

Final Report on:

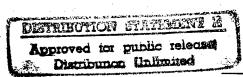
Hot Gas Erosion and Wear of Materials

Sponsored by:

THE UNIVERSITY OF MICHIGAN &

ARMY RESEARCH OFFICE

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ANN ARBOR, MICHIGAN

SEPTEMBER 25-27, 1996

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WORKSHOP ORGANIZERS: JOHN C. BILELLO, ROBERT R. REEBER, AND STEVEN M. YALISOVE

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Final Report:

Workshop on:

Hot Gas Erosion and Wear of Materials

Sponsored by:

The University of Michigan & Army Research Office

Ann Arbor, Michigan September 25-27, 1996

WORKSHOP ORGANIZERS:

JOHN C. BILELLO & STEVEN M. YALISOVE UNIVERSITY OF MICHIGAN

AND
ROBERT R. REEBER

ARMY RESEARCH OFFICE

INTRODUCTION

Robert R. Reeber, PhD
Materials Engineer
Army Research Office
Research Triangle Park, NC 27709

The Army-after-Next will require improved durability and reliability for its systems. Soldiers in the field will face known as well as new threats and can benefit from as yet undiscovered scientific advances. A principal objective of this workshop was to identify possible directions for shorter and longer term Army-funded research that has a high likelihood for impacting the Army mission.

The next generation of gun tubes will require sustained high rates of fire at temperatures exceeding 3500 K. The scope of the materials problem for such systems can be illustrated by evaluating what known high melting point materials are currently available. These are listed in Table 1.

TABLE 1
MELTING TEMPERATURES OF REFRACTORY MATERIALS

| Metal | Melting Point (K) | | Melting Point (K) |
|--|-------------------|---------------------------------|-------------------|
| Chromium | 2130 | Hf ₃ Si ₂ | 2923 |
| Hafnium | 2500 | Ta₅Si | 2773 |
| Niobium | 2740 | TiC | 3054 |
| Molybdenum | 2888 | YN | 2973 |
| Tantalum | 3288 | ZrC | 3803 |
| Osmium | 3303 | HfC | 4233 |
| Rhenium | 3453 | TaC | 3600 |
| Tungsten | 3673 | ${ m TiB}_2$ | 3123 |
| ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~ | | ZrB ₂ | 3473 |
| | | HfB ₂ | 3523 |
| | | TaB ₂ | 3473 |
| | | TiN | 3220 |
| | | ZrN | 3260 |
| | | HfN | 3580 |
| , , , , , , , , , , , , , , , , , , , | | TaN | 3360 |
| | | NbC | 3660 |

Advanced materials problems and cost estimates are given below in Table 2.

TABLE 2 MATERIALS PROBLEMS

| Material | Potential Problem | Cost |
|-----------------------------|---|------|
| Metal | High Temperature strength and ductility | M |
| Ceramic | tensile strength and thermal conductivity | H |
| Ceramic Matrix Composite | differential thermal expansion | Н |
| Metal Matrix Composite | " " and brittle shock | Н |
| Cermet | brittle shock | Н |
| Intermetallic | brittle shock | Н |
| Gradient Material | ? | VH |
| Nanolaminate | ? | VV. |

Given our current understanding of complex phase equilibria of ultrahigh temperature structural materials and their cost of development we have an extremely difficult problem meeting the projected requirements. The empirical nature of multicomponent high melting point materials design means that data requirements are large. Parameter space for the complex phase equilibria of a five component system is represented by five dimensions in composition space. This does not include the need for understanding performance and failure criteria for specific compositions. The research challenge is to develop theoretical/semiempirical underpinnings, verified by experiment, that can short circuit traditional approaches for providing design information.

New families of ultrahigh temperature refractory materials, for greater than 3000 K service, would provide major improvements in fuel efficiency. Such materials, although not low cost, could have increased durability and improved mission capabilities in many other areas of importance to the Army.

Two panels of civilian and Army materials specialists have addressed these needs and provide the following summary reports.

HOT GAS EROSION AND WEAR OF MATERIALS

PANEL REPORT SHORT TERM NEEDS AND ISSUES FOR ENHANCED MATERIALS PERFORMANCE

Professor John Conrad, Chairman University of Wisconsin, Madison, WI

Short term was defined as 5 to 10 years for the purpose of this panel. The panel made assessments of Army gun tube needs and the applicability of a variety of processes and materials. The gun tube erosion problem involves complex interactions between the tube coating, explosive charge, duty cycle and the projectile. It is important to consider the overall aspects of the system.

Environmental issues for specific processes are of concern in any development, but they are dependent on regulatory actions and therefore were not considered further by the panel. Current large gun tube technology consists of electroplated hexavalent hard chrome deposited at rates of 1mil/hour (for the whole gun tube) with a variety of post processing procedures. Such coatings contain incipient cracks. Much of the data documenting this process dates back to World War II. Nevertheless, some possibilities still exist for further optimization.

For the short term, improvements in the existing chrome electroplating and new processes involving tantalum, molybdenum and tungsten were considered. The greatest near term relevance was ascribed to tantalum, because of its high melting point and high ductility. Any new process should have full bore coating rates comparable to chromium plating.

General Recommendations:

- 1. Characterization of coatings is extremely important. Improved testing methodologies, including a high rate wear test, are needed. Also better ways are required to more precisely define critical design parameters.
- Improved models can offer low cost approaches to minimize the number of large scale empirical experiments necessary for final validation. Such models require information on high strain rate deformation, high temperature thermomechanical and thermophysical properties, effects of high dynamic pressures, thermal shock, thermal fatigue, including number of duty cycles, and erosion in the relevant environment. Furthermore, new propellants have excess amounts of hydrogen. This is potentially deleterious to certain materials systems.
- 3. Differing problems at the gun muzzle and breech and with respect to smooth bore versus rifled tubes may require somewhat different solutions.
- 4. New opportunities exist for multilayer and graded structures, designed nanoarchitectures. These may be limited by cost and manufacturability considerations.

Table 3 provides a list of potential processes for gun tube hot gas erosion protection. The panel rated the potential of each process. Specific recommendations are listed below.

Recommendations for proposed gun tube manufacturing processes:

- 1. Tantalum molten salts and sputtering (triode and magnetron) are not so amenable to full barrel coating. Tantalum has properties that appear, in 20mm firing tests, to be significantly better than the current chromium electroplate.
- 2. Current chemical vapor deposition processes are too high in temperature and going to lower temperature CVD could present problems. In the longer term, investments for designer organometallics could have favorable results. A review of current technology in this area has been recently published by M. Trkula of Los Alamos National Laboratory.
- 3. Laser methods do not seem practical in the short term for the geometry required and were referred to the Long Term Research Panel as a research topic..
- 4. Centrifugal SHS utilizes a thermite reaction of a slurry while the part is spun to create a functionally graded material. The method is currently used in Japan, the Ukraine and several small US companies. In Japan the interior of pipes that are 15 feet long and 10 inches in diameter have been coated. The coating could have thermal conductivity problems. If systems other than Fe_2O_3 and Al going to Al_2O_3 and Fe are available, this process is considered to have some short term potential.
- 5. Explosive welding processing is currently available in the US as art for conventional metals and alloys. It has been extensively developed in Japan and the Ukraine (Paton Institute). The requirement of a minimum of 10% ductility could be met by tantalum sleeves. The potential exists to manufacture such sleeves by CVD, sputtering and e-beam. Such combined processes were considered to have significant short term potential, especially for smooth bore cannon.
- 6. E-beam methods for direct use were considered longer term potential because of geometry problems. Nippon Steel does have a commercial process for manufacturing stainless steel tubes for gun barrels with this technology.
- 7. Hard chrome parts in borehole geometries have been nitrided by plasma source ion implantation. Empire Chrome Company in Chicago has been working on this with the University of Wisconsin. This PSII treatment provides some significant wear life extension. Other hybrid methods may provide similar benefits.
- 8. Trivalent Chrome electroplating is now viable for decorative chrome. Although current processes are considered to have expensive chemistry and a narrow process window, at a recent June 96 Electroplaters Society Meeting in Cleveland six different investigators. reported independent approaches for depositing hard trivalent chrome. The material being deposited is heat treatable and can be put on during an early stage of part processing. During heat treatment chromium diffuses partially into the steel forming a reliable diffusion bond. It is expected that in 5 years an improved trivalent hard chrome process should be available.
- 9. Army participants indicated that internal evaluations of preliminary tantalum sputtering approaches investigated by Benet Laboratory looked promising. Better lab scale tests are needed to relate to what occurs in gun tubes. It was suggested that a review was needed by outside experts to further assess this process and identify any potential problems. Such a review could provide impetus to Army decision makers in their determination to aggressively push ahead with the work.

TABLE 3 MATERIAL/PROCESS EVALUATION

| Process | Rate | Cost | Potential |
|------------------------------------|----------|-----------|---|
| Electroplating | Moderate | Low | State of Art for Hexavalent Chromium |
| Chemical Vapor Deposition | L to M | M to High | Long Term |
| Sputtering | L | H | Near to Long Term |
| Laser Ablation | M to H | M to H | Long Term |
| Explosive Welding | M | M to H | Near Term |
| Centrifugal SHS | M to H | ? | Near Term |
| Nitriding | M to H | ? | Optimize |
| Organo-Metallic-CVD | M to H | M to H | Long Term |
| Ion Beam Assisted Deposition | L to M | Н | Optimize |
| Superplastic Forming | H | M to H | |
| Plasma Welding | ? | ? | ? |
| Metal Plasma Torch | ? | ? | Includes Rebuild |
| Combined Processes | ? | ? | Near to Mid-Term |
| Chrome 3+ | M to H | M | Mid-Term |
| LT molten salt bath electroplating | M to H | M to High | Long Term |
| Other | ? | ? | ? |

HOT GAS EROSION AND WEAR OF MATERIALS

PANEL REPORT BASIC RESEARCH NEEDS

Dr. James McCauley, Chairman U.S. Army Research Laboratory Aberdeen, MD

Defining Research Goals

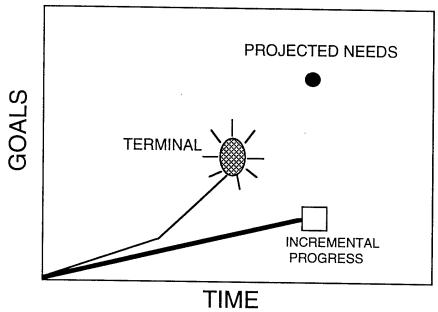
The basic research panel was charged with the following questions: 1. How can we more effectively plan research targeted for the goals of this workshop? 2. How can we accelerate the adoption of cost effective advanced materials into Army systems? A non-trivial task is to address what assumptions must be made to provide for the materiel needs of the Army-After-Next. The success, or failure, of technology options chosen will impact strategic choices available to senior level Army planners.

Several examples were cited from past industrial practice as models for technology insertion. Developments in electronics, specifically the exponential/logistics relationship between transistor density versus time and advances in materials strength-density vs. year were the examples provided. These are valid models for the private sector where perceived financial benefits are sufficient incentives; whereas in the Army mission performance has been the critical issue. Reduced resources, in combination with new requirements, has increased the emphasis on cost reductions for new systems.

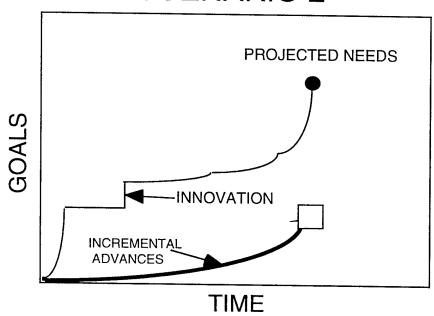
Today research, development and engineering planning can often be restricted to a linear paradigm that proceeds from one empirical solution to another. Based upon perceived strategic need, a better approach would be to predetermine the performance goals required for a given system and then go backwards to see what property requirements are mandated.

Figure 1 and Figure 2 schematically represent different strategic scenarios for providing similar fire support in the field. The mission capabilities for both would have different costs attached. Each development scheme requires new research ideas and technology to be successful. At this time their feasibility has a degree of uncertainty. The object of this report is to identify options for reducing the risk of these scenarios to acceptable limits.

Figure 1
SCENARIO 1



SCENARIO 2



Each R&D path requires different materials and processing challenges. A goal is to look at performance requirements for a system and have the capability to model it at different scales from atomistics through the microstructural changes produced by processing and or induced by service (i.e. growth of cracks etc.). The challenge is to provide an understanding that includes first principle theories and/or empirical and semiempirical representations utilizing available databases. Knowing the why of how the performance capabilities change with improved materials properties and novel design changes is essential.

The following generically summarizes the panel's considerations and recommendations:

a. Potential Army Applications for Erosion Resistant Materials

These include:

- 1. opaque or transparent and radiation resistance, light weight armor made from ultra hard superhard materials,
- 2. signature control from nanolaminate materials through novel design concepts,
- 3. ultrahigh temperature (>4000K) wear resistant gun tube materials,
- 4. generically lightweight structural materials for combat vehicles and helicopters,
- 5. robots for many applications- one person commanding expendable robotic drones through verbal commands,
- 6. projectile materials where sabots are coated with multiple coatings, and or the coating on a bullet coats the tube thus protecting it for the next round,
- 7. the impact of smart shells on barrel lengths, firing rates, need for rifling.
- 8. new classes of high temperature (>3500K), degradation-resistant materials for ultrahigh efficiency engines.

b. Property and Design Database Status:

Providing quantitative algorithmic representations of the interrelationships between performance, system design and materials properties is a complex process requiring accurate and comprehensive data for advanced materials. In spite of the fact that the government has heavily supported advanced materials research and development for over 30 years, such materials are not utilized extensively. The costs for generating comprehensive design databases for new materials is excessive. It is often difficult to integrate databases. Different groups do not necessarily want to freely combine their databases with other sometimes competing organizations. Additionally, the theoretical underpinnings for such integration are not adequate, or do not exist. Databases lack credibility, either because they lack characterization information, or because they don't have sufficient information for the needs of the designer.

RECOMMENDATIONS:

Materials Property and Design Databases:

- 1. Existing database systems need to be reviewed to ascertain whether we are really getting what we need from DOD and other databases.
- 2. Applications of recent breakthroughs in information theory and human intuition are required to define Army system requirements and consequential database information. An advanced gun tube or armor mandates an appropriate model. If reliable data are not available fuzzy logic methodology may exist, or be developed. This could guide R&D by modeling/extracting which path has the best chance for success.
- 3. New approaches are required for understanding, including first principle theories as well as empirical and semiempirical representations, how diverse physical and mechanical materials properties are interrelated.
- 4. More comprehensive high temperature/pressure databases are needed for specific advanced materials such as tantalum and tungsten. These can be used as a benchmark for other advanced materials.

Modeling and Simulation:

- 1. Property data is required for specific applications under actual conditions (large scale testing is necessary to validate research results).
- 2. An understanding is required for designs that interrelate the nano, meso, micro, macro structure scales with systems performance during service. This would permit the design of nanoarchitectures that control stress concentrations. Such an approach can provide significantly improved properties including processing non-equilibrium materials and nanomaterials into net shape components.

Processing:

- 1. There are rapid prototyping requirements for proofs of concept of advanced materials as well as their potential end product manufacturing routes (research prototyping).
- 2. Costs can be reduced by net shape and in-situ/intelligent processing of advanced materials.
- 3. Issues of reproducibility, and making materials cheaper and better, can be addressed by very detailed quality control and non-destructive characterization.

Important Properties:

- 1. The atomistics and thermochemical aspects of wear must be related to the specific conditions. Ordinary and high rate wear for specific applications are significantly different.
- 2. Joining/welding of new/novel materials to other materials/substrates can be a challenge especially when the joint may be another discrete material. Improved methods are required to nondestructively characterize joints, interfaces, and gradient materials.

- 3. The effect of cycles, or number of rounds, on wear is not completely understood. Many times cycling effects can be significantly different than monotonic temperature/pressure testing.
- 4. Large testbed success is generally required to convince senior decision makers that a viable candidate exists.

Summary:

It is clear that designing integrated materials systems requires project teams with appropriate skills (processing, modeling, design, simulation, lab and field testing). Such teams are necessary to test contending scenarios. Providing support for external research, which should be complementary to internal team efforts, can bring fresh perspectives and additional innovative solutions to complex problems. Advanced materials opportunities present major materials challenges. These, if solved, will provide significant improvements for mission capabilities as well as lead to civilian sector spin-offs.

WORKSHOP PROGRAM

HOT GAS EROSION AND WEAR OF MATERIALS

Sponsored by: The University of Michigan - Army Research Office at Webers Inn, Ann Arbor, Michigan

WEDNESDAY MORNING

SEPTEMBER 25, 1996
Robert Reeber, Army Research Office, Session Chair

| 7:30 a.m. | Registration and Continental Breakfast |
|------------|---|
| 8:50 a.m. | Opening Remarks — <u>John Bilello</u> , The University of Michigan, Co-Chair |
| 9:00 a.m. | Materials Design for the Army-after-Next Wear and Erosion in the 21 st Century — Robert Reeber, Army Research Office, Co-Chair |
| 9:30 a.m. | An Introduction to Interior Ballistics — Glenn P. O'Hara, Benet Labs |
| 10:00 a.m. | Discussion and Coffee Break |
| 10:45 a.m. | ARL Gun Tube Thermal Management and Erosion — Paul Conroy, ARL, Aberdeen Proving Ground |
| 11:25 a.m. | Formation of New Phases by Rapid Heating and Cooling in a Ballistic Compressor — John Dash, Portland State University |
| 12:00 p.m. | Lunch (catered) |
| | WEDNESDAY AFTERNOON SEPTEMBER 25, 1996 Carolyn Aita, University of Wisconsin (Milwaukee), Session Chair |
| 1:30 p.m. | Synthesis of Covalent Light-Element Coatings Using Novel Deposition Chemistry — John Kouvetakis, Arizona State University |
| 2:00 p.m. | Erosive Wear Coatings — <u>Larry Fehrenbacher</u> , Technology Assessment and Transfer, Inc. |
| 2:45 p.m. | Discussion and Coffee Break |
| 3:30 p.m. | Deposition of Protective Films on Structural Materials Using Laser Assisted |
| | Deposition Processes — Henry White, University of Missouri (Columbia) |
| 4:15 p.m. | Non-Equilibrium Synthesis by Laser for Tailored Surfaces — <u>Jyoti Mazumder</u> , University of Michigan |

THURSDAY MORNING

SEPTEMBER 26, 1996
Steve Yalisove, University of Michigan, Session Chair

| 7:30 a.m. | Registration and Continental Breakfast |
|------------|--|
| 9:00 a.m. | New Direction - Farther, Faster, Longer — Richard Kamakaris, Picatinny Arsenal |
| 9:30 a.m. | Plasma Synthesis of High Temperature Hard Ceramic Coatings — John Dash, Portland State University |
| 10:00 a.m. | Discussion and Coffee Break |
| 10:30 a.m. | Reactive Sputter Deposition: Engineering on an Atomic Scale — Carolyn Aita, University of Wisconsin (Milwaukee) |
| 11:15 a.m. | Novel Methods for Optimizing Performance in High Temperature Coatings Via Texture Control — Steve Yalisove, University of Michigan |
| 12:00 p.m. | Lunch (catered) |

THURSDAY AFTERNOON

SEPTEMBER 26, 1996

John Bilello, University of Michigan, Session Chair

| | ·· - - |
|-----------|---|
| 1:15 p.m. | Ion Beam Processing as an R & D Tool for Synthesizing Non-Equilibrium Alloys — <u>James Hirvonen</u> , ARL, Aberdeen Proving Ground |
| 1:55 p.m. | Mechanical Properties and Crystal Bonding — John Spence, Arizona State University |
| 2:35 p.m. | Dynamic High-Pressure Synthesis and Processing of Wear-Resistant and Refractory Materials — Naresh Thadhani, Georgia Tech |
| 3:15 p.m. | Discussion and Coffee Break |
| 3:45 p.m. | Mechanical Properties of Thin Films and Hard Coatings via Light Scattering — R. Sooryakumar, Ohio State University |
| 4:15 p.m. | The Joy of Stress — John Bilello, University of Michigan |
| 5:00 p.m. | POSTER SESSION (See Last Page for List) |
| 6:15 p.m. | Dinner (no host) |
| | |

FRIDAY MORNING SEPTEMBER 27, 1996

Robert Reeber, Army Research Office, Session Chair

7:30 a.m. Continental Breakfast

8:50 a.m. Panel Meetings - Critical Issues, Robert Reeber, ARO

<u>Panel #1 — NEAR TERM NEEDS & ISSUES</u>
<u>John Conrad</u>, University of Wisconsin (Madison), Panel Chair

Panel #2 — THE ARMY-AFTER-NEXT (2040 A.D.)

James McCauley, ARL, Aberdeen Proving Ground, Panel Chair

10:30 a.m. Discussion and Coffee Break

11:00 a.m. Panel Report Summaries, Robert Reeber, ARO

11:30 a.m. Critical Analysis & Summary

12:00 p.m. Lunch (no host)

2:00 p.m. Tour of the University of Michigan Materials Science & Engineering Department

3:30 p.m. Adjournment

POSTER SESSION ABSTRACTS

Innovative Concepts for Gun-Barrel Protection Based on Multilayer Coatings and Liner Casting Technology — Frank Kustas, Technology Assessment & Transfer, Inc.

Residual Stresses in Production Electrolytic Chromium Deposition — Sabrina Lee, Benet Laboratories

Thermal and Erosion Modeling of Gun/Ammunition Systems — Bert Pflegl, Benet Laboratories

Ion-Assisted Coatings for Enhancing Wear and Corrosion Resistance of Engineering Materials — Kumar Sridharan, University of Wisconsin (Madison)

High Temperature Thermal Expansion, Bulk Moduli and Self-Diffusion for Tantalum and Tungsten — Kai Wang, University of North Carolina (Chapel Hill)

REACTIVE SPUTTER DEPOSITION: ENGINEERING ON AN ATOMIC SCALE †

Carolyn Aita

University of Wisconsin Milwaukee, Wisconsin

Reactive sputter deposition is widely used to grow ceramic films at temperatures much below their fabrication temperature in bulk. In addition, it is used to produce metastable ceramic phases, and new artificial structures, including nanolaminates and nanocomposites. An understanding of the growth environment is essential for this deposition method to be used effectively, controllably, and reproducibly. However, the growth environment is complex, does not lend itself to even rudimentary in situ diagnostics, and has not historically been a topic of active study. The research we present here is a step towards remedying this situation. We have developed "phase maps" (process parameter-growth environment-film property relationships) for a number of binary oxide and nitride systems. Common features among these systems, as well as differences, are identified. Kinetic paths that lead to specific structures (e.g., amorphous versus crystalline growth, production of denser albeit metastable crystalline phases) are proposed in terms of reactions that occur at the sputtering target, within the plasma volume, and at the substrate. Lastly, in addition to serving as guides for other binary systems, we show how these maps can be used for prediction of structural and chemical order in ternary and higher systems.

[†] Supported under U.S. Army Research Office Grant Nos. DAAG-29-84-K-0126, DAAL-03-89-K-0022, and DAAH -4-93-G-0238.

THE JOY OF STRESS

John C. Bilello and Steven M. Yalisove

University of Michigan Ann Arbor, Michigan

Film growth doesn't have to be a stressful experience! Properly controlled residual deposition and/or growth stresses can be used as one of the system parameters which can be manipulated to enhance performance. Optimal internal stress control in monolithic, and in multilayer, films can be used to create new coating systems that otherwise would be completely unstable. It is also necessary to control the interface stresses between the coating and substrate since even the best coating system, in terms of surface properties, would be useless if it delaminated readily. Examples of stress optimization experiments will be given. This presentation will discuss advanced laser optical scattering methods as well as high-resolution, high-energy x-ray diffraction techniques for measuring, controlling, and manipulating residual stresses to improve old and to create novel coating systems.

ARL GUN TUBE THERMAL MANAGEMENT AND EROSION

Paul J. Conroy, G. E. Keller, P. Weinacht, and M. J. Nusca

US Army Research Laboratory Aberdeen Proving Ground, Maryland

Current tank gun ammunition for the M1A1 tank is being designed to maximize the kinetic energy of the projectile at launch. This direct fire requirement along with new extended range artillery requirement have reintroduced gun bore erosion as a significant design issue because erosion will limit the number of rounds that can be effectively and safely fired over the life of the gun tube. The present briefing includes the description of the ballistic environment, the interior ballistic modeling of the continuum mechanics, a history of ARL's work in thermal management, and ARL's current efforts in erosion modeling including a brief description of the ARL thermochemical erosion model for gun tubes. Preliminary results comparing a fielded kinetic energy tank round and a candidate next-generation tank round are presented. Historically, the currently fielded "solutions" did not result from or in identifying the fundamental cause of the erosion, and some discrepancies between the flame temperature correlations and the erosivity were never resolved. It is believed that significant additional work is required in the area of material interaction with gases to adequately describe erosion of the gun tube surface. Attempts to model erosion have been and are currently being made although the specific surface reactions, kinetics, and thermodynamics, are not well known under ballistic conditions. Fundamental computational non-continuum surface chemistry appears to be a tool which could closely describe the physics at the surface and provide input to a macroscopic chemical model. A tool of interest to validate the computational chemistry could be the ballistic compressor, which can reproduce the ballistic environment for a particular gas species interacting with a particular material.

FORMATION OF NEW PHASES BY RAPID HEATING AND COOLING IN A BALLISTIC COMPRESSOR

John Dash

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A free-piston type ballistic compressor capable of producing gases at temperatures as high as 6000 K and pressures as high as 3000 atmospheres for about one-half millisecond has been used to study effects on materials. These effects were studied with an atomic force microscope, scanning and transmission electron microscopes, and an energy dispersive spectrometer. The gases used were either pure argon, a mixture of argon and hydrogen, or pure hydrogen. The H-Ar mixture produced drastic changes in surface morphology and structure of pure iron foils. Particles about 50 nm long and 10 nm diameter were observed in the microstructure. A resonant N-p reaction was used to estimate the hydrogen content. This result and electron diffraction indicate that the particles are iron hydride.

Single crystal, body-centered cubic chromium thin films were exposed to pure hydrogen at about 1800°C and 550 atm. Second phase particles of hexagonal structure were observed to form. The surface chromium content of stainless steel was drastically reduced by exposure to hot, dense Ar, and a new phase was observed.

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EROSIVE WEAR COATINGS

Larry Fehrenbacher and Frank Kustas

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Erosive wear is a pervasive and continuing performance and maintenance dilemma for military systems ranging from gun barrels to helicopter blades to turbine and diesel engine parts. The complex interaction of impinging solid particles of varying physical and chemical characteristics in gaseous environments of different chemistries, velocities and temperatures has precluded the use of analytical models for the selection of materials with acceptable overhaul intervals. A large empirical database exists for both solid materials and traditional coatings (plasma spray) and surface treatments (gaseous diffusion and ion implantation) used to mitigate erosive wear. A review of the empirical relationships between hardness, microstructural characteristics and erosion behavior is given for several cermet and ceramic coatings and surface treatments. Dense multilayer ceramic/ceramic and ceramic/metal coatings appear to be excellent candidates for improved erosion resistance. Recommendations on fundamental research and exploratory development areas for multilayer wear coatings are preferred.

ION BEAM PROCESSING AS AN R & D TOOL FOR SYNTHESIZING NON-EQUILIBRIUM ALLOYS

James K. Hirvonen

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Energetic ion beam processing is a powerful, yet under-utilized research tool, for the controlled production of highly non-equilibrium (metastable, amorphous) near-surface alloys and coatings (both metals and ceramics). Several of these systems exhibit beneficially enhanced physical (friction, wear) and chemical (corrosion, oxidation) properties. The nonequilibrium nature of these surface alloys (and coatings) can often be attributed to the high quenching rates (> 10^{15} K/sec) within each ion cascade due to a) the ions ultra-short (< 10^{-12} s) stopping time and b) the locally high equivalent temperatures (> 10^3 K; ~ T_m) that ions produce as they displace lattice atoms coming to rest in the substrate. Individual cascades overlap at high ion doses to form continuous surface alloys whose composition(s) can be orders of magnitude different than equilibrium phases. In addition, the composition and morphologies of these surface alloys and coating can be controlled using direct ion implantation, ion beam mixing, or ion beam assisted deposition (IBAD). More recently, ion processing of surfaces using intense pulsed ions derived from plasmas has been employed to alter the surface composition and structure of metals and ceramics in a manner perceived to be more amenable for treatment of large areas. The status of employing ion beam techniques for basic studies of novel surface alloys will be reviewed and will indicate directions for future studies to eventually provide wear/erosion resistant surfaces

NEW DIRECTION - FARTHER, FASTER, LONGER

LTC Richard G. Kamakaris

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Crusader will be the indirect fire support system providing cannon artillery fires to the United States Army's maneuver forces on the battlefields of the next century. Crusader is the Army's flagship development effort and consists of two major combat vehicles: the 155mm Self-propelled Howitzer (SPH) and its Resupply Vehicle (RSV).

This presentation will consist of an overview of the Crusader system with emphasis on the requirements placed on the main armament system, the XM297E2 155mm cannon. The XM297E2 is being developed by Benet Labs, Watervliet Arsenal, New York and the Armaments Research, Development and Engineering Center (ARDEC) located at Picatinny Arsenal, New Jersey under contract to United Defense-Limited Partnership, Minneapolis, Minnesota, the Crusader prime contractor. Government oversight is the responsibility of the Project Manager Crusader with Product Manager Crusader Armaments responsible for the main armament, both also located at Picatinny Arsenal.

Specific topics will include the requirement for maximum range (40-50 km), maximum rate of fire (10-12 rounds per minute for 3-5 minutes), and sustained rate of fire (3-6 rounds per minute for 60 rounds). Impacts on tube wear life as a result of the Crusader System Operational Mode Summary/Mission Profile will be discussed as well as the design philosophy for the extended range cannon.

Also covered as a part of the presentation are the XM231/232 Modular Artillery Charge System (MACS) propellant and artillery projectile compatibility issues, both of which also contribute to system effectiveness.

SYNTHESIS OF COVALENT LIGHT-ELEMENT COATINGS USING NOVEL DEPOSITION CHEMISTRY

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We are involved in synthesis of new binary, ternary, and quaternary light-element covalent compounds that are potentially hard, strong, and refractory. The materials are primarily synthesized as thin films and coatings by chemical vapor deposition (CVD) of unimolecular precursors. High pressure techniques are also employed to produce dense threedimensional structures and compositions that are metastable. In this presentation we describe the development of a novel synthetic route to polymeric structures of two-dimensional C₃N₄. This method involves thermal decomposition of new molecular precursors such as (C₃N₃N) $X_2[M(CH_3)_3]_2$ (X = Cl,F; M = Sn,Si) via elimination of stable XM(CH₃)₃ species to produce thin films or bulk materials of composition C₃N₄ the highest nitrogen content observed in C-N solids. These materials are primarily sp² hybridized and are predicted to be suitable precursors of high pressure synthesis of tetrahedral C₃N₄. Compositions of C₃N₃B and C₃N₃P analogous to C₃N₄ are also being prepared by using similar precursor chemistries and deposition methods. The C₃N₃B and C₃N₃P systems are obtained by replacing N in the N(CN)3 carbon nitride network by B and P respectively. The B atoms are intended to enhance the stability of the material and the P atoms are expected to promote 3-dimensionality because of the propensity to form PN₄ tetrahedra. Finally we will report synthetic schemes and some preliminary results for preparation of new silicon carbon nitrides (Si₄CN₄) incorporating Si₄C building blocks joined together by nitrogens atoms as well as attempts to deposit (BN)_xCy three-dimensional systems. The ultimate goal of our newly established program is to explore a radically new approach to synthesize superhard thin films as well as to monitor and characterize the film growth process in situ and in real time.

NON-EQUILIBRIUM SYNTHESIS BY LASER FOR TAILORED SURFACES

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Rapid heating and cooling rate associated with laser processing provides a unique opportunity for non-equilibrium synthesis of materials which can provide compositions with extended solid solution. With proper selection of alloying elements and process parameters, materials with tailored properties can be synthesized. This paper discusses the theoretical basis for the mechanisms and the experimental approach for non-equilibrium synthesis of materials tailored for various applications such as wear, high temperature oxidation and corrosion resistance.

Non-equilibrium partitioning due to rapid solidification is explained based on the atom trapping theory. A mathematical model involving heat and mass transfer and non-equilibrium partition co-efficient is used to predict the non-equilibrium phase diagram and establish a relationship between the process parameters and the final alloy composition. Experimental procedure is discussed and the microstructure and properties of non-equilibrium alloys for various applications are described. Microstructure was characterized using various electron optical techniques, such as Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Auger Electron Spectroscopy (AES) and Energy Dispersive X-Ray Analysis (EDAX). Room temperature wear properties were characterized by a line contact Block on Cylinder method, high temperature wear tests were similar to simulated engine test. High temperature oxidation properties were characterized by using Perkin-Elmer Thermo-Gravimetric Analyzer (TGA) where dynamic weight changes were monitored at 1200°C. Corrosion properties were evaluated by a potentio-dynamic method using a computer controlled Potentiostat manufactured by EG&G.

PLASMA SYNTHESIS OF HIGH TEMPERATURE HARD CERAMIC COATINGS

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Highly adherent hard coatings of oxide ceramics for high temperature applications have been formed by an ion-energy-controlled, plasma-based method. Metal plasma produced by a filtered vacuum arc source is directed toward the substrate in the presence of the appropriate oxygen background pressure. For fabrication of multilayers and more complex multi-element film materials, plasma streams from two or more guns are merged together. The ion energy is controlled by repetitively pulse-biasing the substrate, providing a means to enhance adhesion between the substrate and the growing film (by ion mixing at the interface), as well as to modify the film microstructure (by ion assisted deposition).

Here we outline the plasma/ion beam technique and present some examples of films produced. Alumina films have been formed on iron aluminide substrates by using an aluminum plasma gun in oxygen. The as-deposited films, of thickness from 0.2 to 1.5 μ m, were amorphous, and transformed into α -Al₂O₃ after annealing at 1000°C. The film adhesion was typically greater than our instrumental limit of 70 MPa and high temperature (1000°C) cycling did not diminish the adhesion strength or film integrity. In another series of experiments, mullite films (3 Al₂O₃.2SiO₂) were deposited on SiC substrates using mixed plasma streams of aluminum and silicon. Highly adherent films with Al:Si ratio varying from 2:1 to 8:1 were produced, and the adhesion improved upon annealing at 1100°C. Other relevant examples of successful application of our plasma technique include the deposition of intermediate layers for bonding porcelain to Ti alloys, doped and undoped DLC, TiC, and multilayers of DLC and TiC/DLC.

AN INTRODUCTION TO INTERIOR BALLISTICS

Peter O'Hara

Benet Laboratories, Watervliet Arsenal Watervliet, New York

The analysis of guns and gunnery revolves around the study of ballistics, which is commonly divided into four subclassifications; Interior, Intermediate, Exterior and Terminal Ballistics. The problem starts with Interior Ballistics which is the analysis of the thermal-chemical-mechanical process by which projectiles are accelerated for zero to some high velocity in a launch device or gun. The analysis must include the combustion of individual propellant grains (gun powder), as a gas generation process which can build pressures up to 700 MPa (100,000 psi). These pressures accelerate projectiles to velocities in excess of 1200 m/sec in the space of a few meters. The interior ballistic process is extremely energetic and violent but must be kept in strict control to prevent the onset of shock waves or an accidental explosion. Because this is a combustion or defligration, the bulk gas temperature can exceed 3000°C, the resulting products are rich in energy and chemical species which produce an aggressive chemical soup for a few milliseconds. The analysis can proceed as a lumped parameter model or in a 1-, 2- or 3-dimensional framework. This presentation will outline the NOVA series of codes which integrates 13 parameters of the two-phase flow problem, in a 1-dimensional Finite Difference framework.

MATERIALS DESIGN FOR THE ARMY-AFTER-NEXT WEAR AND EROSION IN THE 21ST CENTURY

Robert R. Reeber

US Army Research Office Research Triangle Park, North Carolina

The Army-after-Next will require improved durability and reliability for its systems. Soldiers in the field will face new, as yet unknown, threats and will benefit from as yet discovered scientific advances A principal objective of this workshop is to lay out a roadmap of possible directions for Army-funded research which in the short term have a high likelihood for impacting these longer term needs. The purpose of this talk is to give a perspective on current trends, foreseeable needs, and program constraints as these relate to the synthesis and application of new high temperature capable superhard/superstrong materials.

MECHANICAL PROPERTIES OF THIN FILMS AND HARD COATINGS VIA LIGHT SCATTERING

R. Sooryakumar

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Measurement of the elastic properties of films thinner than a few microns poses serious experimental difficulties because their dimensions are far smaller than wavelengths generated with ultrasonic techniques. Other techniques such as vibrating reed, torsional measurements and bulge tester are destructive since they generally involve removal of the film from the substrate and then subjecting the free standing layer to some macroscopic deformation from which elastic properties are deduced.

Brillouin light scattering has turned out to be a powerful technique in the study of elastic properties of solids and laminar systems. An advantage of such a method is that it probes acoustic excitations whose wavelengths are comparable to typical thin film thicknesses or modulation wavelengths of superlattices, and is hence ideally suited to the study of regions where interesting fundamental phenomena might be expected. The development of the multipass tandem spectrometer some years ago allows the technique to produce detailed spectra even for opaque materials such as metals.

We will provide examples of the use of this method to probe the mechanical properties of thin film structures. Preliminary results from supported diamond-like-carbon films and transition metal coatings will be discussed that include dispersion of the principal surface phonon, wave vector dependence of the mode velocities, and estimates of the elastic constants.

MECHANICAL PROPERTIES AND CRYSTAL BONDING

John C. Spence

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Strong refractory materials are those with a high bond energy per unit volume, and high melting point - they thus contain the highest density of directed bonds. Short, covalent bonds in light atoms satisfy these conditions best. To prevent fracture, a high dislocation velocity might be needed at high temperatures. We have developed both theoretical and experimental techniques to study this complex relationship between bonding and properties. Our experimental methods are based on convergent beam electron diffraction (CBED) in TEM for the measurement of crystal charge density distributions. We match calculated and experimental energy-filtered transmission electron diffraction patterns obtained using a 50 nm diameter, 100 kV electron probe. All multiple scattering effects are included and structure factors refined. Our theoretical work is based on ab-initio quantum molecular dynamics in the local density approximation. Recent results include:

- 1. An explanation for the increased ductility of gamma TiAl with Mn doping at low temperature. CBED measurements for doped and undoped crystals showed decreased covalency as Mn was added, reducing brittleness as the Ti bonds become less directional due to the Mn.
- 2. An explanation in terms of electronic band structure for the effect of impurities on the ideal strength of diamond, silicon and germanium.
- 3. The most accurate charge density map yet obtained for MgO, showing the distribution of the Mg 3s bonding electrons. These results have been used to distinguish state-of-the-art electronic structure computations.
- 4. A new index of bond strength is proposed, based on changes in the mean inner electrostatic potential Vo, which provides a measure of atomic size and shrinkage in the bulk. We also suggest that whereas the band structure energy (involving valence electrons) controls shear and ductility, the longer range coulomb forces are most important for fracture.
- 5. The first accurate ab-initio computation of the fracture stress of a crystal and of the dislocation kink mobility barrier (PRL 74, p.3392 (1995)).
- 6. To obtain charge density maps in acentric crystals, a solution to the phase problem is needed. We have described such a solution and applied it to BeO. Structure factors measured by electron and X-ray diffraction are compared.

Taken together, these results suggest the possibility of predicting the mechanical properties of new materials of known structure. They also provide conceptual guidelines for the design of new materials with wanted properties.

DYNAMIC HIGH-PRESSURE SYNTHESIS AND PROCESSING OF WEAR-RESISTANT AND REFRACTORY MATERIALS

Naresh N. Thadhani

Georgia Institute of Technology Atlanta, Georgia

High-pressure shock-compression of materials produces a unique state of dynamic deformation, not possible by any other loading method. A process occurring under such conditions, can cause (a) phase transformations and chemical reactions occurring during the high-pressure state leading to the formation of metastable phases and compounds, (b) fusion between individual particles of powders producing a highly-activated dense-packed compact, and (c) welding of solid (or porous) substrate clads of dissimilar materials which may not be possible by conventional joining processes. In this talk, a brief overview of these processes will be presented.

The application of shock-induced reaction and transformation processes will be described based on our work on synthesis of the theoretically-predicted carbon nitrides and the B1-type cubic phase of tantalum nitride. Processes of dynamic consolidation of powders of superhard materials including diamond and silicon nitride, and welding of dissimilar solid-solid and powder-solid substrates of wear-resistant and refractory materials, will also be described. The emphasis of the presentation will be on the current understanding of the mechanistic aspects of the individual processes and their correlation with characteristics of the synthesized and processed materials having properties and applications of possible interest and relevance to DoD needs.

DEPOSITION OF PROTECTIVE FILMS ON STRUCTURAL MATERIALS USING LASER ASSISTED DEPOSITION PROCESSES

Henry W. White, S. Zhu, J.E. Chamberlain and F. S. Pour

University of Missouri Columbia, Missouri

The major objective of our work is to grow adherent, protective films on structural metals and alloys. Our primary goals are to synthesize, characterize, and model new and novel materials and film systems from the lighter elements, such as C, B, N, and Be. While some of our initial work has been done on diamond-like materials, it is our ultimate goal to synthesis materials other than polycrystalline diamond and c-BN. We report here the results from two basic deposition techniques. The first technique uses a highly focused beam from a pulsed infrared laser to ionize a gaseous atmosphere (e.g., methane and hydrogen, or simply nitrogen) in the presence of a receiving substrate. Ion densities of 1019/cm3 can be attained. A separate target (e.g., carbon, aluminum, iron) may also be employed for some applications. Two advantages of this process are that (i) films can be deposited at very high rates at ambient conditions, and (ii) non-equilibrium type films can be synthesized. In the second technique, a microwave enhanced CVD system has been used to grow diamond-like films on steel without the use of any diamond seeding step. Films have also been grown by introduction of infrared laser pulses into the growth plasma to modify ionization ratios. Initial work demonstrates that introduction of the laser beam into a methane hydrogen plasma creates changes in the film surface that are clearly visible. Future work includes use of a fast, gated emission spectroscopy to characterize the growth plasmas, the use of a neural net algorithm to relate film properties and growth conditions, and the modeling of film properties using molecular simulation techniques.

NOVEL METHODS FOR OPTIMIZING PERFORMANCE IN HIGH TEMPERATURE COATINGS VIA TEXTURE CONTROL

Steven M. Yalisove and John C. Bilello

University of Michigan Ann Arbor, Michigan

Coating performance in a high pressure-high temperature corrosive gaseous environment can be optimized if the microstructure and macrostructure of the coating can be tailored for the specific application. The basis for this control in sputter deposited coatings has been the zone models for the last decade. Work will be presented which goes far beyond the zone models and explains, from an atomistic viewpoint, the reason for microstructural evolution of refractory metal coatings. The ability to produce the desired stress in coatings which were deposited at low temperatures and have high degrees of texture can now be realized. Methodologies for producing high strength, high toughness coatings with strong textural character will be described along with an atomistic model which elucidates a physical understanding of the process. The ability to control the microstructure is mirrored with the ability to control the residual stress using these techniques. A short summary of our efforts to marry these effects will be included.

POSTER SESSION ABSTRACTS

for the

THE UNIVERSITY OF MICHIGAN

AND

ARMY RESEARCH OFFICE

Workshop on:

Hot Gas Erosion & Wear of Materials

INNOVATIVE CONCEPTS FOR GUN-BARREL PROTECTION BASED ON MULTILAYER COATINGS AND LINER CASTING TECHNOLOGY

Frank Kustas and Larry Fehrenbacher

Technology Assessment & Transfer, Inc. Annapolis, Maryland

Development of revolutionary new technologies, for protection of internal surfaces of gun barrels, is critically needed for the next generation of armaments. Higher muzzle velocities, alternate propellants, higher pressures, and higher temperatures will be needed to satisfy future system requirements. Design of alternate materials and fabrication methods will require a review of material property requirements, followed by detailed analytical modeling that considers thermodynamic properties (for prediction of corrosion, oxidation and hot-gas resistance), physical properties (for prediction of thermal shock and thermal stress resistance) and mechanical properties (for prediction of abrasive wear resistance). Functional gradient materials (FGM) offer a method to mitigate differences in thermal expansion between metals and ceramics; design of FGM is currently being employed for thermal barrier coatings and the same methodology can be leveraged for coatings to reduce gun barrel erosion. A functional gradient with a higher metal content near the barrel surface and higher hardness ceramic content near the erosion surface will offer a compatible coating that is resistant to the gun barrel environment. This type of coating can be fabricated by physical vapor deposition (PVD) of discrete multilayers by magnetron sputtering. Employing unbalanced magnetron sputtering results in the fabrication of very high-density films with improved mechanical properties and adhesion compared to normal sputtered films. Thin (2 - 5mm) magnetron-sputtered carbide/metal coatings have demonstrated superior properties compared to much thicker production Cr electroplate. New coating fabrication methods, such as movement of an internal post or cylindrical magnetron within the gun barrel (which acts as the vacuum chamber and a node) will be required to produce uniform coating on the inside of the barrel. New methods of sputtering target usage will be required for fabrication of internal radius multilayers. Concepts such as consecutive sputtering targets or split targets will be needed.

RESIDUAL STRESSES IN PRODUCTION ELECTROLYTIC CHROMIUM DEPOSITION

Sabrina L. Lee

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Enduring the high pressure and high temperature chemical environment of the bore of a gun tube during operation, aqueous electrolytic chromium has thus far survived as the chosen metal for wear and erosion protection of the bore. This is because it possesses many excellent properties such as high hardness, erosion and corrosion resistance, and low coefficient of friction. However, electrolytically-deposited high contraction chromium has problems because of the inherent cracks generated during deposition. Improved low contraction chromium has fewer cracks, but these cracks grow and new cracks develop during operation. These cracks allow the propellent gases to penetrate the coating and expose the base metal causing failure of the component. Excellent work has been performed to optimize chromium electrolytic deposition parameters by hardness, ultimate tensile strength and cathode current efficiency measurements, but residual stresses in electrolytic chromium deposition on A723 steel have not been characterized.

Our recent x-ray investigation indicates strong (111) fiber texture and almost perfect inplane azimuthal symmetry in high contraction chromium, and near random crystalline orientation in low contraction chromium. In addition, high level of tensile residual stresses were observed. Two approaches were taken for residual stress evaluation in highly textured cubic crystals: 1) A Matlab matrix inversion method to solve for residual stress and unstrained lattice parameter using a single family of reflections. This method is applicable to fiber-textured or epitaxial coatings with cubic crystalline structure; 2) assuming Hill-Neerfeld isotropic elastic models, a modified sin²Ψ method was adapted to multiple families of reflections. The two methods yielded similar residual stress levels due to the relative low anisotropy factor in chromium.

Relaxation of residual stresses in wear and erosion coatings cause cracking, buckling, peeling of the coatings and debond from the substrate. Continued research efforts in residual stress distribution analysis, correlation with observed microstructure, and optimization of deposition parameters and deposition processes contribute to the advancement of future coating technology. The techniques are applicable to aqueous electrolytic deposition, cylindrical magnetron sputtering deposition and plasma spray processing of chromium and other refractory coatings, alloys and ceramics.

THERMAL & EROSION MODELING OF GUN/AMMUNITION SYSTEMS

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and

Dr. Stuart Dunn and Dr. Douglas Coats

Software & Engineering Associates
Carson City, Nevada

The Thermal & Erosion Modeling technology base program at Benet Laboratories has generated a finite difference based computer code for the prediction of temperatures within a gun barrel due to its firing history. The program has also investigated the performance of standard instrumentation used for thermal data collection. Using the results of interior ballistics models as input, this code has repeatedly demonstrated accuracies on the order of 1 degree centigrade. This model is useful for predicting the heat build up in gun barrels and calculating the thermo-mechanical performance of gun barrels subject to the heat and pressure loading of the launching charge.

Working together with Software & Engineering Associates, which has extensive experience in modeling nose tip and rocket nozzle erosion in the rocket industry, the team has created a unified computer model for predicting the thermo-chemical erosion in gun barrels. This program has shown reasonable accuracy in predicting bore surface regression in limited comparisons with test data. The code is capable of calculating heat energy transferred at the bore surface and the series of chemical reactions occurring at the gas-metal interface. The calculation of the boundary layer performance includes the effects of mass addition due to thermo-chemical and thermo-mechanical ablation.

Future work, including the effort to adequately predict and model the effects of through cracks in the bore surface coatings, will be discussed. This work should be of interest and substantial benefit to those interested in high temperature/ pressure/chemistry gun tube erosion problems and those seeking to address material performance in this environment.

ION-ASSISTED COATINGS FOR ENHANCING WEAR AND CORROSION RESISTANCE OF ENGINEERING MATERIALS[†]

Kumar Sridharan, J.R. Conrad, R. Breun, M.M. Shamim, R.P. Fetherston, and A. Chen

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Plasma Source Ion Implantation (PSII) is a non-line-of-sight, cluster-compatible ion surface modification technique that has been shown to improve wear and corrosion resistance of materials. In the implantation mode high energy ions are implanted into the near surface regions of the part causing chemical and microstructural change that lead to hardening of the part's surface. In the plasma-assisted deposition mode, overlay coatings such as diamond-like carbon (DLC) and titanium nitride can be deposited with interface mixing to promote coating adhesion. The presentation will cover these issues with specific examples and discuss commercialization efforts. Research initiatives to apply the process as an environmentally clean alternative to wet chemical bath electroplating procedures will be presented.

[†] The work is partially supported by the U.S. Army Research Office Grant No. DAAH 04-94-G-0238.

HIGH TEMPERATURE THERMAL EXPANSION, BULK MODULI AND SELF-DIFFUSION FOR TANTALUM AND TUNGSTEN

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Tantalum and tungsten are two of the refractory bcc metals. Their thermal expansion, bulk modulus and self-diffusion at high temperatures are important physical properties. Based on an empirical $cB\Omega$ -model, Varotsos and his coworkers have related self-diffusion with other bulk thermodynamic properties. They calculated self-diffusion coefficients for several bcc metals: Na, Li, I. W, and Nb. It has been shown that the bulk modulus B_T at any temperature can be related to the diffusion coefficient as

$$B_{r} = -B_{T}^{o} \exp \left(-\int_{o}^{T} \alpha dT\right) \ln \left(\frac{D}{D_{o}}\right) \frac{kT}{h_{act}}$$

therefore,

$$B_g - B_T \left(1 - B_T \frac{\alpha^2 VT}{C_P} \right)^{-1}$$

Here α is the coefficient of thermal expansion, C_P the specific heat, B_r^o the linear extrapolation of B_T to zero temperature, h_{act} the activation enthalpy, and V the molar volume. When data for thermal expansion and specific heat are available, the bulk modulus at any temperature can be estimated. Falter and Zierau applied this method to K and W. They found strong correlations between thermoelastic and diffusion behavior and were able to calculate the bulk modulus of W from diffusion, thermal expansion, and specific heat data. Since then, improved thermal expansion and specific heat data for W at high temperatures have been measured and modeled. With this information we have recalculated the high temperature bulk modulus for tungsten and compared the results with previous work. Our estimate of the adiabatic bulk modulus as a function of temperature is about 8% higher than earlier results at the highest temperature. Diffusion data over a limited temperature range are also utilized to calculate the bulk modulus of tantalum. Its thermoelastic and diffusional behavior are closely related. Utilizing available thermoelastic data, the relationships allow the calculation of tantalum self-diffusion coefficients over a broad temperature range.

APPENDIX

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