LEAD AGENCY: U.S. Army

LAB: U.S. Army Research Laboratory - Materials Directorate

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PROBLEM STATEMENT: Eliminate or reduce usage of environmentally harmful chrome and cadmium electroplating processes. Conduct applied research and development to demonstrate that metal or ceramic coatings deposited by physical vapor deposition (PVD), and/or ion-beam-modified surfaces are equivalent or superior in performance and are a cost-effective & environmentally acceptable alternative to electroplated Cr and Cd for military applications.


BACKGROUND: Hard chrome is primarily used in DoD related manufacturing to (1) coat high wear surfaces such as bearing shafts and hydraulic components and is principally performed by Original Equipment Manufacturers (OEM's) and (2) rebuild and remanufacture of out-of-tolerance components at maintenance depots. For the former, the use of hard chrome has actually been increasing because of the general requirement enhanced performance. For the latter application, many components are returned to the depots for refurbishment that are worn, corroded, or eroded by use. The components are reworked by removing the damaged metal, stripping off any old hard-chromium coatings, building them up with hard-chrome, and then machining them to final tolerance. Corpus Christi Army Depot (CCAD) coats more than 0,000 types of components annually with hard-chrome for this purpose. Most of these components are re-plated several times during their service lives.

Gun tube wear & erosion have been a long-standing military unique problem. A practical objective has been to achieve gun tube wear life comparable to fatigue life, though wear & erosion caused the unexpectedly short tube life for the new 8" and 155 mm gun systems. Advanced gun systems under development (such as Liquid Propellant and Rail Guns) will push requirements to even higher standards. New protective coatings with even higher melting points (refractory metals) are needed to challenge the use of more energetic propellants with higher flame temperatures.

Cadmium electroplating is also used by both OEM's and by DoD maintenance depots to impart corrosion resistance and lubricity to a wide variety of parts, although several alternatives exist for certain applications. These alternatives include electrodeposited Zn and Zn alloys and ion-vapor-deposited (IVD) aluminum. The Anniston Army Depot, Anniston, AL, has recently installed two IVD systems and is replacing Cd with IVD-Al for some components of armored vehicles. CCAD has also recently installed an IVD system, and is currently replacing Cd on many non-flight critical parts. An Air Force study acknowledges that IVD-Al will not easily replace more than about 50% of the Cd-plating requirements. The Army has authorized electroplated zinc as an alternative to cadmium for grade 8 fastener application. Exceptions include selected electrical/electronic applications where Cd-plated fasteners are required and high strength steel components. A recent study by the Army Research Laboratory, Watertown Site, showed a Zn-Ni alloy provided better resistance than zinc and exhibited a comparable coefficient of friction. While the Cd plating alternatives have reached a certain degree of
maturity, several issues still need to be resolved. The Aviation Troop Command, (ATCOM), St. Louis, recently outlined the problems to be addressed which include: fatigue and Environmentally Assisted Cracking (EAC), torque-tension requirements for fasteners (before and after exposure), close tolerances, and ability to reach recessed areas. Thus there still exists the strong (& urgent) need for further coating development & characterization efforts.

**TECHNICAL APPROACH:** Vacuum-based PVD coating techniques are known to produce the highest quality coatings, with widespread use of high vacuum techniques in the microelectronics industry having broadened the industrial base for large scale systems with a concomitant reduction in cost. The most advanced types of PVD coating techniques utilize what can be called "ion-assist" whereby energetic charged particles are incident on the workpiece during the coating process. Two variations on ion-assisted PVD are (1) ion-beam-assisted deposition (IBAD) whereby a directed beam of energetic particles from an ion gun are coincident on the workpiece with the depositing vapor atoms, and (2) magnetron sputtering whereby vapor atoms are produced by sputtering from an electrode with ions being accelerated from a plasma by application of a negative bias to the workpiece. These two techniques produce coatings that are highly adherent, fine grained, generally pin-hole free and fully dense, and which can be deposited at relatively low temperatures on virtually any type of solid material. The deposition rates for these types of coating techniques are sufficiently high that they could be expected to economically replace both chrome platings deposited by OEM's and electroplated cadmium. For these applications, the types of coatings to be investigated would be TiN, (Ti, Al)N, CrN, Ta and diamond-like carbon, all of which have been previously investigated for corrosion and wear applications. However, the deposition rates are not high enough to replace the chrome plating operations in military depots which are intended for re-build of components. For this application, the proposed solution is to rebuild the component using an alternative electroplating technique such as electroless nickel, machine it to final tolerance, and then apply one of the above PVD coatings to provide significant wear and corrosion resistance.

Ion implantation has been shown to significantly improve the corrosion and wear behavior of a variety of materials. Virtually any element can be implanted into substrate materials although only a few will be selected for this program. Previous research conducted at ARL has shown that nitrogen implantation into hard-chrome coatings increases the surface hardness and significantly reduces the tendency of the coatings to form microcracks when subjected to loads or stresses. This will be further investigated under this program as well as ion implantation of thin-dense-chrome coatings, a proprietary of Armoloy, Inc., which is an electroplating process that does not produce toxic effluents. Previous efforts in this area have investigated alternative electroplated coatings, such as Zn alloys as Cd replacements. The only significant exception to this is the development of IVD aluminum. It is interesting to note that large-scale IVD-Al systems have been available for over 16 years, yet DoD is still funding R&D work to investigate and implement this process. Electroless nickel coatings are also being investigated as a replacement for chrome, but nickel is on the EPA "toxic enemies" list so it should be considered as an interim process. An important issue in developing new types of coatings in any system is whether it will have any effect on any other system components. If a chromium coating is replaced with another coating which demonstrates superior performance in laboratory tests, will it have a detrimental effect on its mating part? This potential problem will be considered in the selection and evaluation of actual components. This overall program is considered to be of medium technical risk.

**RELATIONSHIP TO OTHER SIMILAR ONGOING WORK:** The Basic Industry Research Laboratory (BIRL) at Northwestern University has been awarded a substantial contract ($1.5M over two years) entitled," Hard-Chrome Coatings: Advanced Technology for Waste Elimination." This proposed SERDP program is designed to investigate other coating techniques and thus there will be virtually no duplication of effort. One of the POC's (BDS) on this proposal has collaborated with the PI on the DARPA contract. Extensive collaboration/coordination between the two programs will ensure that DOD will obtain the optimum solution(s) to this problem. This program is also closely coordinated with the
NDCEE demonstration program for Ion Beam Processing. There is currently a proposed ESTCP effort to take both the BIRL and SERDP program results beyond their current 6.2 phase and fully transition the process to the depot level.

**TASKS/ACTIVITIES:** The focus of the project will be the characterization and evaluation of the coatings in comparison to electroplated chromium and cadmium coatings. Evaluation of coating performance must include laboratory simulation of battlefield and global environments, with a baseline comparison with hard-chrome coated components. Properties such as hardness, adhesion, and density will be determined for each coating. Measurements related to actual performance will be correlated with the type of electroplated coating intended to be replaced and the actual end-use application. Thus, testing will include 1) sliding wear tests with realistic loads, speeds, and use of lubricants, 2) erosion tests, 3) corrosion tests using electrochemical and/or salt spray methods, and 4) low-cycle or high-cycle fatigue, or rolling-contact fatigue, and 5) hot-hardness tests. In addition to evaluation of coated test coupons, actual components will be selected for coating and evaluation. The POC's have assembled a team to address all of the tasks related to coating deposition, characterization, and evaluation. The tasks are listed with the activities expected to perform them. An (A) or (N) following the activity denotes whether the Army or the Navy will be the primary contact.

Corrosion Science Group, ARL(A): Deposition of IBAD and plasma sprayed coatings; cohesion, adhesion, and porosity measurements on all coatings; surface analytical measurements; corrosion by electrochemical impedance spectroscopy, galvanic corrosion studies; erosion tests; coefficient of friction measurements; rolling contact fatigue measurements.

Surface Modification Branch, NRL(N): Deposition of IBAD coatings; hardness, density, and adhesion measurements on all coatings; composition measurements on compound coatings and determination of impurities, if any; other surface analytical measurements; sliding wear tests; corrosion tests.

BIRL, Northwestern University: Deposition of magnetron sputtered coatings; high temperature wear tests using Falex tester; deposition of HVOF coatings (A).

Jet Process Corporation, New Haven, CT: Deposition of PVD coatings (N).
Armoloy of Connecticut, Inc.: Deposition of TDC coatings (A)
Naval Air Warfare Center, Trenton, NJ: Fatigue testing of coated samples (N).
Corpus Christi Army Depot (CCAD): Deposition of cadmium and chromium coatings onto test specimens; selection of two helicopter components (in consultation with ARL) for coating; rig testing of coated components (A). Flight-test arrangements will be made with the ATCOM and the NASC.

**EXPECTED PAYOFF:** Coatings developed under this project should demonstrate performance that exceeds that of electroplated coatings, thus reducing the frequency of rework. This will further reduce the costs associated with the new processes. As an example, if a 2.5 X increase in service life by using ion implantation can be achieved, estimates based on CCAD data show these re-work savings on only three bearings and gears used in the AH-1/UH-1 helicopter drive trains would total over $1.2 M yearly. The potential on a DoD wide basis would be many times greater. It is also intended to use this technology for gun tubes which are routinely Cr electroplated to provide wear resistance the bore. The costs of alternative coating technologies should not be compared with the current cost of Cr and Cd coating, but with their expected future costs, taking into account regulations projected into the future. The Basic Industry Research Lab cost analysis has concluded that for operations with equivalent throughput, the operating cost for a PVD facility would be 20% less than for a plating operation (based on info. from CCAD, McClellan AFB and on their own calculations for PVD operations).
TRANSITION PLAN: A detailed transition plan will be developed early in 1995, in close cooperation with the field activities, CCAD and CPNAD, as well as other activities (Army MSC's and RDEC's, NAWC's, the Joint Technology Exchange Group and the Aerospace Chrome Elimination Group). Additional selected components will be coated, with some subjected to additional rig testing, and the remainder installed in actual operating aircraft. Cherry Point NAD expects to install a large PVD coating system in early 1995, which will coincide well with the technology transition. Since it will not be possible to individually evaluate (qualify) the replacement coatings for every component that is currently electroplated, a key aspect of the transition plan is to provide information and data, including coating deposition specifications, to agency engineers so that new coating technologies can be certified for use in broad areas.