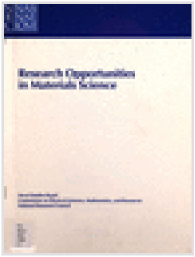

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RESEARCH OPPORTUNITIES

IN MATERIALS SCIENCE

Panel on Research Opportunities
in Materials Science
Naval Studies Board
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and Resources
National Research Council

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PANEL ON RESEARCH OPPORTUNITIES IN MATERIALS SCIENCE

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PREFACE

The Panel on Research Opportunities in Materials Science was established by the Naval Studies Board in response to a request from the Office of Naval Research (ONR). That request called for the establishment of a series of panels representing the scientific disciplines for which the ONR has support responsibility, each with the specific assignment of assisting the ONR to identify promising research initiatives for future consideration. The materials panel met on August 17 and 18, 1987, to carry out its part of that overall assignment.

Throughout its deliberations the panel members were keenly aware of the Navy's unique dependence upon materials science. No other Service nor institution that comes to mind matches the United States Navy and its Marine Corps in the range of environmental and operational conditions under which its materials must function with ever-increasing effectiveness. We have but to contemplate the pressure range from synchronous orbit to the Marianas Trench, the temperature range for the superconductivity of old to a nuclear fireball, the speed range from a SOSUS array through near-gravitational escape to a laser pulse, and the construction range for a microchip to an aircraft carrier. Of the vast array of materials types and characteristics thus implied, the panel concentrated its attention on areas that are both pertinent to the ONR materials program goals, as presented by the Materials Science Division, and within the fields of expertise of the panel members.

The panel wishes to express its gratitude to the ONR and Naval Research Laboratory (NRL) representatives for their informative briefings and illuminating discussion. It also wishes to compliment each organization and laboratory on a well-conceived and well-organized program of very high quality research in materials science. And finally, as representatives of the materials community, we wish to recognize, with appreciation, the leadership role the ONR has played in supporting and encouraging university research in this area. We hope that the suggestions in this report will prove helpful in maintaining the current level of excellence.

John B. Wachtman, Jr., Chairman
Panel on Research Opportunities
in Materials Science

SUMMARY

In the introduction, which follows this section, the panel has offered a few "institutional" suggestions that it believes will further strengthen an already admirable research program. Under "Recommended Areas of Opportunity," the panel has presented the findings that resulted from its specific task; that is, to identify new research opportunities that it believes the ONR should seriously consider in shaping its future research program in materials science. Those areas in which the panel has made specific suggestions are the following:

1. Structural Composites Involving Fibers and Whiskers
2. Nanocomposites
3. Intermetallics
4. Electronic Materials
    - Ferroelectric Studies
    - Dielectric Ceramics
    - Piezoelectric Materials
    - Pyroelectrics
5. Electro-Optical and Magneto-Optical Materials
    - Bulk Crystal Growth
    - Thin-Film Growth
    - Multilayer Structures and Artificial Crystals
    - Magneto-Optical Materials
6. High-Temperature Ceramic Superconductors
7. Microstructure, Process, and Property Modeling, with Computer Assistance
8. Chemical Synthesis of Microscale Materials
9. Protective Films/Corrosion Science

INTRODUCTION

In virtually every field of technological endeavor from antisubmarine warfare to hypersonic flight and advanced communications, the rate-controlling step in development of new technology is the discovery, or synthesis, of materials that are capable of performing effectively under the imposed conditions of service. Fundamental to the surmounting of these materials barriers are the basic research programs of major funding agencies such as the Office of Naval Research (ONR).

According to the basic research (also known as 6.1) resource distribution documents available to the Panel on Research Opportunities in Materials Science, the major thrust (60 to 65 percent of budget) of all research programs of the ONR is "long-term research to advance the state of knowledge across the spectrum of disciplines relevant to long-term Navy needs." A second thrust (20 to 25 percent of budget) involves research on specific applications having the potential for early use by the Navy, while a smaller thrust (15 percent of budget) focuses on long-term, high-risk, high (potential) payoff projects. Materials research (under the Materials Science Division) represents a total of approximately 9 percent of the $350.8M total budget for FY 1988. Additional materials-related research is included in other "subelements," notably physics, electronics, mechanics, and chemistry. Although the panel did not review the contributions of these subelements, it would be helpful to future review panels to have a more unified view of the total ONR materials effort, as the field of materials is so highly interdisciplinary. Without such information, it is difficult to assess the degree of "coverage," coordination, and coupling among the various subelements having an interest in materials.

The quality of staff in the Materials Science Division (MSD) is extraordinarily high. The leadership of the director is clearly evident, and the program managers are innovative, energetic, and technically very sound. As indicated above, other divisions at ONR support some aspects of materials research, for example, the Chemistry, Physics, Mechanics, and Electronics Divisions. It is to the credit of the MSD staff that they are aware of these other activities and work with the staffs of other divisions to support exciting multidisciplinary research through the Accelerated Research Initiatives.

The presentations by the individual program directors were impressive, and individual programs show evidence of strong leadership and guidance. However, the extensive approval structure and review process employed by the Navy has the potential for overmanagement, which could reduce the freedom and productivity of individual program managers in initiating and monitoring research programs (a traditional strength of ONR program managers).

The panel is concerned that separation of activities now included in the Applied Research Program (ARP) from the major program areas of the MSD may have resulted in loss of coordination and effectiveness. Thus it recommends that consideration be given to merging the elements of the ARP with the appropriate basic programs from which they originally emerged to provide closer coordination while assuring effective utilization of new materials discoveries.

To make the output of research more readily accessible, and to avoid repetition, every reasonable effort should be made to capture research data in computer-accessible form. Maximum effectiveness requires care in the design of data-collecting documents. Interaction with database experts at the National Bureau of Standards could simplify the design of such documents. The availability of more complete computerized databases will do much to facilitate mathematical modeling and the development of expert systems for materials selection and processing.

Present programs include financial support of summer students, postdoctoral fellows, IPA appointees, and visiting scientists. The panel urges continuation and extension of these programs as budgets permit.

RECOMMENDED AREAS OF OPPORTUNITY

STRUCTURAL COMPOSITES INVOLVING FIBERS AND WHISKERS

The potential for structural composites has long been recognized, and the Department of Defense has been a leader in their development. The potential for still further progress is great and justifies continuing efforts. Present and anticipated advantages of structural composites include high stiffness-to-weight, high strength-to-weight, high-temperature capability, good corrosion resistance, special electromagnetic properties, and the ability to tailor combinations of properties to meet special requirements.

The increasing demands of military systems necessitate that engineered structural materials in the form of fiber-reinforced and particulate-reinforced composites be developed to meet the stringent operational requirements. Basic studies are needed in many areas for better understanding of composites in terms of microstructure, micromechanics, and the processing variables needed to optimize properties.

Research should be directed to all major composite systems:

- metal matrix;
- ceramic matrix;
- polymer matrix (especially thick section); and
- carbon-carbon.

Key issues include understanding how wetting influences the characteristics of the fiber-to-matrix interface, which in turn affects mechanical properties such as toughness and strength, corrosion mechanisms (both aqueous and high-temperature), as well as protective coatings, and processing control to improve reliability and reproducibility.

There are problems with the use of structural composites that vary in degree of seriousness with the type of composite and the type of application. Generic problem areas include special fracture modes, property deterioration in service, problems with joining and with openings, control of quality in processing and resulting reliability in service, and cost.

Although the past Navy composites program, taken in conjunction with other government-supported programs on structural composites, is sound, there are opportunities to move more rapidly toward achieving the potential of structural composites and solving some of the associated problems. Interface control is a key area. Coatings can be used to reduce damaging chemical reactions and to adjust the fiber-to-matrix bond strength to optimum values. Techniques such as chemical vapor deposition (CVD) need to be combined with modern instrumental characterization techniques in specific fiber-to-matrix systems to study and develop optimum combinations.

An associated area of opportunity is that of making an entire composite by chemical synthesis techniques. The potential exists for producing shaped composite parts. One approach would involve the use of a mold within which the composite would be grown in a series of steps. Fibers or whiskers could be grown first from the vapor by a catalyzed growth process. Single-layer or multilayer coatings could next be applied by a CVD process. Finally, the matrix could be added by a CVD infiltration process or by simple fluid infiltration.

Nondestructive evaluation (NDE) of composites continues as both a partially solved problem and an opportunity. Modern computer-aided analysis and control techniques make it possible to analyze in great detail the response of a composite to NDE interrogation (acoustic, electromagnetic, etc.). A new dimension is added by the recent introduction of artificial intelligence approaches. Thus an extremely detailed "signature" can be recorded, analyzed, and used to control complex processing parameters. This procedure offers promise for control in processing and assessment of deterioration in service.

Another need and corresponding opportunity is that of developing an integrated process of design with composites in parallel with research on development of the composites themselves. Such new composites may offer not only new advantages but new limitations. An example is the emerging class of ceramic matrix composites intended for structural use above 1000°C. An argument for their development is their presumed ability to survive a momentary overload that takes them into a matrix-cracked condition. This argument presumes that the cracked composite will survive under the normal design load long enough for service and replacement. However, a cracked composite is subject to greater oxidation and other chemical attack. What is needed in response is a program coupling experimental work on postdamage deterioration with design-for-service so that rational goals can be set for performance of a composite material.

In addition, more attention should be given to hierarchical levels of composite synthesis to include both the molecular-scale and the macroscale for polymer-matrix composites. The principal objective would be to develop molecular-scale reinforcement in liquid crystal polymers as a means of improving transverse and through-thickness properties, joints, and transition sections. Further, greater attention should be given to through-section property variations in thick-section composite structures, especially in advanced polyamide and LCP matrices.

NANOCOMPOSITES

These materials offer an ability to prepare desired blends of material properties having special additional property benefits resulting from the ultrafine microstructures produced. In electronic applications, the nanoscale of the substructure can result in major modification of the properties of the individual component phases. Examples are the modification of stable ferroelectricity to super paraelectric behavior in dielectrics and the extensive flux pinning by phase boundaries in superconducting ceramics. Strength and toughness are improved for most materials at relatively low temperatures because of reduced lengths for slip, twinning, and crystallographic cracking mechanisms within the microconstituent phases. On the one hand, processing or fabrication of such materials is easier at relatively high temperatures because of diffusion-enhanced grain boundary plasticity and sintering mechanisms. This is particularly true of superplastic deformation behavior at appropriate temperatures and deformation rates. On the other hand, low-temperature vapor deposition of thin film and, also, sol-gel techniques appear ideally suited to the fabrication of electronic ceramics whose properties should be intimately connected with the thermal histories as well.

The advantages (or disadvantages) of amorphous versus nanocrystalline composite properties are important to investigate and assess. Relevant issues include material stability and the dependence of any particular property on crystallinity of the material. The reduction or local enhancement of chemical heterogeneity, say, relating to internal friction and corrosion behaviors, is important. Surface and interface properties of such materials require examination by advanced techniques, including scanning tunneling microscopy. Important new concepts from clustering theory, relating to subcapillarity effects, should be incorporated within the research program.

INTERMETALLICS

Indications are that the semibrittleness of intermetallic compounds will be overcome by new processing techniques such as rapid solidification, dynamic compaction, and improved powder metallurgy methods. These techniques provide for consolidating dense, near-net shapes. Of particular interest for airframe and engine applications are the titanium aluminides and niobium aluminides. These materials have a high strength-to-weight ratio, can readily serve as the matrix for fiber composite reinforcement, and have very good high-temperature oxidation resistance provided the aluminum content is sufficiently high that adherent Al_2O_3 scales form during oxidation.

Research on the mechanisms of plastic flow and ductility improvement, processing optimization, and alloying will assist in establishing a basic understanding of the properties achievable for these materials. Fundamental work is needed on partial dislocation structures, dislocation pile-ups, twinning behavior, and grain boundary properties, with or without solute alloying additions.

ELECTRONIC MATERIALS

The Materials Science Division at the ONR has been responsible for major advances in high band gap insulated ceramic materials used in dielectric, piezoelectric, pyroelectric, and electro-optic applications. Fundamental to most of these applications are the multiaxial ferroelectrics in the perovskite and tungsten-bronze structure families.

<u>Ferroelectric Studies</u>: Current work on both dielectric and piezoelectric applications highlights the role of reversible ferroelectric domain motions in enhancing properties in polycrystal ceramics.

New theoretical and experimental work is needed on improper ferroelectric walls to explore possible dyadon (elementary excitation of a ferroelastic domain wall) contributions to dielectric, elastic, and piezoelectric response as a function of domain size in both ferroelectric and antiferroelectric crystals.

Models for relaxor ferroelectrics have progressed to the level where it should be possible to predict limits for dielectric and electrostrictive properties and to develop composition systems to explore these limits.

Experimental work is needed to test predictions of possible ferroelectricity in ABF_3 perovskites.

Dielectric Ceramics: Rapid evolution toward thin-film structures suggests the need for new materials (possibly antiferroelectrics) with much reduced saturation at high electric fields ($E \sim 10^4$ to 10^5 V/cm). This need is coupled to the requirement for low processing temperatures needed in fabricating film structures and for integrated multicomponent approaches for ceramic packaging of semiconductor integrated circuits (ICs). New ceramics with metallic conduction offer the possibility of all-ceramic multilayer capacitors (MLCs) for dielectric and electrostrictive applications. Payoffs from the basic work would be ultraminiature MLCs, capacitors that could be integrated into IC packages and eventually deposited directly onto silicon and gallium arsenide.

Piezoelectric Material: Extension of phenomenological analysis applied to lead-zirconium-titanate (PZT) could facilitate separation of intrinsic and domain contributions in lead-lanthanum-zirconium-titanate (PLZT) piezoelectric and relaxor ferroelectric compositions. New theoretical and experimental work on electrostriction is needed. For composite transducers, design rules for transmitter structures need to be formulated. Electrostrictors have demonstrated zero aging, and biased operation in MLC configuration could provide high-stability transducers for Navy use. Taken with the better understanding of domain wall contributions, these approaches could lead to high coupling (>95 percent), more stable transducers, and large area senders for active sonar at low frequency.

Pyroelectrics: Sharp transition (first order) ferroelectric perovskites with T_c near room temperature are required for solid state thermal imaging systems. Nanocomposites offer the possibility of separating pyroelectric and piezoelectric responses. Thin films will be required in these point, line, and area detectors. These studies would facilitate the development of high-sensitivity, high-resolution, solid state images for thermal radiation.

Electronic Polymers: In addition, particular attention should be given to identifying directions for exploiting new understanding of conduction mechanisms in electronic polymers. The work of Professor Alan Heger and his colleagues at the University of California at Santa Barbara explaining electrical conductivity exceeding that of copper along aligned macromolecular structures deserves focused attention.

ELECTRO-OPTICAL AND MAGNETO-OPTICAL MATERIALS

The ONR program in electroceramics should be expanded into the area of electro-optics, where there are a number of potential Navy applications. Both bulk single-crystal research and epitaxial thin-film synthesis are required to take full advantage of electroactive materials in optics. Because of problems related to light scattering at grain boundaries and crystalline imperfections, crystals of higher structural quality and compositional control are required than are generally needed for dielectric, pyroelectric, and piezoelectric applications.

Bulk Crystal Growth: A number of crystalline materials having high electro-optical properties are now known. Many of them fall into perovskite and tungsten-bronze structural classes. The optical quality of bulk single crystals is generally quite poor, or single crystals may not even be currently available. Research to improve crystal quality by fundamental studies of the growth process, the liquid-solid interface shape, impurity segregation, and stoichiometry control are likely to result in improved crystals that permit utilization of the electro-optic properties in devices. Bulk single crystals of these or related materials will also be useful as substrate materials for the epitaxial growth of thin films.

Thin-Film Growth: Techniques developed for the growth of semiconductor materials and multilayer structures such as molecular beam epitaxy, metal-organic chemical vapor deposition, and atomic layer epitaxy have not yet been used to advantage for the growth of oxides or other wide-gap electro-optical materials. Such research will also have an impact on the growth of superconducting films, and insulating films for semiconductor processing (i.e., encapsulants, diffusion masks, and passivation layers).

Thin-film deposition techniques can be used to integrate optical and electronic devices. Deposition onto silicon and gallium arsenide is a particularly interesting challenge from this point of view. In many instances, low-temperature deposition will be desirable (<500°C), so that photon-assisted, plasma-assisted, or other deposition enhancement techniques should be studied.

From the scientific standpoint, epitaxial growth of electro-optical materials should include studies of interface formation, nucleation, and the growth of layers on lattice mismatched substrates. In-situ characterization techniques developed by the semiconductor industry are already available and are, in general, readily applied to oxides.

Multilayer Structures and Artificial Crystals: Some of the property enhancements demonstrated in composite structures can be designed directly into thin-film multilayer structures during epitaxial growth. Once epitaxial single-crystal growth is achieved, then compositionally modulated structures on a nanoscale can be fabricated to achieve specific material parameters. By reducing the scale of composition modulation to unit cell scale (as, for example, in the germanium-silicon system), completely new crystalline properties not found in materials from the melt or from solution can be expected.

A number of vapor-deposited compositionally modulated alloy systems (e.g., copper-nickel, gold-nickel, copper-palladium, and silver-palladium) exhibit a strange elastic characteristic. The biaxial modulus plotted against the wavelength of layered copper-nickel specimens is determined from a miniature bulge test and is found to peak sharply at a wavelength of about 20 angstroms. This "supermodulus effect" represents a phenomenal increase in stiffness, amounting to a factor of 2 to 4 over that of a homogeneous copper-nickel alloy, and indicates that a significant change compared to stiffness in bulk materials has taken place. As yet, we have no generally satisfactory theory for this unexpected enhancement in stiffness.

Magneto-Optical Materials: An exciting research and development area for magnetic alloys lies in the magneto-optical recording of information. Vacuum-deposited amorphous films of rare-earth/transition-metal alloys, such as GdCo, TbFe, GdTbFe, and GdTbCo, have the property of switching the direction of magnetization on a very fine scale, under the influence of a weak external field, when heated locally to 100° to 200°C by a pulsed laser-beam signal. After the beam is removed, the reversed domains persist because of hysteresis, and so the recorded bits are "stored" for subsequent reading by magneto-optical (Kerr polarization rotation) effects. This application is expected to be in wide commercial service soon; it has the advantage of high bit density, noncontact recording and reading, and selective erasability by laser-beam heating in an oppositely biased external field.

The opportunities for creative metallurgical research on these thin-film amorphous alloy systems are immense--e.g., deposition techniques, compositional control, microstructural uniformity, amorphous-state stability and aging effects, corrosion mechanisms and protection, and new alloy chemistries. And once again, the emerging impact of thin-film metallurgy is noted.

Payoff: Successful growth of high-quality thin electroactive single crystals will have immediate impact in the area of optical switching, modulation, information storage, and related integrated optical applications using electro-optic, magneto-optic, and acousto-optic effects. The films will be important for piezoelectric transducers, pyroelectric infrared detectors, and dielectric capacitors without the complicating effects of grain boundaries. The fabrication of short-wavelength heterojunction lasers may prove feasible if transport and doping studies are carried out in parallel with crystal growth. Alternatively, second-harmonic generation of gallium arsenide lasers in nonlinear optical waveguide structures provides a means of up-converting injection lasers into the blue spectrum.

HIGH-TEMPERATURE CERAMIC SUPERCONDUCTORS

This revolutionary discovery has captured the imagination of scientists and engineers worldwide. Approximately $40M of FY 1987 U.S. federal support was quickly reprogrammed to initiate basic and applied research in this area. The key federal agencies supporting this research are the Department of Energy, Department of Defense (Navy, Air Force, Army, Defense Advanced Research Projects Agency), and National Science Foundation.

The Materials Science Division of the ONR is participating with the Defense Advanced Research Projects Agency (DARPA) in a major initiative aimed at processing and fabricating thin- and thick-film and bulk superconductors. The DARPA funding is directed to achieve results that will lead to demonstrations and manufacturing of electronic devices, magnets, motors, and the like, as quickly as possible. The ONR support will aim at developing the underlying basic science in materials synthesis, processing, and structure/property relationships.

With this background in the ONR's Materials Science Division, the keen interest and talented personnel in the Physics, Chemistry, and Electronics Divisions, and the very substantial and excellent in-house superconductivity research being undertaken at the NRL, the Navy is particularly well-positioned to enhance its basic research effort in high-temperature superconductors. The panel recommends that this topic be considered by the ONR as a multidisciplinary Accelerated Research Initiative (ARI), with a broad fundamental approach including theory, chemical synthesis, stability and protective coatings, electronic devices, and ceramic processing of bulk and thin-film superconductors. An ARI duration of from three to five years is recommended.

As part of the accelerated programs in high-temperature ceramic superconductors, the panel suggests that the ONR develop a focused thrust in pursuing thin-film devices such as Josephson junctions and SQUIDS. Special attention devoted to the synthesis and characterization of thin films and the processing science associated with the formation of highly dense structures for these types of devices will help to accelerate their development and application to Navy missions. Consequently, increased emphasis on this type of research in the ONR would be most appropriate.

MICROSTRUCTURE, PROCESS, AND PROPERTY MODELING, WITH COMPUTER ASSISTANCE

A broad range of new developments encompassing innovative material structures with new properties, new and improved methods of material processing, and material uses in appreciably extended service conditions all require that special attention be given to the benefits of modeling various aspects of these considerations, particularly, with assistance from advanced computer methods. The Nobel Prize-winning effort at the NRL of computer-assisted complex crystal structure determinations is a positive example of foresight applied earlier in this important fundamental subject area. The new ceramic superconducting materials, newly synthesized organic explosives, microalloyed structural steels, microtwinned electronic ceramics, and ordered intermetallic materials are examples for further structural or microstructural analysis.

Modeling of hypothetical microstructures and properties should be connected intimately with exploratory efforts to develop new ceramic, structural steel, and intermetallic materials. The effort should include thin-film and three-dimensional composite microstructures extending down to the nanoscale. Of particular concern is the use of modeling to bridge the gap between continuum mechanics analyses of microscopic material properties and other fundamental calculations based on atomic or molecular potentials. Such computer-assisted modeling should usefully connect as well with the use of modeling and computer methods in other branches of science and engineering.

CHEMICAL SYNTHESIS OF MICROSCALE MATERIALS

Novel chemical synthesis routes for engineering materials offer several potential advantages. Nonequilibrium materials can be produced with compositions, phases, and/or microstructures lying outside the normal range associated with conventional processing techniques. Low processing temperatures made possible by chemical routes offer the opportunity of combinations not previously possible. For example, it may become feasible to put very hard diamond or diamond-like inorganic films on polymers to improve their resistance to mechanical damage.

An area of special promise is the chemical synthesis of thin films. Such films have many current and potential uses. Hard ceramic films on cutting tools have proved their technical and commercial usefulness. Wear-resistant films on metal parts produced by CVD or PVD (physical vapor deposition) techniques are being introduced into automobiles. Although corrosion protection by self-passivation is preferable, chemically synthesized protective films are required for applications such as semiconductor passivation. Films can also perform electrical and optical functions.

Several such applications are described under other sections of this report, but the general subject of chemical processing is singled out here for focused attention both because there are common features of processing technology and because there are opportunities for synthesis that go beyond single films.

Chemical synthesis routes offer many other possibilities for tailoring microstructures in addition to layer structures. The sol-gel approach allows for preparation of microporous materials down to a very fine scale (e.g., 4 nm or less). Variations on this technique offer possibilities for assemblages of phases with grain sizes in the tens of nanometer range.

Very fine scale ceramic powders and coated powders offer potential for improved forming of green (i.e., unfired) ceramics and for improved sintering. Taken together, these advantages offer the promise of both improved average property values and improved reliability, including reduced scatter in properties.

The synthesis of novel layers of a variety of materials can be carried out by electrochemical means. This group of processing techniques has the advantage of precise and simple control of processing parameters, low cost, and capability to be carried out, in many cases, at ambient or low temperatures. Opportunities now exist because of new developments in pulse deposition, supercritical fluid deposition, molten salt deposition, nonaqueous deposition, and anodic oxidation.

These techniques have resulted in the production of compositionally modulated layers, metal-ceramic composite layers, deposition of organic coatings, deposition of alloys, and deposition of difficult-to-plate metals (aluminum, tantalum). Opportunities exist to produce compound films such as titanates, niobates, and tantalates for electronic applications.

PROTECTIVE FILMS/CORROSION SCIENCE

The Navy suffers substantial costs ($1.9B annually) and decreases in effectiveness and safety because of the environmental degradation of metallic materials. It is widely recognized that almost all corrosion processes are controlled by the interaction of the thin (<5 nm) protective films that are produced on metal surfaces of structures with the environment in which the structures exist. In aqueous environments, such films are called passive. It is the breakdown of these passive films that leads to the failure of metallic structures, largely by localized corrosion (pitting, crevice corrosion, stress corrosion, etc.).

In recent years, especially promising opportunities have arisen that enable the in-situ study of passive layers at atomic and near-atomic levels of resolution. There is a strong necessity to carry out such studies without removing the observed surface from the aqueous environment in which it is formed because a number of studies have shown that some properties of the passive layer change when a surface is removed from the environment for ex-situ study.

The opportunities provided by development of these in-situ surface study techniques will permit the exploration of a number of crucial issues in corrosion science:

1. The effect of the structure of the passive film on its ability to resist breakdown. (Are effective passive layers crystalline or glassy?)
2. The effect of alloying constituents on the structure, composition, thickness, and electronic and mechanical properties of the passive layer, and the way these characteristics affect the breakdown process.
3. The effect of substrate structure (crystallographic orientation, grain boundaries, defects, inclusions, presence of other phases, etc.) on passive film properties and the determination of breakdown sites. The newly developing fractal processing approach should be applied to this problem.

Two new in-situ surface study techniques that show special promise for attacking the issues just listed are:

1. Scanning Tunneling Microscopy. This technique has been shown to be capable of examining a surface in an aqueous environment with a resolution approaching the atomic or nearly atomic scale. It thus becomes feasible to examine the

breakdown process as it takes place as a function of the atomic structure of the surface observed.

2. X-ray Absorption Spectroscopy. In-situ study of the passive film by new x-ray absorption spectroscopic techniques has become possible with the establishment of a number of synchrotron light sources with high enough photon fluxes to enable measurements on surfaces immersed in aqueous environments.

Two techniques are being applied: (a) extended x-ray absorption fine structure (EXAFS), which can measure nearest neighbor distances and atomic coordination in thin films; and (b) near-edge x-ray absorption fine structure (NEXAFS), which can measure electronic transitions in passive layers. These techniques are especially useful for the study of passive layers, because they are capable of examining the glassy structures possessing the most effective passive layers.

In addition to examining conventional metallic materials, these and other new in-situ techniques (e.g., Raman spectroscopy, spectroscopic ellipsometry, electrochemical noise, and holographic heterodyne interferometry) should be applied to the study of the passive film on the new metallic materials (e.g., intermetallics, rapidly solidified alloys, and metal matrix composites).

The opportunities outlined above should be applied to the passivation of semiconductor surfaces (especially the compound semiconductors such as gallium arsenide), which should be examined from the corrosion science point of view, because, thus far, the problem of providing a dielectric film on gallium arsenide with low interfacial defect densities, an important problem in MOS-FET technology, has not been solved.

Finally, the panel recognizes the continuing roadblock of stress-corrosion cracking (environmental enbrittlement), and wishes to point to the striking progress made recently in connection with ultrahigh-strength martensitic steels through the use of lanthanum and rapid solidification.