the engineer's focus as to which material properties are the most telling about a candidate elastomer's probability of success.

Managing Environmental Effects

If selecting an elastomer for a seal application were strictly a matter of mechanical performance, the evaluation and selection process would be more straightforward. The majority of synthetic elastomers, both organic and inorganic, were each specifically developed to address the limited thermal or chemical performance of their immediate predecessors.

Making the Right Selection

One of the greatest truisms of materials selection (for any material class or application), is that *there is rarely a single best choice*. The results of a material downselect activity are usually much more complex, frequently rendering the final choice dependent on a series of trade-offs and intangible factors. It has been said that experience is the best teacher of all - no place is this truer than in the material selection process. Engineers and designers naturally tend to become loyal to certain materials – accruing hands-on experience through successive projects, ultimately developing a comfort level with them. This can be both a

Table 6. Seal Service Profiles for Different Applications.

Aircraft	• Accrued service life of systems/components measured in flight hours. • Highly maintenance-intensive: frequent service intervals, unscheduled repairs. • Hydraulic seals, other critical seals replaced with similar regularity.
Missiles	• Vast majority of a missile's life is spent in storage (up to 20 years) • Storage followed by a single brief flight (seconds→minutes→hours) • Elastomers mainly used as environmental seals (protects internal components of the missile during long-term storage). • Seals expected to last for the duration of the missile's service life.
Land Systems	• Performance requirements vary greatly among land systems (e.g. tanks, personnel carriers, trucks, Humvees). • Common seal applications– internal combustion engines, drive trains, hydraulics, lubrication, environmental seals, etc. • Service intervals for these vehicles are regularly spaced (months to years). • Most seals are replaced periodically per the vehicle's maintenance protocol
Sea Systems	• Hull and superstructure seals must withstand long-term corrosion/degradation effects of seawater, salt fog, and biological organisms. • Hull seals must also perform long-term while submerged. • Seals in systems near reactors must resist low-level radiation effects. • Seals in mechanical and power systems replaced per maintenance schedules.
Space Systems (unmanned)	• Seals must last for the duration of the vehicle's projected service life. • Seals must be highly resistant to thermal extremes and outgassing • Elastomers used as passive vibration dampers, reducing the vibrations caused by the propulsion system during orbital maneuvers. • Mitigate the effects of thermal expansion mismatch between components.
Space Systems (manned)	• For reusable manned space vehicles (i.e. the Space Shuttle), seals may be replaced after every mission, after several missions, or during major upgrades; depending on the seal's function and criticality. • For single-flight vehicles (i.e. Soyuz or Shenzhou), seals need last for single flight only (mostly used to maintain the integrity of the cabin environment).
Space Systems (launch vehicles)	• Launch vehicle o-ring seals and gaskets must be able to withstand and dampen the shock and vibration loads placed on assemblies by the rigors of transport to the launch site. • The service life of launch vehicle seals is short, but critical. They must perform as specified for the several minutes of powered ascent, until they are jettisoned along with their booster.

benefit and a detriment to good design principles and to the end product.

What happens all too often when a material is expedited through the selection process, favoring familiarity and expedience over sound material selection principles, is that some of its shortcomings and limitations are overlooked. The temptation to take such shortcuts is great – especially when a company has used the material in question for many years on a number of projects without incident. The risk of such neglect is choosing a substandard material, ultimately posing a threat to the performance or safety of the system. A less obvious impact is the lost opportunity from overlooking a superior material choice. On balance, past experience is still, by far, the best source of information when selecting a material; but it is a *part of* and *not a replacement for* good materials selection practices.

Service Life

The ultimate measure of a material's effectiveness is how long it will be able to function in its application (at the specified level of performance) before its eventual degradation hampers overall system performance. Service life or more specifically, service life requirements are application-dependent. These *requirements* are mission-driven, specifying seal service lives ranging from hours to years, or even for the entire life of the vehicle or system. Service life requirements are in large part dictated by a system's mission or operating profile, as illustrated in Table 6.

Shelf Life

What is easy to overlook is that not all of the eventual degradation experienced by an elastomeric seal occurs during its time in service. From the moment they are first produced, all elastomers start to degrade. Obviously, degradation proceeds more slowly when these materials are sitting on a shelf in a factory or depot than in service, but the fraction of total useful service life expended during that time on the shelf is not insignificant (*and does subtract from remaining useful service life*).

The length of time that an elastomeric material can be kept on the shelf before it is unusable is known as *shelf life*. While elastomer service life data are not readily available, the opposite is true for shelf life data. Manufacturers (and others) freely publish this information.

Elastomeric seal materials are sold either as discrete parts or as bulk materials (typically in the form of a viscous caulk or paste). The definitions of shelf life for the two are somewhat different. For discrete parts, shelf life is the length of time before these parts are no longer acceptable for use, and are thus discarded. The longer these parts sit in storage, the shorter the remaining service life when installed. Shelf life for a bulk material is defined as the maximum allowable time a material can be stored before it must be applied or discarded. This is even more critical for two-part sealants, which are mixed just before application and subsequently undergo a curing reaction. Expired two-part sealants will not cure properly, thereby invalidating their use.

NOTES

† Latex is the sap drained from rubber trees, which when coagulated, forms rubber.

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Recent US Patents

The following is a list of recent patents issued by the United States Patent and Trademark Office in the area of materials. Interested readers can obtain further information by accessing the Patent Office's website: http://www.uspto.gov.

6,760,606	Auxiliary material for superconductive material
6,760,523	Tape based high fiber count cable
6,760,515	All optical display with storage and IR-quenchable phosphors
6,760,245	Molecular wire crossbar flash memory
6,760,215	Capacitor with high voltage breakdown threshold
6,760,208	Distributive capacitor for high density applications
6,760,198	Magnetic multilayered films with reduced magnetostriction
6,760,194	Head gimbal assembly with piezoelectric microactuator
6,760,189	Soft magnetic film having high corrosion resistance, magnetic head including the same, and method for making the soft magnetic film
6,760,165	System and method for manufacturing an assembly including a housing and a window member therein
6,760,092	Method for fabricating an array substrate for a liquid crystal display with an insulating stack made from TFT layers between crossed conductors
6,760,021	Multi-dimensional image system for digital image input and output
6,759,990	Compact antenna with circular polarization
6,759,965	Light indicator
6,759,945	Variable transmittance birefringent device
6,759,935	Coil-embedded dust core production process, and coil-embedded dust core formed by the production process
6,759,919	Low intermodulation film microwave termination
6,759,841	Hall-effect current detector
6,759,803	LED light source with lens and corresponding production method
6,759,800	Diamond supported photocathodes for electron sources
6,759,799	Oxide-coated cathode and method for making same
6,759,751	Constructions comprising solder bumps
6,759,750	Method for integrating low-K materials in semiconductor fabrication
6,759,748	Wiring structure of semiconductor device

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AFRL/ML Nanotechnology R&D Efforts to Advance Aerospace Systems for the Next Century

Benjamin D. Craig
Richard A. Lane
AMPTIAC
Rome, New York

History has witnessed innumerable advances in aeronautics and space technology since that first powered flight in December of 1903. A fair percentage of the major technological innovations of the twentieth century were in support of, or applicable to aerospace systems in some way. At the outset of this new century, several nascent technologies hold great promise to advance America's leading edge to ever-higher levels. Arguably, this is nowhere more true than in the field of nanotechnology. Having evolved beyond a technical curiosity, nanotechnology is getting a fresh look from the scientific and engineering circles of the aerospace community, as they seek ways to harness its potential benefits for aircraft applications; as well as for launch vehicles and spacecraft.

INTRODUCTION

The Air Force Research Laboratory (AFRL) has been involved with numerous projects in nanotechnology, researching and developing new technologies to advance the military's aerospace capabilities. This article contains an overview of their recent nanotechnology research intended to support aerospace applications; it is broken up into sections covering four technology areas including fabrication methods, materials, functional devices, and modeling and simulation.

Nanostructures refer to some element of a material or material system that is 1 – 100 nm in size. This includes grain size, particle diameter, fiber diameter, or layer thickness. Nanostructured materials and devices have the ability to enhance and/or produce novel material properties in most areas, such as mechanical, chemical, thermal, optical, electrical, and magnetic. Advances in nanostructure fabrication as well as the ability to analyze such small structures are improving our understanding of the relationship between nanostructure and material properties. These advances will subsequently result in better nanostructured designs with enhanced performance. (Refer to the MaterialEASE article in the *AMPTIAC Quarterly*, Vol. 6 No. 1, for a more in depth discussion of nanostructure-property relationships, as well as nanofabrication and analysis methods.)

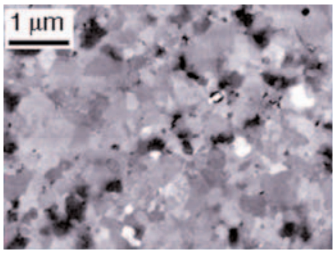
FABRICATION AND MACHINING TECHNOLOGIES

The fabrication of precise stable nanostructures along with the ability to transition such methods to marketable large-scale processes is truly the key to success for nanotechnology. Numerous nanofabrication methods have been studied, including powder synthesis and deposition, solution and gas phase deposition, and mechanical deformation processes. Nanomachining techniques using an atomic force microscope (AFM) have also been used to produce nano-sized patterns for electronic and photonic devices.

Fabrication of Large-Scale Nanophase Aluminum Alloy Structures

Nanophase aluminum alloys have the ability to provide high strength lightweight structures and components for aerospace applications. It has been established that nanophase metals offer increased strength and toughness over conventionally fabricated metals. Such aluminum structures have the potential to replace high cost, heavier metals such as titanium. There is a need to develop fabrication methods which can be scaled-up to produce bulk nanophase materials.

Success has been demonstrated using both a cryomill powder synthesis and equal channel angular extrusion (a mechanical deformation process) to produce large scale aluminum alloys.



Material	Yield Strength (MPa)	Elongation (%)	Reduction in Cross-Section (%)
7075-T6	505	11	10
Nanophase Al 1st Generation	550	10	20
Nanophase Al 2nd Generation	830	5	10

Figure 1. **Structure and Property Enhancement of Nanophase Al Alloys.**

The nanosized grain structure and subsequent increase in mechanical properties produced in the study are shown in Figure 1. Such bulk structures will reduce the overall weight, and ultimately the cost of spacecraft. Nanophase aluminum alloys are deemed applicable for several structures and components including an LH_2 rocket engine fuel pump.

Polymeric Fabrication Techniques

There are two primary fabrication methodologies used to produce polymeric-based nanostructured systems. One is a controlled dispersion of preformed nanoparticles, while the second involves in-situ chemical formation of nano-sized structures. Spatial control of nanostructures during fabrication is crucial in the development of functional materials, such as electronic and photonic devices. Research has been conducted into the fabrication of polymeric structures, using both an electrostatic self-assembly method, and a dielectrophoresis method. The controlled deposition of silver into a polymeric template* to produce conductive fibers has also been under investigation.

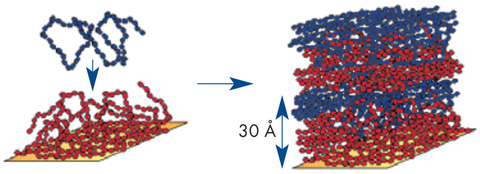


Figure 2. Self-assembly of Polymeric Layered Structures.

There is a great interest in fabricating thin film photovoltaic devices from electroactive polymers, due in large part to its potential to create lightweight, low cost, flexible solar cells and photodetectors. An electrostatic self-assembly technique has been utilized to produce such devices. In this process, layers of oppositely charged species are sequentially deposited onto a substrate from water-based solutions, via the electrostatic attraction between layers. This behavior is depicted in Figure 2. The advantage of this method is the control of film thicknesses, architecture, and composition at the nanoscale. This in turn, affords the creation of efficient photovoltaic devices. One such fabricated device, included an indium tin oxide (ITO) substrate, followed by an electron donating layer of polyphenylene vinylene/sulfonated polystyrene (PPV/SPS), an electron accepting layer of polyallylamine hydrochloride/carbon (PAH/C_{60}), and a top electrode layer of aluminum. Figure 3 shows the measured current (I) of this fabricated structure as a function of voltage potential (V).

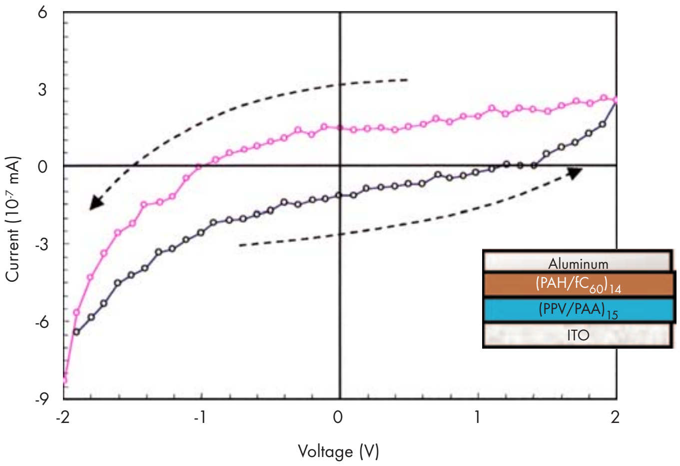


Figure 3. Current-Voltage Characteristics of a Solar Cell Fabricated Using the Self-assembly Method.

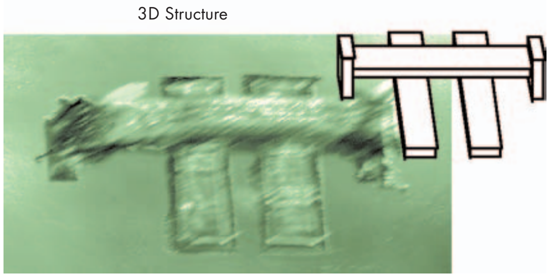
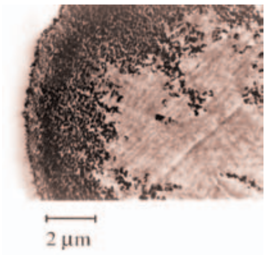


Figure 4. Prototype Optical Switch Structure.

The use of dielectrophoresis (non-uniform electric fields) is under evaluation for the fabrication of well-defined two- and three-dimensional structures with controlled dimensions and compositions. This method can be readily automated to allow manufacturing of functional devices for use in photonics, high density data recording, and for elements to build more complex systems. A prototype optical switch is represented in Figure 4. Challenges anticipated in the development of this method include the construction of electrodes required for the efficient organization of the nanostructures, and mitigating the electrical forces developed during the organization process which could, in fact, nullify the dielectrophoresis effect.

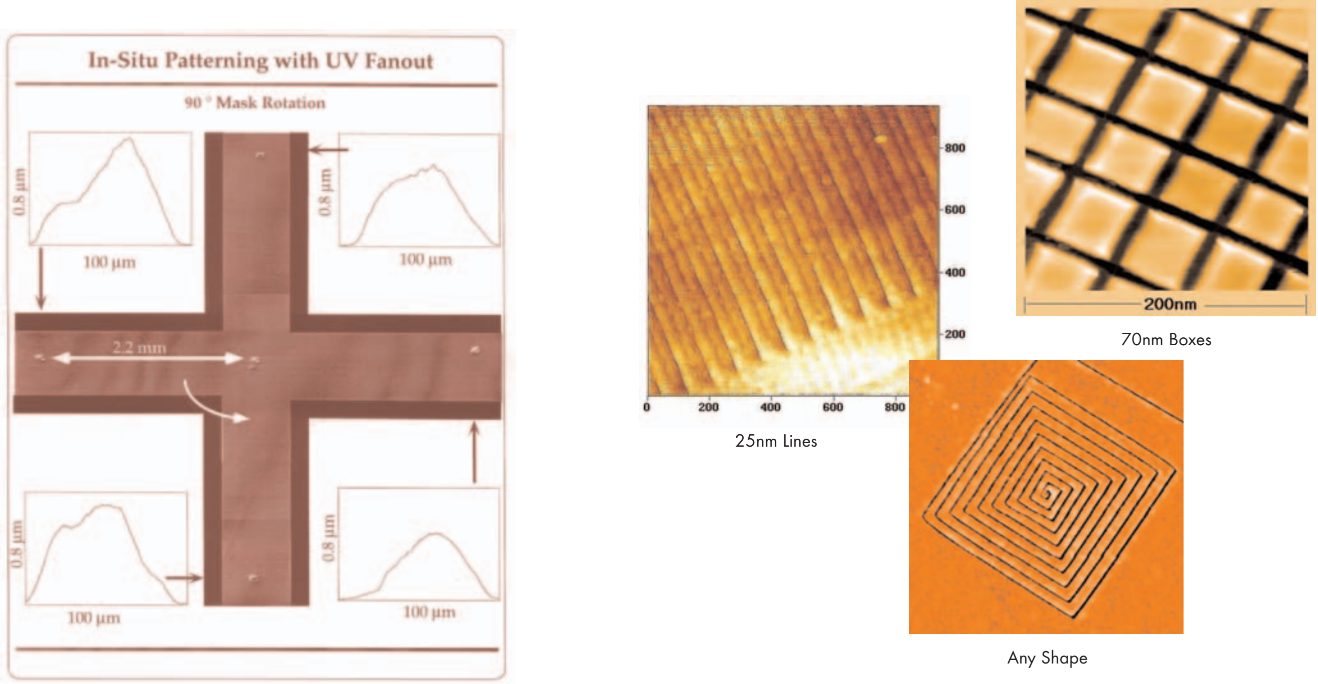
In-Situ Deposition of Conductive Fibers

Nanostructured conducting fibers hold the potential for numerous applications. They are lightweight, and may be used as signal fibers for embedded sensors, electromagnetic shielding, and smart structures. Such fibers have been fabricated by depositing silver nanoparticles in-situ into a polymer template structure; creating an interpenetrating silver network parallel to the fiber axis. Spatial control is achieved through precise fiber swelling and infiltration of the silver precursor and reduction agents. Silver infiltrated polyphenylene-benzobisthiazole (PBZT) fibers have been produced with conductivities exceeding 10^4 S/cm. The Ag/PBZT composite fiber also maintains the high strength of the polymer. Tests have revealed approximately a 200 times increase in strength and a 50% reduction in weight compared to the current aerospace signal wire cores (see Figure 5).



Material	Modulus (GPa)	Strength (MPa)	Strain (%)	Conductivity (S/cm)
PBZT fiber	95.2	900	1.98	10^{-12}–10^{-14}
Ag/PBZT fiber	51.8	1050	3.29	2.5×10^4
Ag fiber	76	55	60	6.3×10^5

Figure 5. Structure and Property Enhancement of an Ag/PBZT Conductive Fiber.



Laser-Assisted MOCAD

AFM Nanomachining

Figure 6. Fabrication of Nano-Sized Patterned Elements.

Fabrication of Patterned Structures via in-situ Deposition and Nanomachining

Methods to construct nano-sized patterns in materials include in-situ deposition (bottom-up) and machining (top-down) of structures. Research has produced nanostructures using a laser-assisted metal-organic chemical vapor deposition (MOCVD) method and also a specialized AFM apparatus as a lithographic tool. The AFM apparatus may be used on a number of different materials while the laser-assisted MOCVD method is specifically used for III-V (columns of the periodic table) compounds. The laser-assisted approach uses an ultraviolet excimer laser on a holographic optical element for patterning two dimensional structures deposited by MOCVD. The next-generation, laser-assisted MOCVD is expected to extend the technology to three dimensional patterns using a Stranski-Krastanov† growth technique to preferentially seed quantum dots.‡ The AFM nanomachining method has the capability to design and fabricate three dimensional nanometer size patterns with excellent uniformity. Figure 6 includes structures developed using the two techniques.

NANOMATERIALS

What distinguishes nanomaterials from conventional materials, aside from their nanoscale structure, is that they tend to exhibit significantly better properties. This section discusses some of the efforts that are being pursued by AFRL to develop novel nanomaterials, optimize their properties, and harness the advantages they offer.

Nano-Engineered Magnetic Materials

In support of the More Electric Aircraft (MEA) initiative, AFRL has developed magnetic materials with improved properties, relative to conventional magnetic materials. The MEA concept focuses on developing an electrical power system that can handle primary actuation loads (e.g. flight control, landing gear actuation, etc.) to replace the main hydraulic systems, as well as the pneumatic, electric and mechanical power transfer systems. This would lead to a reduction in weight, an improvement in aircraft reliability, maintainability, and supportability; and would also reduce the amount of time required for ground support and maintenance.

The main MEA components include aircraft integrated power units (IPU - see Figure 7), magnetic bearings, and internal starter/generators (IS/G), which eliminates the need for a gearbox and reduces the A/C frontal area. These MEA systems require magnetic materials with higher strength and higher temperature capability. For example, the soft magnetic

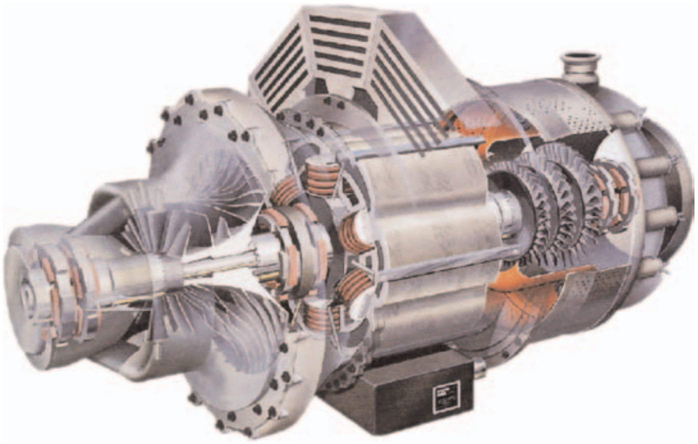


Figure 7. Conceptual Design of an Integrated Power Unit (IPU).

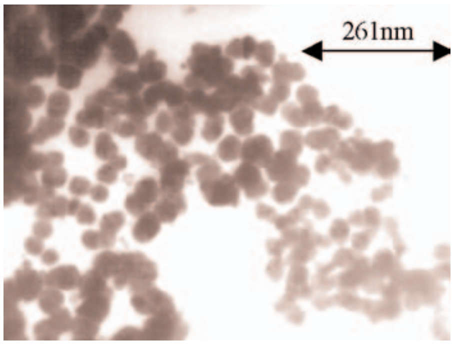


Figure 8. TEM of an FeCo Alloy Nanopowder Prepared Using a Chemical Decomposition Process.

materials will be used in 450°C to 600°C environments, and in rotors that are subjected to hoop stresses of approximately 90 ksi. To meet these requirements, nanoscale magnetic powders were produced and consolidated to create entirely new nanocrystalline magnetic materials. (Figure 8 shows a TEM of an iron-cobalt alloy nanopowder.) The microstructure of the new magnetic materials was controlled by using nanoscale powders and appropriate compaction methods to consolidate the material. Ultimately, the mechanical and magnetic properties of the new materials were optimized for use under conditions of high temperature and stress.

Nanofilled Polymers and Composites

Unlike conventional polymer composites, which employ reinforcing materials that are typically sized no less than a micron in any one dimension, polymer nanocomposites utilize organic and inorganic reinforcement schemes that are sized on the nanoscale. As a result, polymer nanocomposites display unique properties that are fundamentally different from their conventional counterparts. A primary disadvantage of traditional composites is that some of the favorable characteristics of the base polymer, such as the processability and certain mechanical properties, are sacrificed to some extent when the reinforcement scheme is applied. In the case of polymer nanocomposites, however, the base polymer retains its inherent properties to a much greater degree, provided the distribution of the nanoscale reinforcements is relatively uniform. Additionally, the properties of the base polymer can be improved through strict control of the distribution and arrangement of nanoparticles, all while maintaining the processability and low-cost characteristics of the polymer.

AFRL has also been investigating the development, processing, and applications of polymer-layered silicate nanocomposites. These rigid, particulate-toughened matrix resins for advanced, fiber-reinforced polymeric composites show improvements in impact resistance, coefficient of thermal expansion (CTE) control, and suppression of microcracking, as well as increased modulus, and ultra-low permeability. The unique properties are especially remarkable since they have been observed upon incremental additions of the layered silicate (1-5 vol. %) compared to their conventional counterpart which has greater than 20 vol. % loading.[1] These nanocomposites also exhibit great thermal stability, better ablation properties, and improved barrier properties in gaseous environments.

AFRL is developing polymer nanocomposites with self-passivating, self-healing, and ablative capabilities. Nanolayered silicates form a ceramic passivation layer on the surface of the polymer when they are exposed to certain aggressive environments. These ablative nanocomposites can survive temperatures in excess of 2000°C with less than 2 vol. % nanofiller. These materials also exhibit enhanced barrier properties and can withstand the harsh environments of space, including atomic oxygen, UV radiation, and electron/proton bombardment.

The nanofilled polymers and composites currently under development are potentially suitable for a number of applications including lightweight tanks and ducting, space-durable membranes, EMI shielding, smart fabrics, photonic crystals, embedded antennas, multifunctional materials, and sensor protection.

Nanostructured Inorganic Clusters

AFRL has successfully developed a new group of polymeric materials, as part of their effort to develop lighter weight, higher performance materials for space applications. This new group of nanostructured inorganic cluster materials, called polyhedral oligomeric silsesquioxanes (POSS), can be fabricated into hybrid organic/inorganic polymer materials. The POSS monomers are essentially silica molecules with covalently bonded, reactive functional groups. These functional groups can be polymerized or the monomers can be grafted on to existing polymers. Nonreactive, organic functional groups are also contained on the POSS monomers to achieve solubility and compatibility with other polymeric systems. Figure 9 shows the chemical structure of the POSS monomer and the physical structure of POSS containing polymers.

Up to 50 wt. % POSS can be incorporated into conventional plastics (thermoplastics and thermosets) by copolymerization or blending without affecting the processability of the material. As a result, this can improve the thermal, physical, and mechanical properties of most plastics. Since the size of POSS clusters are on the nanoscale, the improvements made by incorporating them in a plastic can be achieved without negatively affecting the desirable properties of the base polymer. Some of the property enhancements for POSS containing polymers include:

- Atomic oxygen & UV resistance
- Increased operating temperature
- Lower density
- Increased strength
- Increased modulus
- Reduced thermal conductivity
- Reduced flammability

The new POSS polymeric materials are suitable for use in satellites and other space systems, since they have relatively low densities and high moduli, and have also exhibited resistance to space environments, such as atomic oxygen, UV radiation, etc. The POSS polymeric materials can also be used in lubricants, and have elevated decomposition temperatures (590°F) – much higher than current conventional lubricants (400°F). These novel POSS materials can also be used for numerous other applications, such as nanostructured pulsed plasma fuel additives, solid rocket motor ablatives, and jet canopies.

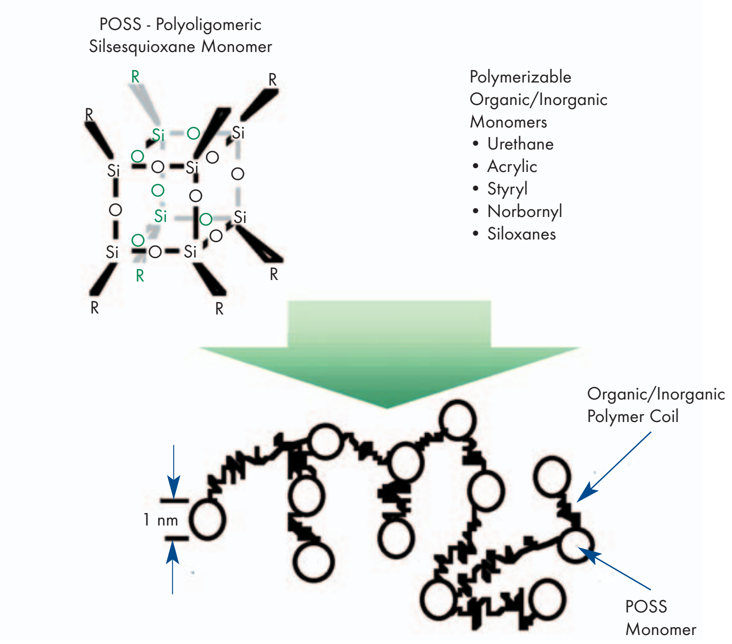


Figure 9. **POSS Containing Polymers.**

Highly Organized Carbon Nanotube Arrays

The carbon nanotube has become the quintessential symbol of materials nanotechnology, primarily because of its extraordinary photogenic qualities and intriguing properties. AFRL has actively been exploring the wide-ranging potential benefits that carbon nanotubes have to offer, including their unique electrical, thermal, and mechanical properties. Carbon nanotubes have been used to create novel materials with specific properties and as reinforcements for composite materials.

POSS enabled materials can be used in conjunction with other materials or by themselves to impart very unique properties to systems. One such unique combination is an array of carbon nanotubes anchored on an aluminum base, as shown in Figure 10. The objective of this effort was to explore the unique physics of carbon nanotube arrays and test the potential of the nanotube band gap for infrared detection capability. It was determined that the optical band gap was related to the nanotube diameter, as shown in Figure 11. This demonstrates that carbon nanotube arrays are suitable for use as infrared imaging detectors, since they are capable of high resolution and are wavelength tunable. These arrays also show potential for field emission displays since they are lightweight and require little power. They may also find application in data storage devices due to their high density and low power capability. Ultimately, the arrays may be used to form ultra-dense nanoelectronic networks.

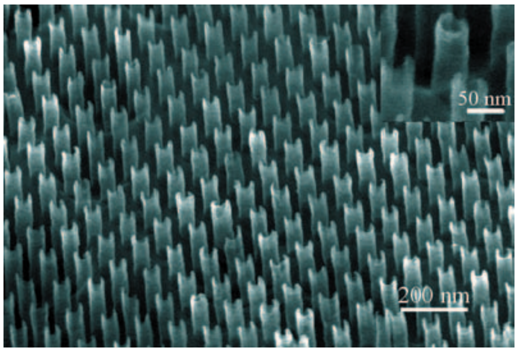


Figure 10. **Carbon Nanotube Array on Aluminum.**

Another AFRL investigation looked at metal-filled nanotubes for room temperature superconductivity. These metal-filled nanotubes take advantage of basic nanotube properties, such as high current, low weight, and high strength, and now have the added advantage of improved magnetic properties. The room temperature current versus voltage characteristics of the metal-filled nanotubes seem to mimic the behavior of low temperature metallic superconductors. Figure 12 shows the "staircase-like" increase in current with increasing voltage. Although the search for a room temperature superconductor continues, metal-filled nanotubes offer another path for further research.

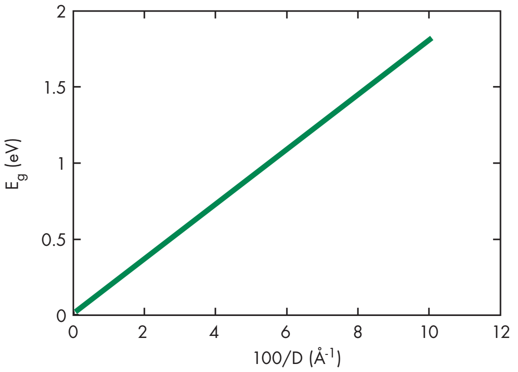


Figure 11. **Optical Band Gap Vs. Nanotube Diameter.**

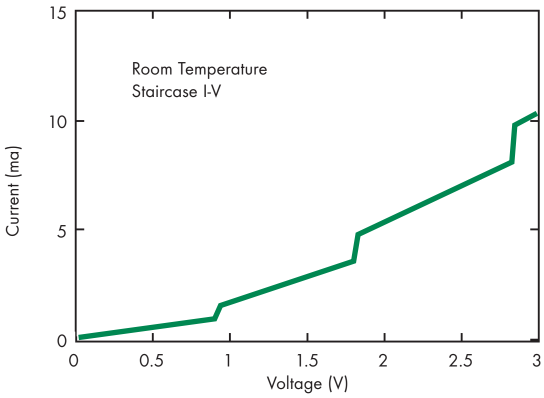


Figure 12. **Current-Voltage Characteristic of a Metal-filled Carbon Nanotube.**

Carbon Nanotube Reinforcement

AFRL has an ongoing project to improve the structural, thermal, and electrical properties of polymer matrix composites (PMCs) by employing carbon nanotubes as a reinforcing material (Figure 13). In order to realize these property improvements, there are several obstacles to overcome involving the alignment of the nanotubes, surface modification methods, material characterization methods, and composite fabrication methods. Expected property enhancements include increased strength, modulus, fracture toughness, thermal conductivity and electrical conductivity, as well as multifunctional capability.

The potential of this technology is to enable space systems

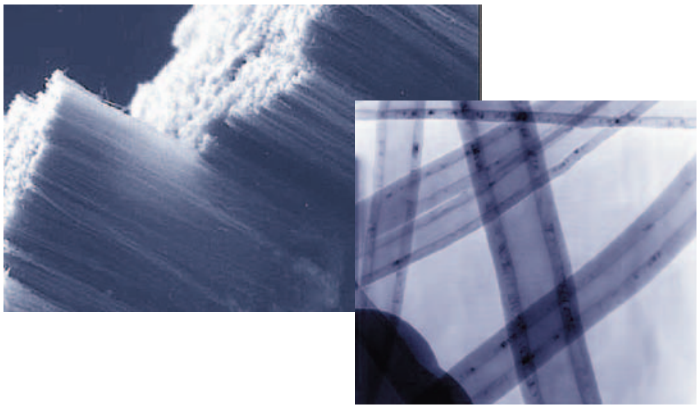


Figure 13. Pictures of Nanotube Bundles and a Close-Up of Nanotubes.

designs to have small and/or highly efficient thermostructural materials. Possible applications include satellites and mirrors, microsatellites, reinforcements for space sails, and space tethers.

Nanostructured Coatings

Nanostructured coatings are novel new materials that have unique properties not normally available from conventional coatings. With nanostructured coatings, for example, typically mutually exclusive properties can be blended, such as hardness, toughness, and low friction capability. An example of a nanostructured coating that provides unique properties is shown in Figure 14. Solid lubricant nanoparticles and hard crystalline nanoparticles are embedded in an amorphous metal matrix to transform high friction, hard materials into hard and lubricious coatings. This results in a tough, hard (wear resistant) coating with an improved resistance to brittle failure. Another benefit of these nanostructured coatings is that they can be developed to maintain their properties over variable and extreme environments.

With further development, nanostructured coatings could have a significant impact on space and satellite systems. For example, they could easily triple the lifetime of control moment gyros, reduce energy consumption and torque noise of mechanical components, enable high speed flywheels, and could also tailor surface chemistry for oils/additives. For pins, latches and gears, nanostructured coatings could prevent failure caused by storage and launch loads, and could potentially increase the lubricant lifetime by an order of magnitude.

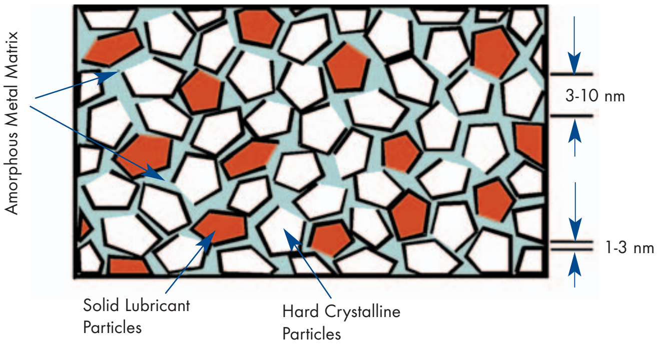


Figure 14. Example of a Nanostructured Coating.

Nanostructured Coatings for Improved Nanotribology of MEMS

MicroElectroMechanical Systems (MEMS) have shown continued success in development and application, but are not without their own obstacles (a MEMS device is shown in Figure 15). Friction, stiction (which is the unintentional adhesion between two surfaces), and wear, for example, have prohibited some MEMS devices from operating as intended while limiting the performance and design of others. AFRL researchers have been looking into nanostructured coatings for a suitable solution to these problems. As a result, AFRL has developed monolayered lubricants that have both bound and mobile phases. These low friction, wear resistant nanostructured coatings are self-assembled monolayers (SAMS) capable of self-healing due to their replenishable gas phase. MEMS devices can now handle extreme environments, (e.g. space, humidity, and high temperature) more easily because these new nanostructured coatings have modified the surface forces and chemistry to reduce or eliminate friction, stiction, and wear. As an added benefit, the new coatings can prevent electrical contact degradation in general. The lubricant system has been observed to remain effective at high temperatures, in a vacuum, and in high humidity environments. The surface treatments required to apply these nanostructured coatings is compatible with other MEMS processing methods.

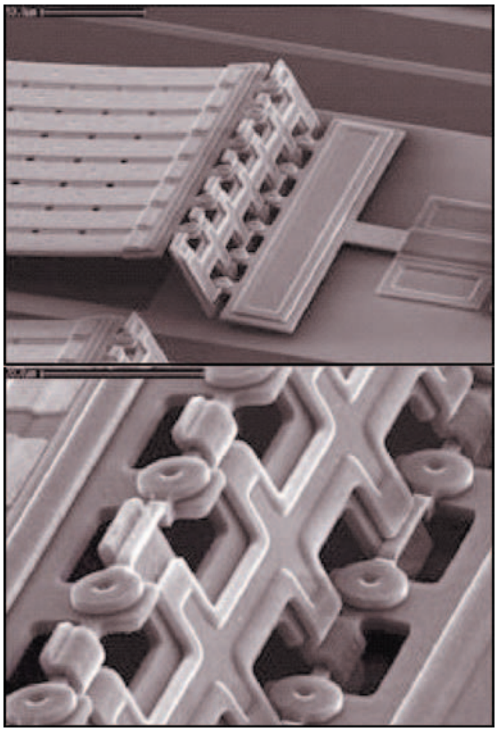


Figure 15. MEMS Electrostatic Lateral Output Motor.

These nanostructured coatings can have a major impact on MEMS device development and application, because they enable MEMS operation in space and other extreme environments and also extend the operational life of these devices. Overall, MEMS are extremely important, as they can increase capability of satellite and other space systems by integrating and miniaturizing sensing and actuation systems. This results in a reduction in weight (consequently reducing the cost) and an improvement in the reliability of these systems.

Nanostructured Polymeric Electrolyte Membranes for Fuel Cells

Proton exchange membranes (PEMs) provide a transport media for protons to migrate between the cathode and anode

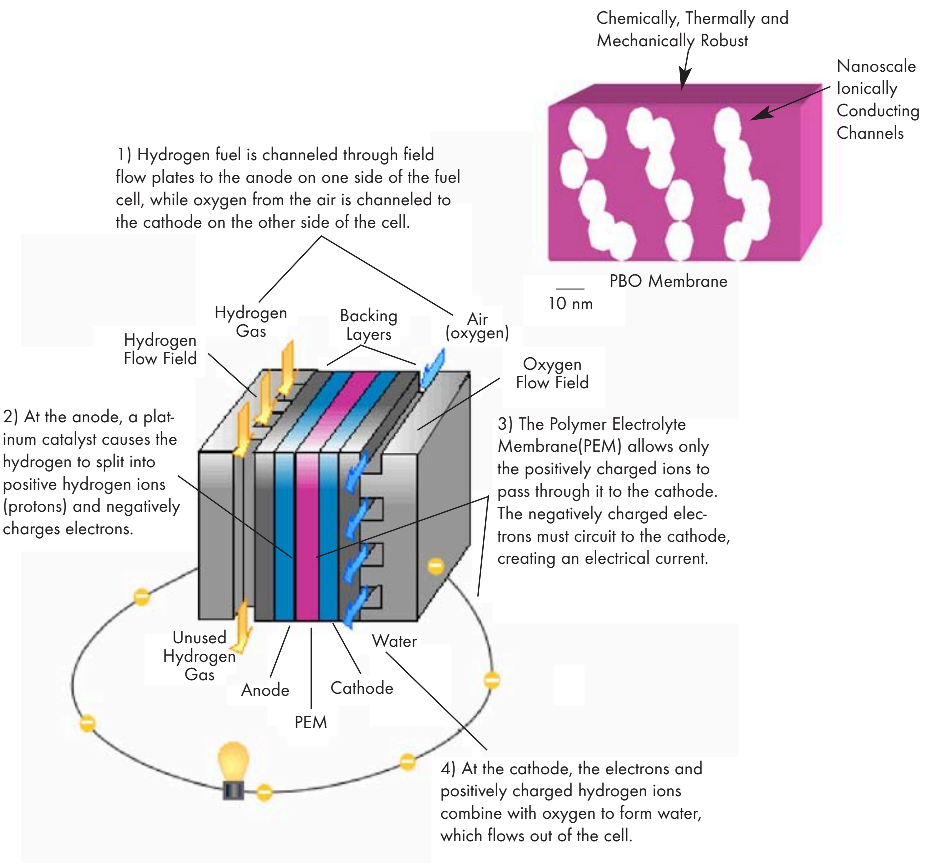


Figure 16. **Polymer Electrolyte Membrane Fuel Cell Structure[2].**

in a fuel cell, as depicted in Figure 16. The membrane is nanostructured to provide hydrophilic regions that conduct protons, and fluorinated hydrophobic regions to provide stability. Nanostructured films of polyphenylene-benzobis-oxazole (PBO) have been produced for membrane applications having the capability to surpass currently used fluoropolymer type membranes. The PBO membranes have been shown to have good performance at 80°C and only 10-20% relative humidity. Optimization of the PBO membrane and research on PBO nanocomposite membranes are also expected to increase the temperature range of operation, beyond the current capability of fluoropolymer membranes.

ELECTRONIC AND PHOTONIC DEVICES

With the development of fabrication tools able to produce structures as small as 0.1 nm, research is now ongoing to develop electronic and photonic components that are smaller, faster, and more efficient. Studies have been underway at AFRL to produce semiconductor devices using self-organized quantum dots and nanostructured photonic devices for optical data links, data management, and electronic displays.

Self-Organized Quantum Dot Semiconductors

Quantum dot semiconductor devices have a strong potential for being transitioned into numerous applications including room temperature lasers and infrared detectors, single electron transistors, and terabyte quantum memory storage devices. Success has been achieved in controlling the size, composition, and arrangement of quantum dots in semiconductor heterostructures. Self-organized quantum dots can be fabricated using the Stranski-Krastanov mode whereby growth of lattice mismatched materials occurs by a strain-induced coherent relaxation creating dislocation-free islands, or quantum dots, as seen in Figure 17. By controlling the arrangement, size, and composition of these quantum dots, electro-optical devices with enhanced performance may be designed.

Nanolayered and Nanotemplated Photonic Devices

Photonic devices are made from materials in which the dielectric constant is modulated on a length scale comparable to the preferred wavelength of the electromagnetic radiation. As the size of photonic structures approach the wavelength of light (< 1 micron), it becomes difficult to confine photons in the dielectric structure. A possible solution to this problem is to create periodic or quasi-periodic dielectric structures which control the transmission, reflection, and dispersion of the photons. Two such devices are under research, each using a different fabrication approach to produce nanostructures that enhance the device's performance. One method is to deposit nanometer-thick layers of materials to enhance properties for optical data links and management applications. The device shown in Figure 18 has produced an increase (~3.2 times) in the electro-optic coefficient over current devices.

High-speed switchable gratings have been produced by spatial control of phase separation§ on the nanoscale. Templates are used to fabricate phase-separated structures for developing holo-

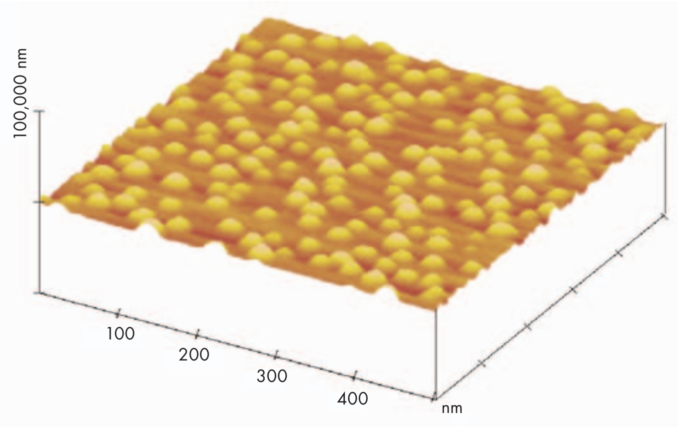


Figure 17. **Self-Organized Quantum Dots.**

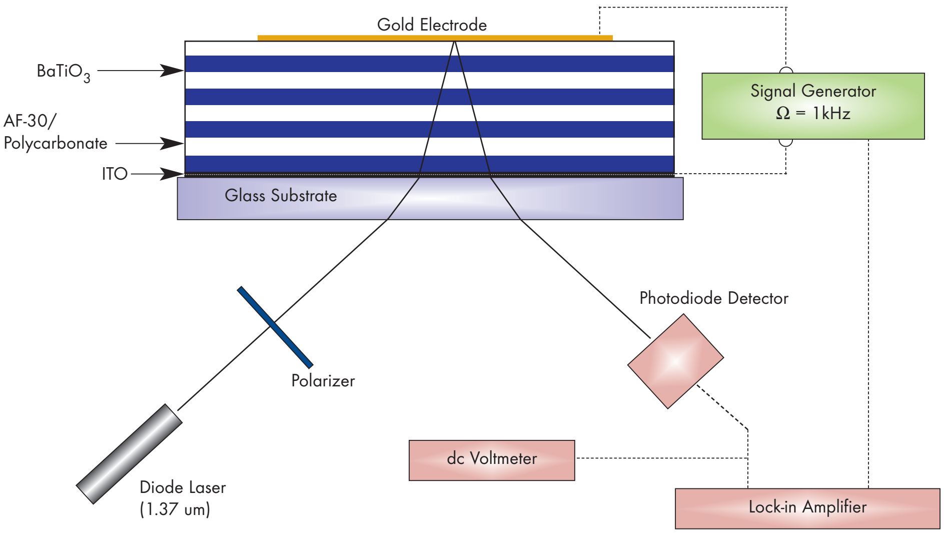


Figure 18. **Nano-Layered Photonic Device.**

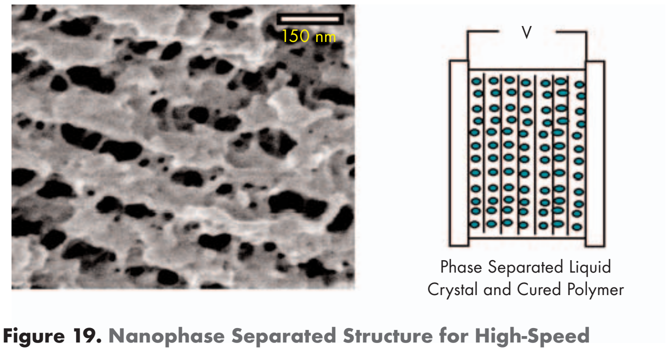


Figure 19. **Nanophase Separated Structure for High-Speed Switchable Gratings.**

Figure 20. **Potential Applications of High-Speed Switchable Gratings.**

graphic optical elements switchable by an induced electric field (Figure 19). These devices can be used to produce optical displays for many applications, including cockpit avionics and helmet-mounted displays, as shown in Figure 20.

MODELING AND SIMULATION OF NANOMATERIALS

Fabrication and testing of nanomaterials is not always a simple task. In fact, testing the mechanical properties of some nanostructured materials has proven to be nearly impossible. For example, using existing tools it is not possible to grasp the ends of a single nanotube to perform a tensile test. Therefore, the modeling and simulation of nanomaterials is extremely important in advancing the understanding of how these materials behave under specified conditions. The following discusses some of AFRL's efforts to explore nanomaterials in the theoretical realm.

Theory of Nanocrystalline and Multilayer Metals

A fairly well-observed anomaly that could be considered the primary advantage of nanomaterials is the improvement in mechanical properties as the material's structure shifts from a microscale size to a nanoscale size. For example, a material with a grain size less than 100 nm shows markedly better mechanical properties compared to materials with conventional grain sizes, which are on the microscale. Multilayered materials also exhibit a similar quality, where the mechanical properties are better if the layers are less than 100 nm thick, as compared to multilayered materials with thicker layers.

AFRL has investigated this critical length scale through modeling and simulation for mechanical properties in metallic alloys. ("Critical" denotes an unusual change in properties based on the size scale of the material's crystallographic structure.) Furthermore, they have developed a theoretical model that accurately predicts the anomalous increase in strength with decreasing thickness and strength limits in metallic multilayer systems. AFRL has demonstrated nanostructured Cu/Nb multilayered materials that can be artificially grown by vapor deposition and naturally-occurring multilayer microstructures in lamellar TiAl (shown in Figure 21). These unique materials show promise for advanced turbine blade shells.

Multi-Scale Simulations: Nanostructured Materials

Modeling and simulation are often used to advance the understanding and enable better development of fabrication techniques. AFRL has applied modeling techniques, ranging

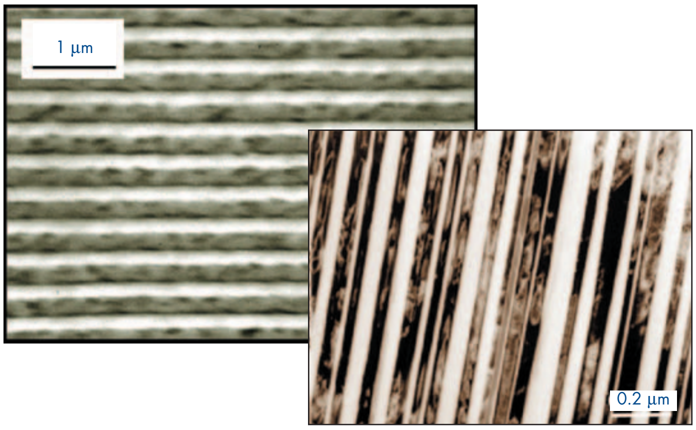


Figure 21. **Vapor Deposited Cu/Nb Multilayer Material (Left) and Lamellar TiAl (Right).**

from the molecular scale to mesoscale**, to examine the development of nanostructured materials. This research has provided a basis for understanding and tailoring nanostructures to enable advancements in fabrication, processing, and characterization of polymeric nanocomposites, nano-inorganic clusters, polymer dispersed liquid crystals, and nanotribology. Among other benefits, the result of the research will lead to improved fabrication of nanocomposites (Figure 22) and the understanding of nanoscale reinforcement (Figure 23).

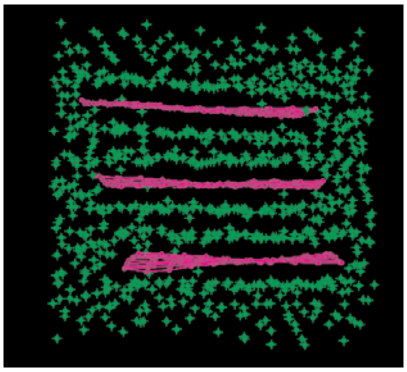


Figure 22. An Example of Simulating the Formation of Polymer-Silicate Nanocomposites.

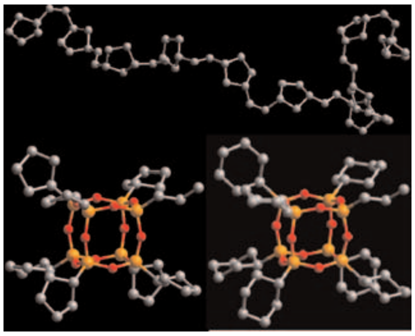


Figure 23. The Effects of POSS Inclusions on the Mechanical Properties of Polynorbornene.

AFRL has also been using modeling and simulation to study the structure-property relationship in polymer-dispersed liquid crystals. The research has focused on attempting to understand the nanoscale structure development of polymer-dispersed liquid crystals, which are fabricated via holography from nanoscopic liquid crystal droplets that are aligned in polymeric resins. Specifically, their objective is to determine the influence of the nanostructure of agile diffractive filters on switching voltage. These material systems show potential for use in applications such as display and telecommunications technology.

Other research has focused on the nanotribology of self-assembled multilayers for MEMS applications (Figure 24). Specifically, AFRL has looked at reducing stiction†† by elucidating molecular aspects, cooperative mechanisms and interfacial interactions associated with the flow of chains in a nanoscopic slit.

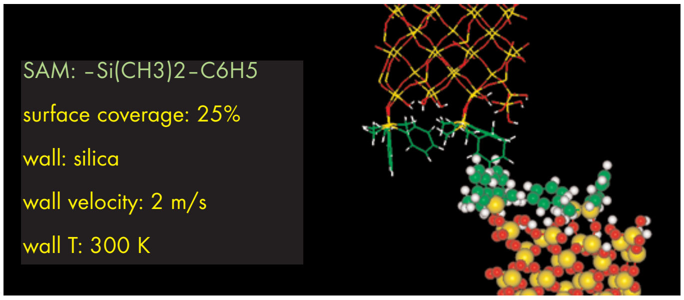


Figure 24. Nanotribology of Self-Assembled Multilayers for MEMS.

In addition to the computer modeling and simulation of materials, another aspect of computational material science is the design of materials. AFRL initiated an effort to develop and apply mathematical and computational methods to design materials at the nanoscale. The program includes projects focused on the integration of materials properties across length- and time-scales for macromolecular systems, biologically inspired materials design (biomimetics), complex materials (e.g. liquid crystals), and advanced scientific computing/simulation algorithms. A general success of the program is that it has demonstrated the design of nanomaterials for Air Force applications with newly developed multiscale approaches, and thus has had a wide-spread impact on the fundamental design of nanomaterials. Specifically, large-scale and long-time molecular dynamics using fast multipole and multigrid methods have enabled simulations of liquid crystals at the nano-level. Furthermore, an effective fragment potential method has enabled the study of nano-optical materials in the condensed phase. Finally, newly developed optimization techniques have enabled large-scale biomolecular structure determination.

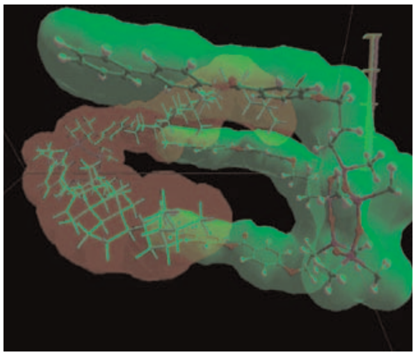


Figure 25. Computer Simulations Allow for Molecular Modeling.

Microscale analysis of a material's structure can provide valuable information, but analysis of a material's structure on the nano- or even the atomic-level can yield extremely valuable information about the material's characteristics. AFRL has attempted to extract atomic-level structural and quantitative compositional information from high resolution transmission electron micrographs (HRTEM) with success (Figure 25). This has enabled the analysis of nanostructure interfaces for many different material systems. The nano-interfaces are characterized through the analysis of a series of HRTEM images by a series reconstruction method. This capability is essential to the development of novel materials by nanostructural engineering, and enables studies on the relationship between processing, nanostructure composition and materials properties. Furthermore, it is critical to the understanding of the properties of interfacial layers or other aperiodic structures (irregularly occurring structures) on the nanoscale.

SUMMARY

Nanotechnology has the ability to impact every component used in aerospace systems. The research into fabrication methods, materials, functional devices, and modeling will lay the path for future aerospace technologies. Higher strength metallic and polymer composite structures can improve flight performance through lighter weight aircraft and spacecraft. Nanostructured coatings can provide better protection against the harsh space environment, and wear resistant properties for moving components. A higher operating temperature ability of materials can push the levels of engine performance and airspeed. Electronic and photonic materials hold the capability to improve flight controls, communications and radar, radiation shielding, and self-diagnostics. Nanostructured polymers also provide membranes in fuel cells for power systems. Although nanotechnology is still very much in its infancy, where the high majority of work is in the research phase, it has the potential to push levels of performance on all fronts, and enable the development of more efficient and reliable aircraft and spacecraft.

ACKNOWLEDGMENTS

The authors would like to thank the Air Force Research Laboratory and its scientists and engineers for contributing much of the information and figures that were included in this article.

NOTES & REFERENCES

* A template is a pattern or mold for the deposition of a material into a precise geometrical configuration.

† Stranski-Krastanov (S-K) is one of three documented forms of heteroepitaxial growth. In its simplest form; S-K growth is characterized by the growth of one or more two-dimensional layers; followed by the growth of three-dimensional islands on top of the previous layers.

‡ Quantum dots are three-dimensional growths, or islands, resident on the substrates of semiconducting materials. Grown at the nanoscale, quantum dots are able to harness the quantum effects of their constituent materials, allowing them to perform operations in a fraction of the time of conventional electronic components.

§ Phase separation is the process of selectively removing constituents of a material.

** While not rigidly defined, *Mesoscale* is generally a level of scale that encompasses more than a few thousand atoms, but less than billions or trillions of atoms (*AMPTIAC Newsletter*, v.5, n.2).

†† Stiction is friction that inhibits the relative motion between two components in a mechanical system.

[1] R.A. Vaia, *Polymer Nanocomposites Open a New Dimension for Plastics and Composites*, *AMPTIAC Quarterly*, Vol. 6 No. 1, Spring 2002

[2] www.fueleconomy.gov/ feg/fcv_PEM.shtml

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Government Personnel

Technical Manager/COTR
Dr. Lewis E. Sloter II
Staff Specialist, Materials & Structures
ODUSD(S&T)/Weapons Systems
1777 North Kent St, Suite 9030
Arlington, VA 22209-2110
(703) 588-7418, Fax: (703) 588-7560
Email: lewis.sloter@osd.mil

Defense Technical Information Center (DTIC) POC
Melinda Rozga, DTIC-AI
8725 John J. Kingman Rd, Suite 0944
Ft. Belvoir, VA 22060-6218
(703) 767-9120, Fax: (703) 767-9119
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Associate COTRs

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Dr. James Murday
Naval Research Laboratory
4555 Overlook Ave, S.W. Code 6100
Washington, DC 20375-5320
(202) 767-3026, Fax: (202) 404-7139
Email: murday@nrl.navy.mil

Alion Science and Technology Personnel

Director, AMPTIAC
David Rose
201 Mill Street
Rome, NY 13440-6916
(315) 339-7023, Fax: (315) 339-7107
Email: drose@alionscience.com

Deputy Director, AMPTIAC
Christian E. Grethlein, P.E.
201 Mill Street
Rome, NY 13440-6916
(315) 339-7009, Fax: (315) 339-7107
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David Brumbaugh
201 Mill Street
Rome, NY 13440-6916
(315) 339-7113, Fax: (315) 339-7107
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John W. Lincoln Award Presented

Mr. Ward D. Rummel, President and Trustee, D&W Enterprises, Littleton, Colorado, was presented the 2003 John W. Lincoln Award. It was given in recognition of his outstanding work over many years in advancing technology associated with the concept of aircraft structural integrity. He was specifically recognized for his outstanding work and leadership in the area of nondestructive evaluation, including advancement of the area of quantitatively characterizing the ability of a nondestructive evaluation/inspection system to detect damage by defining the Probability of Detection (POD) of the inspection method. The Award was presented at the 2003 USAF Aircraft Structural Integrity Program (ASIP) Conference in Savannah, Georgia on 2 December 2003. The Award, which consists of a gold medal and a certificate of recognition, was named in honor of the late Dr. John W. (Jack) Lincoln of the Aeronautical Systems Center, Wright-Patterson Air Force Base, Ohio. Dr. Lincoln was a pioneer and major contributor to the development and application of durability and damage tolerance design to insure the safety and longevity of both military and commercial aircraft. The Award has been presented previously to Dr. Lincoln (1996), to Mr. Charles Tiffany (1997), to Mr. Thomas Swift (1998), to Professor Jaap Schijve (1999), to Professor Alten Grandt, Jr. (2000), to Dr. James Newman (2001) and to Mr. Royce Forman (2002). A plaque with the names of the recipients is on display at Wright-Patterson Air Force Base, Ohio.

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