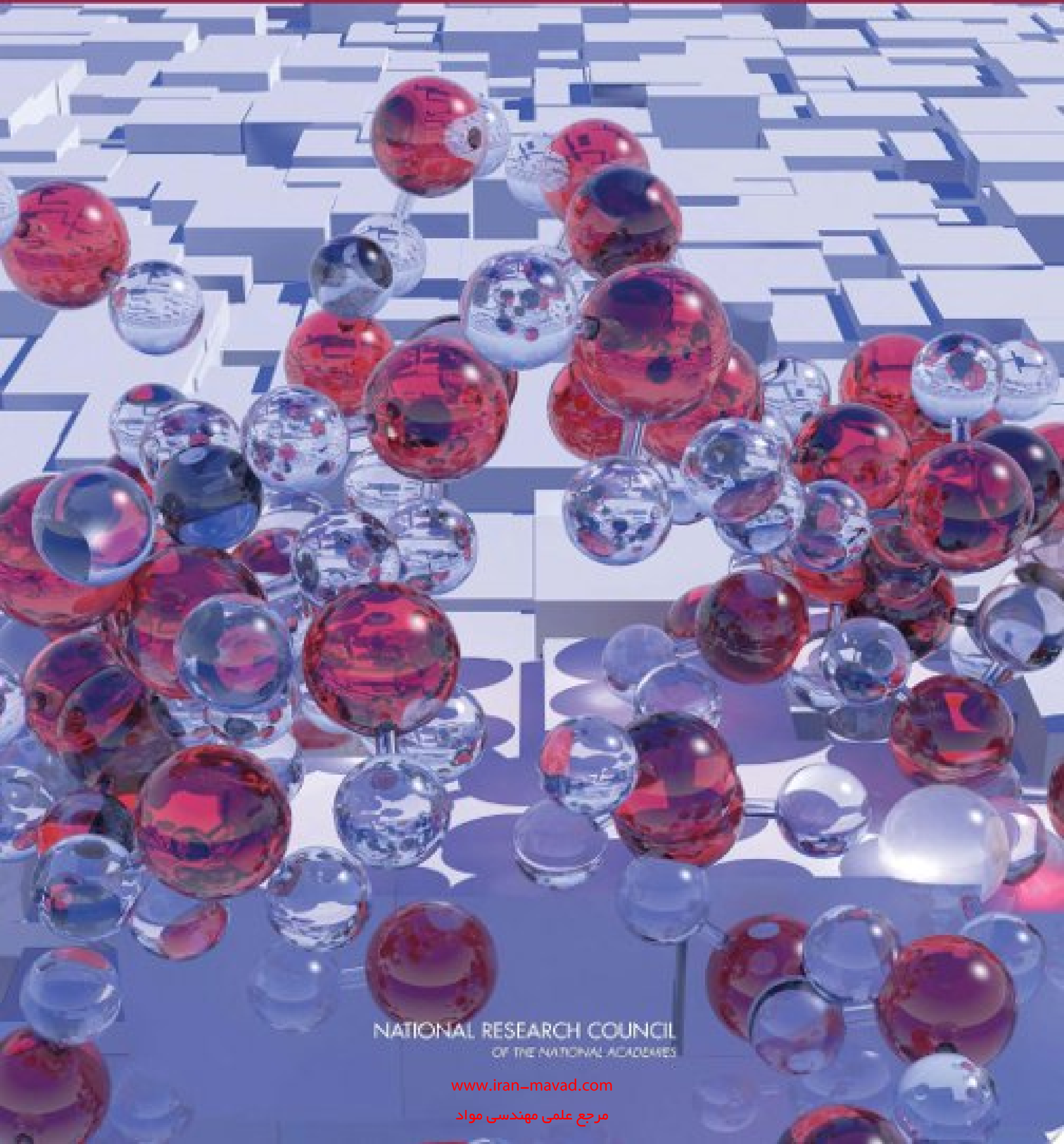
RESEARCH OPPORTUNITIES IN CORROSION SCIENCE AND ENGINEERING



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RESEARCH OPPORTUNITIES IN CORROSION SCIENCE AND ENGINEERING

Committee on Research Opportunities in
Corrosion Science and Engineering

National Materials Advisory Board

Division on Engineering and Physical Sciences

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OF THE NATIONAL ACADEMIES

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Preface

Corrosion science and engineering is a complex and broad subject that is not well defined and is still evolving as the subject itself expands beyond the traditional one, “the destructive oxidation of metals,” to the subject of this report, “environmentally induced degradation of a material that involves a chemical reaction.” The newer subject matter encompasses a wide spectrum of environments and all classes of materials, not just metals, and it intentionally excludes degradation due to nonchemical processes such as creep, fatigue, and tribology.

Some technologists perceive the corrosion research field as moribund, but others, including the members of the National Research Council’s Committee on Research Opportunities in Corrosion Science and Engineering, see the field quite differently—as exciting, poised to make huge leaps. This optimism is based on many converging forces, including the better understanding of nanometer-level chemical processes, instrumentation not previously available that enables the investigation of various phenomena, advances in heuristic- and physics-based materials modeling and simulation, and—especially important—societal expectations that the quality of life will continue to improve in all dimensions.

The degree to which the committee successfully addressed its ambitious charge—to posit grand challenges for corrosion science and engineering and to suggest a national strategy to meet them—will be judged by the readers of this report. The committee hopes that this report will catalyze action to revitalize the corrosion science and engineering field.

Developing a national strategy for any technical field is a highly ambitious goal, as is prioritizing the work that must be done to realize that strategy across all the federal agencies. During its deliberations, the committee realized that thrusts in corrosion science and engineering research must be linked to engineering applications in order to focus research and development efforts. What the committee was able to do was to develop a framework for a national strategy by identifying four corrosion grand challenges that serve as an approach to organizing new basic and applied corrosion research. Because most of the engineering applications in aggressive environments historically used metals, the committee was able to identify more corrosion research opportunities related to metals than to nonmetals. To the extent that it could do so, and based on the experience of its members and the information provided to it, the committee also identified corrosion research opportunities for other materials systems. It expects that an appropriate mechanistic understanding of environmental degradation of nonmetals will lead to proactive approaches to avoiding corrosion or mitigating its effects, basing its ideas on the long experience with corrosion in metallic systems. However, although a few specific such activities are cited in this report, it will be the work of another body to identify research needs and opportunities related to corrosion in nonmetallic systems.

Constituted in the fall of 2008, the committee was given the following the tasks:

- Identify opportunities and advance scientific and engineering understanding of the mechanisms involved in corrosion processes, environmental materials degradation, and their mitigation.
- Identify and prioritize a set of research grand challenges that would fill the gaps in emerging scientific and engineering issues.
- Recommend a national strategy for fundamental corrosion research to gain a critical understanding of (1) degradation of materials by the environment and (2) technologies for mitigating this degradation. The strategy should recommend how best to disseminate the outcomes of corrosion research and incorporate them into corrosion mitigation.

The committee, which was composed of experts in the field as well as generalists and experts in complementary disciplines, explored accomplishments in corrosion research and its effects and assessed needs and opportunities that could be addressed by future research. The full committee met four times between December 2008 and September 2009: on December 18-19, 2008, at the National Academies' Keck Center in Washington, D.C.; April 1-2, 2009, at the National Academies' Beckman Center in Irvine, California; June 15-17, 2009, at the National Academies' Keck Center in Washington, D.C.; and September 1-2, 2009, at the J. Erik Jonsson Center in Woods Hole, Massachusetts. The committee also held town hall sessions at the annual meetings of the National Association of Corrosion Engineers and the Minerals, Metals, and

Materials Society to raise the technical community's awareness of this study, and it prepared a questionnaire to solicit input from the corrosion community.

This report complements the recent National Research Council report *Assessment of Corrosion Education* (The National Academies Press, Washington, D.C., 2009). Five of the present committee's 14 members either served on the committee that wrote the 2009 report or participated as peer reviewers of that report.

The main body of the present report comprises five chapters. Chapter 1, "Corrosion—Its Influence and Control," sets the stage for the remaining four chapters of the report. It defines "corrosion," describes its societal impact, and discusses some of the successes of corrosion R&D. Chapter 2, "Grand Challenges for Corrosion Research," describes the process the committee used to develop the framework of grand challenges, lists the challenges, and then prioritizes them. Chapter 3, "Research Opportunities," presents examples of basic research (the foundation of addressing all the grand challenges) and applied research that can significantly advance understanding of corrosion and mitigation of its effects, and also describes examples of instrumentation and techniques pertinent to progress in characterizing corrosion processes. Chapter 4, "Dissemination of the Outcomes of Corrosion Research," addresses technology transfer. The last chapter, "A National Strategy for Corrosion Research," summarizes the key findings and recommendations of the report. The six appendixes contain the statement of task (A); results of the committee's questionnaire on corrosion mitigation (B); a discussion on the modeling of corrosion (C); definitions of the acronyms used in the report (D); a summary of current government programs relating to corrosion (E); and biographies of the committee members (F).

David J. Duquette and Robert E. Schafrik, *Co-Chairs*
Committee on Research Opportunities in Corrosion
Science and Engineering

Acknowledgments

The Department of Defense Corrosion Policy and Oversight Office initially requested this study. It was ultimately sponsored by that office and by the National Science Foundation, Division of Civil, Mechanical and Manufacturing Innovation within the Engineering Directorate and the Department of Energy, Basic Energy Sciences.

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the National Research Council's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this report:

Fiona M. Doyle, University of California,
Jeremy L. Gilbert, Syracuse University,
Thomas P. Moffat, National Institute of Standards and Technology,
Joe H. Payer, University of Akron,
Kathleen Taylor, General Motors Corporation (retired),
Shelby F. Thames, University of Southern Mississippi, and
Gary Was, University of Michigan.

Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations, nor did they see the final draft of the report before its release. The review of this report was overseen by George Dieter, emeritus professor of mechanical engineering, the Glenn L. Martin Institute Professor of Engineering at the University of Maryland. Appointed by the National Research Council (NRC), he was responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the institution.

The committee also thanks the guest speakers at its meetings, who added to the members' understanding of corrosion and the issues surrounding it:

Graham E.C. Bell, Schiff Associates,
Stanley A. Brown, U.S. Food and Drug Administration,
Luz Marina Calle, National Aeronautics and Space Administration,
Ram Darolia, Consultant,
Daniel Dunmire, Department of Defense,
Brian Gleeson, University of Pittsburgh,
Jonathan Martin, National Institute of Standards and Technology,
Joe H. Payer, University of Akron,
Lewis Sloter, Department of Defense,
John Vetrano, Department of Energy, and
Paul Virmani, Department of Transportation.

In addition, the committee thanks the corrosion experts who attended its town meetings and those who responded to its online questionnaire. Their candid comments were instrumental in allowing the committee to achieve a balanced understanding of the research and development needed to advance the field.

The excellent support of the NRC staff is especially appreciated. Special thanks go to Erik Svedberg, who was indispensable to our accomplishing this study.

Contents

APPENDIXES

Summary

The field of corrosion science and engineering is on the threshold of important advances. To better comprehend corrosion and its effects, researchers have embraced emerging advances across many fields of science and technology to gain understanding of the mechanistic effects of these interactions on materials behavior and to relate this understanding to the underlying structure, composition, and dynamics. Accelerated progress in corrosion research is anticipated as a result of the stunning ongoing increase in the ability to tailor composition and structure from the nanoscale to the mesoscale; to experimentally probe materials at finer levels of spatial resolution as well as the dynamics of chemical reactions; and to model computationally intensive problems that unravel the nature of these reactions and the response of materials to the environment. Corrosion science today is presented with unprecedented opportunities to advance fundamental understanding of environmental reactions and effects from the atomic and molecular levels to the macro level. Advances in lifetime prediction and technological solutions, as enabled by the convergence of experimental and computational length- and timescales and powerful new modeling techniques, are allowing the development of rigorous, mechanistically based models from observations and physical laws. Advanced techniques for the manipulation of information and for analysis are critical to furthering our state of knowledge in corrosion science and engineering. Important in this regard are the development and handling of large data sets to extract knowledge and trends, to visualize emergent phenomena, and to comprehensively test predictions from models.

Materials design for corrosion resistance currently relies on expert knowledge and incremental improvements to well-tested compositions and structures. The use of increasingly sophisticated computational approaches to predict stability and properties and to probe reaction dynamics in complex environments can make materials design more effective and narrow the span of experimental investigation. Furthermore, progress in nanoscience, particularly the ability to synthesize and control precise nanostructures, creates new opportunities for corrosion scientists and engineers to explore the design of materials (including coatings and smart materials) and to establish the critical link between atomic- and molecular-level processes and macroscopic behaviors. Despite considerable progress in the integration of materials by design into engineering development of products, corrosion-related considerations are typically missing from such constructs. Similarly, condition monitoring and prediction of remaining service life (prognosis) do not at present incorporate corrosion factors. Great opportunities exist to use the framework of these materials design and engineering tools to stimulate corrosion research and development to achieve quantitative life prediction, to incorporate state-of-the-art sensing approaches into experimentation and materials architectures, and to introduce environmental degradation factors into these capabilities.

The Committee on Research Opportunities in Corrosion Science and Engineering defined corrosion as the environmentally induced degradation of materials, where "environment" is broadly construed but always includes some element of chemical reaction. There are many corrosion processes that operate over different temperature regimes, environmental conditions, and mechanical stress levels. The public perception of corrosion is generally limited to the degradation of metallic materials in aqueous environments, perhaps with some recognition that gases and condensed phases at high temperatures may also shorten the useful life of engineering materials. However, every material class is affected by corrosion in some way. Although the problem of corrosion is ubiquitous, research to reduce its magnitude has often received only modest attention.

Dramatic changes in societal factors now demand that prevention and mitigation of corrosion damage receive greater emphasis. Our quality of life is increasingly dependent on the application of diverse materials, including metals, polymers, ceramics, and semiconductor devices. This continuing trend is made more significant by the advanced requirements and designs that push past current experience and expose materials to ever-harsher chemical environments. Finally, and perhaps most importantly, increased awareness of the human impact on Earth's environment is raising the public's expectation not only for improved safety and high reliability, but also for green manufacturing and low environmental impact, including sustainability in consumer products, industrial and military equipment, and the infrastructure. When corrosion processes and their products act in direct opposition to these very desirable attributes, their effects must be mitigated. However, while corrosion generally has a societal cost, it also can be beneficial in that naturally degrading materials can provide a positive green effect once the useful lifetime of a device is reached. Environmentally degradable materials will reduce long-term waste storage issues, and the use of corrosion mechanisms may provide a more rapid path to a full life cycle for many products.

The most effective routes to corrosion mitigation rely on knowledge of the underlying mechanisms causing the corrosion. This alone would justify increased attention to the science base of corrosion research; however, understanding corrosion processes would also be beneficial for improving critical technologies such as batteries and fuel cells, semiconductors, and biodegradable materials.

There are many forms of corrosion, and while some are well understood at the macro level, complex interactions among the different forms are yet to be fully clarified. Further, at the detail level there is often relatively poor understanding of corrosion mechanisms, which makes it technically difficult to devise cost-effective engineering solutions to predict, avoid, and mitigate corrosion damage. These difficult problems have often been put on hold in favor of short-term, empirical fixes, but now appears to be an opportune time to readdress complex questions with new techniques. Advances in characterization (using, among other techniques, transmission[1] and scanning[2] electron microscopy, micro- and nanometer electrochemical probe methods, synchrotron beam lines and lasers, x-ray, and neutron spectroscopy and combinations of these methods for simultaneous information gathering) and computation and modeling (first principle, molecular dynamics, multiscale modeling, and informatics) have dramatically broadened the array of tools available. Furthermore, engineering practice has evolved, bringing organization to the science of new materials development—integrated computational materials science and engineering (ICMSE)—and order and predictability to the process of life-cycle management (prognosis[3]).

Lack of fundamental knowledge about corrosion and its application to practice is directly reflected in the high societal cost of corrosion. Although estimates of its aggregate cost vary widely, some studies suggest that corrosion consumes at least 2 to 4 percent of the U.S. gross national product. These estimates do not take into account the ancillary costs to the economy. Ancillary costs include loss of productivity due to deteriorated infrastructure, loss of full operational capability for industrial and military equipment and facilities, and added risk to public safety and

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[1] Ernst Ruska, *The Early Development of Electron Lenses and Electron Microscopy.* ISBN 3-7776-0364-3.

[2] Manfred von Ardenne, Das Elektronen-Rastermikroskop. Theoretische Grundlagen (in German), *Zeitschrift für Physik* 108(9-10):553-572, 1939.

[3] See, for example, Harris Yu, A new stress-based fatigue life model for ball bearings, *Tribology Transactions* 44:11-18, 2001.

welfare.[4] Tackling corrosion cost drivers represents a significant opportunity for the science and engineering community to make a valuable contribution to society.

Sometimes corrosion prediction and prevention do not receive the attention they require during engineering design of structures and systems. This might be because designers anticipate that corrosion problems arising in service can be readily mitigated over time with proper maintenance and repair to achieve desired longevity or because the in-service environment is unknown. The committee envisions a new paradigm in which this traditional reactive approach is transformed into a proactive engineering strategy with (1) appropriate tools used to accurately predict the onset and rate of deterioration of materials in actual or anticipated operating environments, (2) new materials and coatings expressly developed to provide superior corrosion resistance, and (3) design tools used to identify the best, most cost-effective options and to guide the selection of materials and corrosion-mitigation techniques. To support this vision corrosion research should focus on addressing significant gaps in corrosion knowledge so that the results can be applied directly to sectors that are significantly affected by corrosion damage. This means that corrosion science, which seeks to expand the frontiers of basic knowledge, should have its priorities guided by corrosion engineering needs.

Corrosion impacts our everyday life, affecting the health and welfare of the nation and leading to added energy and expense to combat it. Fortunately, a multitude of research and development (R&D) opportunities could lead to making substantial headway in reducing its impact. The committee believes that government-wide as well as society- and industry-wide recognition of the scope of the corrosion problem and a well-defined, coordinated, and reliably resourced program would have a high payoff for the nation. A robust R&D program should have a balanced portfolio of projects providing incremental advancements that result in high return on investment (ROI), as well as high-risk novel projects that could lead to transformative improvement, albeit with a longer time horizon and less attractive ROI in the short term. Because the committee chose to focus on general as well as federal government corrosion issues, it could not also include a separate strategy for each federal entity. The goal was to identify general research needs and organize these into a framework that could be used to facilitate a specific federal response.

This report identifies grand challenges for the corrosion research community, highlights research opportunities in corrosion science and engineering, and posits a national strategy for corrosion research. It is a logical and necessary complement to the recently published National Research Council report *Assessment of Corrosion*

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[4] See, for example, CC Technologies Laboratories, Inc., Report FHWA-RD-01-156 to Federal Highway Administration, Office of Infrastructure Research and Development, 2002.

Education,[5] which emphasized that technical education must be supported by academic, industrial, and government research, as well as technology dissemination to accelerate the implementation of new and emerging technical advances. Although the present report focuses on the government role, this emphasis does not diminish the role of industry or academia.

Grand challenges in corrosion research might be identified from several perspectives. The committee chose to first explore technical challenges that pervade key national priorities such as energy, the environment, health, infrastructure/safety, and national security. These priorities account for an overwhelming portion of discretionary spending in the federal budget and are aligned with federal agencies with defined and related missions. Once identified, these technical challenges were organized by the committee into broad overriding themes, which the committee called the four corrosion grand challenges (CGCs):

CGC I: Development of cost-effective, environment-friendly, corrosion-resistant materials and coatings;

CGC II: High-fidelity modeling for the prediction of corrosion degradation in actual service environments;

CGC III: Accelerated corrosion testing under controlled laboratory conditions that quantitatively correlates with the long-term behavior observed in service environments; and

CGC IV: Accurate forecasting of remaining service time until major repair, replacement, or overhaul becomes necessary—i.e., corrosion prognosis.

The CGCs have been expressed as engineering and technology challenges, and these are deemed to be the drivers and guiding principles of the framework for prioritizing efforts. The committee believes that addressing these challenges will demand an integrated body of scientific and engineering research targeted at specific needs but coordinated to minimize duplication and take advantage of synergism. Figure S.1 is a hierarchical representation of the four CGCs, supported by a body of corrosion science and engineering research.

Between the CGCs and the underlying corrosion science in Figure S.1 is a layer depicting the need for dissemination of corrosion knowledge and research results to those facing the real problems of addressing the CGCs and the related corrosion issues. As in many other fields, there is a need for enhanced communication between researchers and engineers to make the existing knowledge as accessible as possible.

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[5] National Research Council, *Assessment of Corrosion Education*, The National Academies Press, Washington, D.C., 2009.

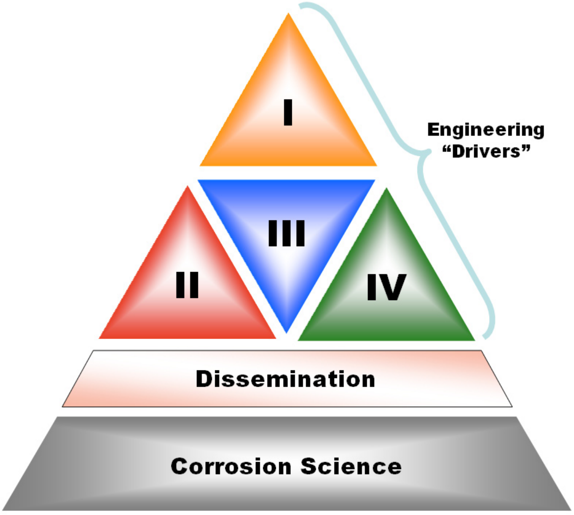

FIGURE S.1 Hierarchy of the four corrosion grand challenges identified by the committee.

The committee recognizes that each federal agency and department must establish its own priorities for addressing the challenges, depending on the relevance of the corrosion damage to their individual missions. The diverse responsibilities of the agencies might include funding such research or performing it as well as taking advantage of what is already known about mitigating corrosion to reduce the costs of such corrosion. Accordingly, the committee recommends that each agency and department use the underlying research opportunities as a framework for prioritization, each according to the benefits expected for its mission and allocating its resources appropriately. To facilitate the rapid dissemination of results, the committee encourages the involvement of industry in the planning and execution of the research and technology development.

> **Recommendation:** Using as guidance the four corrosion grand challenges developed by the committee, each federal agency or department should identify the areas of corrosion research pertinent to its mission and draw up a road map for fulfilling its related responsibilities. In doing so, each should take a cross-organizational approach to planning and execution and should include input from industrial sectors that have experience in handling corrosion.

There are many research opportunities in the CGCs, each having significant gaps in basic understanding that need to be filled. Some of these gaps are listed below.

CGC I: Development of cost-effective, environment-friendly, corrosion-resistant materials and coatings.

- Materials with inherently high corrosion resistance that also possess other important characteristics demanded by the applications of interest.
- Design and modeling of new corrosion-resistant alloy chemistries and structures.
- Durable, environmentally compatible, and cost-effective protective coatings that eliminate or significantly reduce corrosion.
- Materials that biodegrade in a predictable and benign manner.
- Determination of properties and design parameters/rules.

CGC II: High-fidelity modeling for the prediction of corrosion degradation in actual service environments.

- Ability to predict effects of corrosion and the lifetimes of materials subjected to a wide range of service environments.
- Computer modeling of material surfaces at the nanoscale, where corrosion initiates and propagates and where corrosion resistance must be imparted.
- Increasing the fundamental understanding of new corrosion science and its utilization.

CGC III: Accelerated corrosion testing under controlled laboratory conditions that quantitatively correlates to long-term behavior observed in service environments.

- Smart accelerated corrosion testing that accurately predicts performance under a range of exposures, ensuring durability, and early detection of unforeseen corrosion-related failure mechanisms.
- Development of an "environmental corrosion intensity factor" that facilitates quantification of the acceleration provided by test conditions and enables prediction of performance, based on exposure time, in any combination of field environments.
- Hypothesis-driven models to increase fundamental understanding of corrosion science, improve prediction of structural lifetimes, and optimize maintenance programs.

CGC IV: Accurate forecasting of remaining service time until major repair, replacement, or overhaul becomes necessary—i.e., corrosion prognosis.

- Accurate and robust sensors that track and monitor corrosion damage and protection.
- Automated defect-sensing devices for quality inspections.
- Remaining life prediction "reasoners" based on measured corrosion deterioration and knowledge of a material's capability in the particular environment.

- Remaining life prediction for materials that have yet not shown any localized degradation.
- Accurate assessment of alternative corrective actions.

Each of the four challenges is explored in the body of the report. In Chapter 3, the challenges are followed by descriptions of the underlying science and engineering research required to address them. The descriptions reveal that advances across many scientific disciplines will be needed to close current technological gaps, and they clarify the need for a balanced program of traditional single-investigator and multi-investigator efforts that will bring corrosion researchers into collaborative groups that include experts in characterization and computational modeling.

> **Recommendation:** Funding agencies should design programs to stimulate single-investigator and collaborative team efforts and underwrite the costs of realistic test laboratories open to the corrosion community and its collaborators, including industry researchers. These programs should address the four corrosion grand challenges identified by the committee; provide a balance between single- and multi-investigator groups; develop collaborative interactions between corrosion, measurement, and computational experts; and be driven by both science and engineering applications.

A new development model, known as the technology "pull" paradigm, requires the engagement of multiple stakeholders, including researchers, applications engineers, design engineers, and material producers. Their efforts can reach fruition much faster if the technology needs are known in advance, allowing the research to focus on the critical issues. The other stakeholders are those who design the application for the new material and those who produce it in volume. This development model is undertaken by a consortium that engages interested, knowledgeable participants from conception to implementation.

Federal departments such as the DOD and the DOE currently support materials R&D in areas aligned with core mission requirements. Increasingly, these developments involve industry early in the planning process since materials developments are targeted for specific end applications.

> **Recommendation:** Federal agencies should facilitate the formation of consortia of industry, university, and as appropriate, government laboratories chartered to address significant areas of opportunity in corrosion science and engineering. In consonance with best practices, industry should be involved at the earliest practical time in the structuring of these programs so that technology pull can realistically shorten the time between development and reduction

to practice. Also, early involvement by industries will facilitate their active participation as consortium members.

Research is critical but not in itself sufficient to tackle the CGCs. Advances in understanding will have little benefit and negligible ROI if they are not transferred to in-service practice. There are many ways to disseminate research results, but they are typically less than optimal in reaching medium and small firms with few engineers. Several options for enhancing dissemination are discussed in the body of the report. The committee feels strongly that each agency should include a plan for accelerating dissemination of the results achieved in addressing its part of the corrosion road map.

Recommendation: Each agency and department should assume responsibility not only for funding corrosion research but also for disseminating the results of the research.

Actions by the individual agencies are critical to this proposed national strategy, but the variety of materials applications and the broad commonality of the underlying science research suggest that collaboration across agency boundaries will add significant value. The Office of Science and Technology Policy (OSTP) should, accordingly, take the lead in optimizing the government effort. Such an integrated effort would constitute a much-needed national corrosion strategy.

Recommendation: The Office of Science and Technology Policy (OSTP) should acknowledge the adverse impact of corrosion on the nation and launch a multiagency effort for high-risk, high-reward research to mitigate this impact. OSTP should set up a multiagency committee on the environmental degradation of materials. It should begin by documenting current federal expenditures on corrosion research and mitigation and then encouraging multiagency attention to issues of research, mitigation, and information dissemination. Collaboration among departments and agencies should be strengthened by collaboration with state governments, professional societies, industry consortia, and standards-making bodies.

1

Corrosion— Its Influence and Control

INTRODUCTION

With much of the world's population living in close proximity to water and humidity, corrosion of metallic materials has been an inevitable part of the human experience. While the oxidation of iron (rust) is the most easily identified form of corrosion, this oxidation process represents only a fraction (albeit substantial) of material losses. Today, the impact of corrosion on society and the associated degradation of materials are far reaching owing in part to the increased complexity and diversity of materials systems, which include not only metallic materials but also ceramics, polymers, and composites, which are subject as well to environmental extremes. While legacy corrosion concerns remain, advancing technology and the need for global sustainability bring with them new and emerging corrosion issues whose negative impacts must be minimized through appropriate materials selection, mitigation and monitoring, and new materials development. See Figure 1.1 for an example of multiple simple mitigation efforts.

The impacts of corrosion are often described in economic terms. Financial losses have been assessed in several studies which concluded that premature materials degradation costs industrialized nations approximately 3 percent of their gross domestic product (GDP).[1] In the United States it is estimated that between

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[1] Gerhardus H. Koch, Michiel P.H. Brongers, Neil G. Thompson, Y. Paul Virmani, and Joe H. Payer, *Corrosion Cost and Preventive Strategies in the United State,* National Technical Information Service Report No. FHWA-RD-01-156, 2001.

FIGURE 1.1 A mooring ring, shackle, and thimble with rope illustrate three different techniques for combatting the effects of materials degradation,. Originally, the ring and eye bolt were painted, the shackle and thimble were galvanized (zinc coated), and the mooring line was made of nylon. Courtesy of Erik Svedberg.

$2 trillion and $4 trillion are lost to corrosion each decade—on a relative scale, this amount equates to the cost of repairing the infrastructure damage of three or four hurricanes as large as Hurricane Katrina, which caused massive damage in New Orleans, southern Mississippi, and Alabama.

However, the true costs of corrosion to society are even more pervasive and, in practice, difficult to compile. Several studies, including a recent National Research Council (NRC) report on corrosion education,[2] have described both the economic impacts of corrosion and the less measurable impacts such as loss of readiness—that is, the nation's ability to respond militarily or otherwise to emergencies or other situations involving national security. For example, while the maintenance and replacement costs associated with the corrosion of military systems can be

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[2] National Research Council, *Assessment of Corrosion Education*, The National Academies Press, Washington, D.C., 2009, available at http://www.nap.edu/catalog.php?record_id=12560.

readily estimated, the dollar costs associated with the military's inability to respond promptly to a national emergency are difficult to capture directly. Similarly, while the costs of replacing deteriorating bridges and highway infrastructure can be estimated—including the impacts on national productivity and security brought about by failures and traffic congestion during repairs—such estimates require assumptions that are subject to considerable judgment.

Corrosion can affect public health, the environment, and global sustainability in ways that cannot be quantified simply in terms of GDP loss. The deterioration of an early generation of medical devices and implants resulting from interactions with human body fluids, the leaching of corrosion products into the environment, and the weakening of the nation's energy and transportation infrastructures all have impacts that greatly exceed those that are purely financial. The NRC report *Assessment of Corrosion Education*[3] discusses the broader impact of corrosion and educational challenges in greater detail (Figure 1.2).

Interestingly, the physical processes that cause materials to degrade may be harnessed for society's benefit. For example, the fabrication of semiconductor devices relies on a variety of etching, deposition, and oxidation processes often operating at the nanometer level. The ability to precisely control the rates and extent of these processes is critical to that fabrication. Corrosion-associated processes are also relevant to other technologies, both in terms of routes by which to synthesize materials and as a means to understand their performance from a mechanistic standpoint. Examples of materials issues include biodegradability and recycling, battery design and development, nanoporous metals for catalysis and sensing, and fuel cells and gas separation membranes. State-of-the-art corrosion research therefore has the potential not only to contribute significantly to many other fields of science and engineering but also to enable them.

TYPES OF CORROSION

Corrosion has historically been defined as the destructive oxidation of metallic materials. More recent definitions have described corrosion as the degradation of any material and its attendant loss of function by exposure to and interaction with its environment. The committee, mindful of the increased application of nonmetals in important structural applications, chose to define corrosion in the following broader context: Corrosion is the environmentally induced degradation of a material that involves a chemical reaction. Mechanical degradation mechanisms, such as creep, wear, and fatigue, are not considered to be corrosion, although corrosion processes may accelerate these degradation modes. Worth mentioning at this point

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[3] National Research Council, *Assessment of Corrosion Education*, The National Academies Press, Washington, D.C., 2009, available at http://www.nap.edu/catalog.php?record_id=12560.

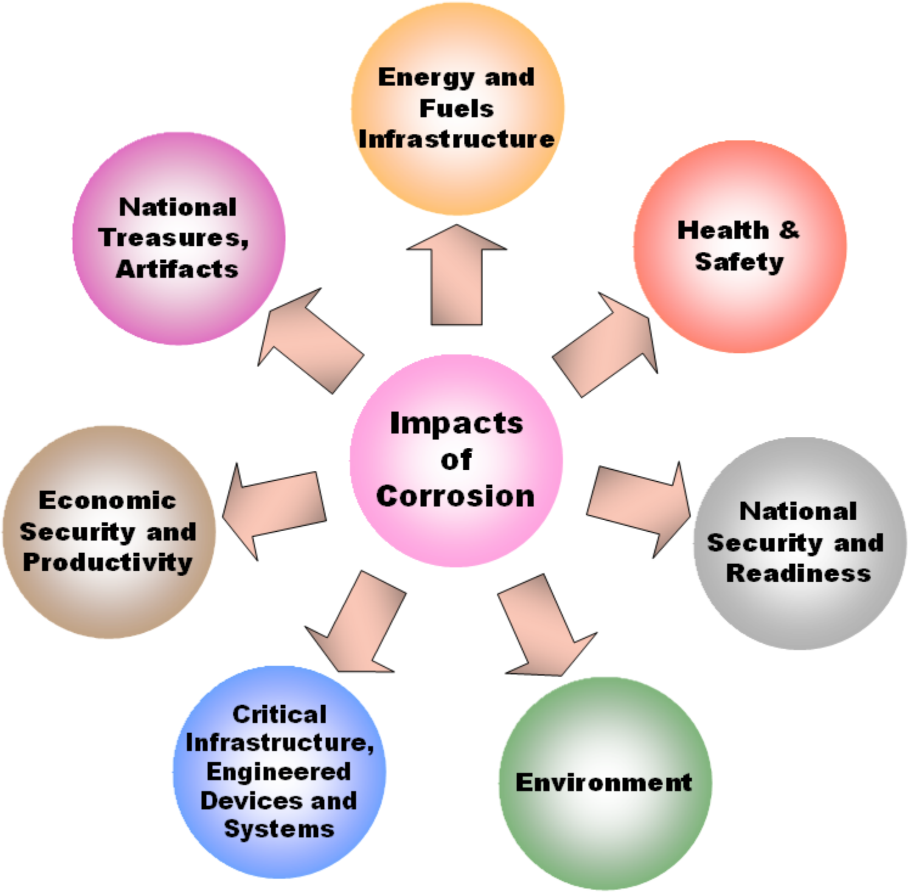

FIGURE 1.2 Corrosion affects nearly every aspect of modern society. In many of these areas, however, its impact is difficult to quantify.

is hydrogen embrittlement, the process by which various metals and alloys become brittle and crack following exposure to hydrogen. Hydrogen embrittlement or hydrogen cracking is often the result of the unintentional introduction of hydrogen into susceptible metals and alloys during formation or finishing operations. The leading types of corrosion are outlined in Box 1.1.

It should be pointed out here that corrosion processes often involve multiple conjoint effects. Rarely does a single mechanism or event drive corrosion; rather, a number of events combine to produce severe effects. Thus, we must keep in mind that corrosion processes usually occur in the context of other factors (loads, wear, crevices, temporally and spatially varying environments, etc.). One such combination of factors can lead to mechanically assisted corrosion in total hip replacements:

BOX 1.1
Types of Corrosion

Metallic Corrosion

- Uniform, or "general," corrosion
- Dealloying
- Pitting
- Crevice related
- Intergranular
- Filiform
- Corrosion by high-temperature gases (oxidation,[1] sulfidation, chlorination, etc.)
- Deposit-induced corrosion, which includes "hot corrosion"
- Galvanic mechanically assisted corrosion
- Stress corrosion cracking
- Corrosion fatigue
- Fretting corrosion
- Tribocorrosion
- Erosion corrosion
- Hydrogen embrittlement, hydrogen-induced cracking, and hydrogen attack

Nonmetallic Corrosion

- Recession of ceramics in the presence of water vapor or volatile compounds
- Diffusion-controlled leaching (ion exchange) in glass
- Glass network hydrolytic dissolution
- Ultraviolet degradation of organic coatings and polymers
- Hydrolysis
- Radiolysis
- Autocatalytic (acid-driven) degeneration
- Metal-ion-induced oxidation

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[1] Oxidation is used here in a very narrow sense to indicate gas-metal reactions that form oxide products.

- Wear (typically fretting),
- Passive oxide abrasion,
- Repassivation,
- Hydrogen ion generation, and
- Crevice environments.

It is the biological inflammatory response to these processes that generates aggressive oxidative environments in vivo (generation of reactive oxygen species, etc.) that combine to lead to severe attacks on medical alloys. Ti alloys can become subjected to pitting in vivo, and Co-Cr-Mo alloys can undergo penetrating intergranular corrosion as well, leading to implant fatigue and fracture.

Another kind of corrosion sustained by medical implants is the metal-ion oxidation sustained by polyurethane pacemaker leads. This failure mode is highly complex and involves water transport across the insulation of the lead, allowing contact with the Co-Cr alloy, which then corrodes by a fretting mechanism. The metal ions, in particular Co^{2+}, then penetrate the polyurethane and oxidize it in a catalytic fashion. This leads ultimately to an electrical breach in the lead and failure of the pacemaker, often resulting in the death of the patient.

EXAMPLES OF CORROSION MITIGATION CHALLENGES

Corrosion may be inevitable, but there are ways to retard it—that is, to slow the kinetics of deterioration. The mitigation strategy for a material must be tailored to the environment and to the composition and structure of the material. Some materials are inherently slow to corrode, especially in the absence of oxygen; others corrode slowly by forming layers of protective corrosion product (Box 1.2).

Materials with different properties will require different mitigation strategies:

- *Metals and alloys without intrinsic corrosion resistance.* Such materials can corrode in otherwise innocuous waters or atmospheres, when dissolved oxygen is present or in which water can be reduced to generate free hydrogen. These metals and alloys usually need to be actively protected. Alloys such as low-carbon steels can be used in thick sections to accommodate the loss of material.
- *Passive metals and alloys.* Usually alloys such as stainless steel or nickel-chromium can be used unprotected in innocuous environments and in a certain range of aggressive environments such as seawater or mild acids, depending on the content of alloying elements. Superpassive metals—such as tantalum, which resists strong hydrochloric acid—also exist but are considerably more expensive. The main issue with passive metals is their propensity for localized—rather than uniform—corrosion.
- *Copper-based materials.* Owing to the thermodynamic immunity of copper, corrosion is normally slow or absent unless oxygen or another strong oxidant is present. Aqueous sulfide solutions are an exception. When oxygen is present or in the presence of acid rain, these materials may react like other nonpassive metals (see Figure 1.3).
- *Certain high-strength alloys.* These alloys can survive at very high temperatures because they form surface layers that protect against oxygen in the application environment or because they are given metallic coatings that perform this function.
- *Glass and ceramics.* Such materials are affected not by electrochemical processes but mainly by simple dissolution of the material. One way of protecting against the corrosion of glass is to add lime: added to soda-glass it reduces solubility in water.

BOX 1.2
Survivor

In his 2007 book *The World Without Us,*[1] Alan Weisman suggests that copper and its alloys are the structural materials most likely to survive for thousands of years in a world suddenly depopulated of human beings. This conclusion, based on a strictly thermodynamic criterion (copper being the most noble structural metal and sometimes found uncombined in nature), may not be correct, however, given that some invented materials, like stainless steel, will also endure for thousands of years because their surface is protected by passivating oxide films.

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[1] Alan Weisman, *The World Without Us*, Thomas Dunne Books, New York, 2007.

FIGURE 1.3 Bronze statue with a protective layer of patina created by slow chemical alteration of the copper content, producing a basic carbonate. The statue has been exposed to the coastal weather outside the city hall of Stockholm. Courtesy of Erik Svedberg.

- *Polymers.* Degradation is due to a wide array of physiochemical processes. One common problem is swelling, where small molecules infiltrate the structure, reducing strength and stiffness and causing a volume change. Conversely, many polymers are intentionally swelled with plasticizers, which can be leached out of the structure, causing brittleness or other undesirable changes. The most common form of degradation, however, is a decrease in polymer chain length. The mechanisms that break polymer chains are ionizing radiation (most commonly ultraviolet light), free radicals, and oxidizers such as oxygen, ozone, and chlorine. Additives as simple as a UV-absorbing pigment (i.e., titanium dioxide or carbon black) can slow these processes very effectively.

Mitigation techniques can be roughly classified as either active or passive. Examples of active mitigation techniques include inhibitors, external cathodic protection, with or without coatings, and sacrificial anodes. Passive techniques include material selection, organic and inorganic coatings, and metallic coatings (including both barrier and sacrificial coatings). One other example of mitigation is control of the environment (oxygen, ions, etc.) such as is sometimes done in boilers when oxygen and ions are removed while inhibitors (amines) are added. The decision to use one technique or a combination of techniques depends on the type of corrosion that is expected, the tolerance for risk, the cost of the technique, the material, the environment, and other factors related to the design of a structure, such as accessibility and size.

The committee assembled and distributed a questionnaire focused on corrosion mitigation in order to better understand the current concerns and problems. The questionnaire, which was made available to key personnel at DOD, MTI, and LMI; the NACE Technical and Research Activities Committees; and directly through the ROCSE Web site, gathered information on the respondents' backgrounds; types of corrosion that were of greatest concern; types, costs, and efficacies of mitigation systems employed; and idealized mitigation systems. Respondents were also given the opportunity to suggest scientific advances that could lead to new and/or better mitigation technologies. Almost 200 people from a wide variety of industry sectors responded to the questionnaire. The majority of the respondents had been involved with corrosion mitigation for more than 15 years managing assets valued at more than $10 million each. A variety of corrosion mechanisms were cited as being troublesome to the respondents, with pitting corrosion the biggest single problem. What most concerned the respondents was safety. Many corrosion mitigation strategies were relied on by the respondents, the most frequent being material selection, monitoring/inspections, external cathodic protection with coatings, organic coatings, and inhibitors. A majority of respondents reported having spent more than $200,000 per year on corrosion mitigation.

Overall, the respondents were at least moderately satisfied with their choice of mitigation technique. In responses to questions about difficulties encountered with the different techniques, some areas of concern became apparent, including sensors for measuring localized corrosion, remote sensing, protection under disbonded coatings, surface preparation requirements for coatings, lack of training, and lack of reliable real-time models to predict lifetimes and damage mechanisms. When asked where future mitigation research should be focused, most questionnaire respondents suggested monitoring and modeling (especially remote monitoring or monitoring of localized corrosion and modeling for lifetime prediction and for new alloy performance), coatings (especially for high-temperature applications or to reduce the need for surface preparation), and development of active systems.

The responses are given in more detail in Appendix B, "Results of the Commitee's Corrosion Mitigation Questionnaire."

SUCCESS STORIES FROM CORROSION RESEARCH

The success stories that follow are not exhaustive. Rather, they were selected to illustrate the impact of advances in science and engineering—emerging tools, analytical approaches, and new materials design, synthesis, and processing—on strategies for material and operational solutions to environmentally induced degradation. These advances have historically helped the community develop an underlying scientific understanding as well as the technological means to mitigate corrosion. The committee is confident that the community will continue to pursue these goals and felt that it was not necessary to arbitrarily limit (or to underestimate) the imagination of researchers by specifying which developments and techniques should be pursued, particularly given the vast range of related phenomena. Rather, historical examples are contained in many of these success stories, which, additionally, offer a glimpse into why future advances hold promise for greater progress in combating corrosion and also illustrate the other factors (such as societal needs, technological drivers, policy, multidisciplinary approaches, and thrusts of critical size) that contribute to successful endeavors to deal with corrosion. The examples begin with general materials development and then move to application-specific success stories.

Corrosion- and Heat-Resistant Alloys

Despite the fact that it is not thermodynamically possible to develop alloys that are totally immune to corrosion, there have been extraordinary developments with respect to heat- and corrosion-resistant alloys in the last century, and—as a result of research efforts—these developments have accelerated over the last few decades. Among the many success stories that are associated with these new materials, one of the most important has been the development of the modern family of austenitic stainless steels.

As early as 1821, Berthier, based on the work of Faraday and Stodart, produced stainless alloys of iron and chromium.[4] However these alloys were extremely brittle and had no structural usefulness. The first useful stainless steels were developed in the beginning of the twentieth century by Monnartz in Germany and Brearley in England,[5] but it was not until the 1912-1914 period that the commercial success of these austenitic steels—primarily based on the addition of 18 percent chromium and 8 percent nickel—was first recognized.[6]

In the 1970s—when strength considerations became an issue for stainless steels—duplex versions were developed, which also increased resistance to chloride stress corrosion cracking. In the 1980s stainless steels with higher molybdenum were formulated to solve problems with localized corrosion encountered in aggressive environments.

This abbreviated history of stainless steels illustrates the successes in the development of iron-based, corrosion-resistant alloys. Developments were accompanied by use of increasingly sophisticated experimental and characterization techniques from advances in allied fields. However, it was also a labor-intensive effort, and the time period—from recognition of the problem, to an understanding of its origin, to the development of the most resistant alloys—was on the order of 80 years. This was hardly an efficient process.

Even with advances in alloy development technologies, it still took almost a quarter of a century to improve the nickel-containing alloys of the 600 family of stainless steels to the more corrosion-resistant versions (e.g., alloys 690, 22, 59, and 2000) that are enabling many applications in extremely aggressive environments found in the chemical industries, nuclear reactors, steam generators, and sour oil and gas production.

The development of heat-resistant alloys was similarly lengthy and inefficient. In the 1970s the protective oxide layers on nickel-based alloys were much improved by alloying them with elements that resulted in a more stable and tenacious layers of alumina versus chromia. It is only now that the concept of alumina protective layers is being applied to more cost-effective and high-temperature iron-based heat-resistant alloys, effectively producing a new class of stainless steels based on the principles of selective oxidation and advanced microstructural control of precipitates for strengthening.[7]

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[4] Louis Kuslan, "Berthier, Pierre," pp. 72-73 in *Dictionary of Scientific Biography*, Charles Scribner's Sons, New York, 1970-1980.

[5] See "Harry Brearley, 1871–1948," Tilt Hammer Web site at http://www.tilthammer.com/bio/brear.html.

[6] *New York Times*, January 31, 1915.

[7] Y. Yamamoto, M.P. Brady, Z.P. Lu, P.J. Maziasz, C.T. Liu, B.A. Pint, K.L. More, H.M. Meyer, and E.A. Payzant, Creep-resistant, Al_2O_3-forming austenitic stainless steels, *Science* 316:433-436, 2007.

In the last few decades, amorphous and nonequilibrium alloys processed using heretofore exotic methods (e.g., spun cooled, sprayed, sputter deposited, and laser surface melted) presented the potential for extraordinary advances in the development of corrosion-resistant alloys. Iron- and nickel-based metallic glasses have been developed whose corrosion resistance rivals that of the best conventional nickel-based superalloys in the low-temperature regime.[8] This advance was enabled by certain glass-forming elements that allow for the addition of large amounts of traditional corrosion-beneficial alloying elements without detrimental effects; the emergence of metallic glass composites; and the benefits of selected minor alloying elements. In addition, multifunctional amorphous and semiamorphous alloys[9] that offer tunable barrier, sacrificial, and chemical-inhibiting capabilities have also been produced. While these materials had long been considered impractical, laser surface treating used by heavy equipment manufacturers has enabled mass production of coatings and bulk metallic glasses and demonstrated routes to practical processing technologies that can produce significant improvements in corrosion protection.

What's Next for Corrosion- and Heat-Resistant Materials?

The emergence of the metallic glasses and alumina-forming stainless steels as potentially highly corrosion-resistant materials is only one example of the progress that is continuing to be made. Both show ways in which lessons learned, new materials developments, the incorporation of modern tools into research activities, and growing understanding of the relationships between structure, materials behavior, and component design can speed the development of such alloys. Key challenges remain, however, in the design or specification of materials for targeted lifetimes in particularly aggressive environments.

Conclusion (Corrosion- and Heat-Resistant Materials)

The most impressive corrosion-resistant alloys in the last half century began to be developed by metals producers. Work on amorphous metals and advanced surface treatments have been funded by university-led efforts or consortia of universities and companies. One area where industry has taken the lead recently is corrosion-resistant rebar materials where cost-effective stainless grades are being

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[8] J.R. Scully, A. Gebert, J.H. Payer, Corrosion and related mechanical properties of bulk metallic glasses, *Journal of Materials Research* 22(2):302-313, 2007; R. Huang, D.J. Horton, F. Bocher, and J.R. Scully, Localized corrosion resistance of Fe-Cr-Mo-W-B-C bulk metallic glasses containing Mn+Si or Y in neutral and acidified chloride solutions, *Corrosion* 66, 035003, 2010; doi:10.5006/1.3360908.

[9] F. Presuel-Moreno, M.A. Jakab, N. Tailleart, M. Goldman, and J.R. Scully, Corrosion resistant metallic coatings, *Materials Today* 11(10):14-23, 2008; M.A. Jakab and J.R. Scully, Storage and release of inhibitor ions from amorphous Al-Co-Ce alloys: Controlled release on demand, *Nature Materials* 4:667-670, 2005.

sought. Unfortunately this work is often not at a fundamental level but instead is aimed at achieving engineering performance without also understanding the scientific underpinning.

The development of corrosion-and heat-resistant alloys over the past century has had huge economic, environmental, and safety impacts. However, as ever greater demands are imposed on materials performance, it will be necessary to come up with new materials at an even faster pace. Given recent and continuing advances in material types, characterization techniques, alloy modeling, and an understanding of fundamental corrosion and kinetic processes, the committee believes it will be possible to rapidly evolve new materials with improved corrosion and heat resistance that are more closely integrated into design for specified lifetimes in particular environments.

Motor Vehicles

Some decades ago, it was common for automobile bodies to rust through within a few years of manufacture, especially where roads were heavily salted. Paint systems failed, pinholes in chrome plating led to the destructive corrosion of fenders, and exhaust systems had to be replaced regularly. Newer cars now come with an extended anticorrosion warranty, and the useful lifetime of a car is more often limited by the mechanical and electrical components than by the external body. Driven in part by competition between manufacturers and regulations against corrosion perforation by the Canadian government, this change has been facilitated by new protective coatings and coating application processes, more corrosion-resistant structural materials, and the incorporation of best design practices. The first company to implement zinc coatings in the automotive industry was Chevrolet, which used it on rocker panels. At the same time Porsche introduced zinc coatings on the steel frames of its cars, and other automotive companies soon followed. Today, these state-of-the-art, multilayer coating systems are not only long lasting but also more environmentally friendly and have resulted in a huge savings to consumers.

Car body panels are now routinely fabricated from two-sided galvanized steel, which provides considerable protection against corrosion. The paint primer layer, universally applied by the cathodic electrodeposition process—in combination with advanced metal pretreatments and galvanizing—results in an almost defect-free, highly protective coating system. Similarly, exhaust systems are made from relatively inexpensive but long-lasting stainless steel, while chrome trim has either been eliminated or galvanically isolated.

Polymeric materials have replaced metals in car bumpers and fenders for both corrosion resistance and weight reduction. To accomplish this, ultraviolet (UV) radiation- and heat-resistant polymers were required. Enhanced resistance to UV degradation also has been incorporated into the protective coatings on the whole car body.

What's Next for Motor Vehicles?

Corrosion science accomplishments continue to impact automotive design. For instance, altered oxide semiconducting properties in new zinc-magnesium alloys with lower self-corrosion rates promise improved lifetimes for the sacrificial galvanic layer. Even extremely corrodible metals such as magnesium are being used for weight savings with no detrimental consequences. In a DOE-supported collaboration with organizations abroad, auto manufacturers in the United States are now designing a car with a front end made completely of magnesium alloy, which is possible owing to advanced surface treatments and an understanding of galvanic isolation. There is also intense work on aluminum/magnesium engine blocks. Corrosion mitigation for these materials will certainly need the attention of the corrosion community.

Conclusion (Motor Vehicles)

Automobiles are an unambiguous example of the successful application of corrosion science and engineering to increase useful service life of an everyday item. Progress has been driven by competition, consumer demand, and regulation, supported by advances in materials and coatings. The trend to more efficient vehicles and the need for lighter materials is once more challenging the community to develop materials that resist corrosion.

Aging Aircraft Airframes

The problem of aging aircraft came to the forefront in the mid-1990s, largely as the result of the report of an Air Force Blue Ribbon Panel.[10] The Air Force had a number of aircraft that were young in terms of fatigue cycles—the typical measure of aircraft age—but old in terms of years since construction. As such, tremendous cost and effort have been required to maintain these airplanes.[11]

Related to this problem was the reliance on the environmentally undesirable, chromate-based corrosion inhibitors that were incorporated into the coatings and

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[10] National Research Council, *Aging of U.S. Air Force Aircraft: Final Report,* National Academy Press, Washington, D.C., 1997, available at http://www.nap.edu/catalog.php?record_id=5917.

[11] For U.S. Air Force aircraft, see National Research Council, *Aging of U.S. Air Force Aircraft: Final Report,* National Academy Press, Washington, D.C., 1997, available at http://www.nap.edu/catalog.php?record_id=5917.

primers used to protect the corrosion-susceptible, high-strength aluminum-copper alloys used in many aerospace applications. Furthermore, few of the fundamental corrosion characteristics of these alloys were known. For these reasons, the Air Force panel identified the need to simultaneously reduce maintenance corrosion costs and replace chromate with a more effective, environment-friendly inhibitor.

To address these issues, the Air Force Office of Scientific Research funded a number of research programs at universities. Multidisciplinary university research initiatives were initiated to study chromate inhibition mechanisms and nondestructive testing. This funding motivated other researchers and funding agencies to get involved in the field, and the number of people working in corrosion-related investigations increased substantially within a few years. At the same time, a special office integrated corrosion management into the Air Force's structural integrity program, so that the impact of corrosion on aircraft was addressed in considerable quantitative detail.

This field was active for about 8 years, from the late 1990s into the current decade, and led to considerable new understanding of the mechanisms of high-strength aluminum alloy corrosion and inhibition. However, many of these suggested improvements have yet to be implemented. Implementation of the new technologies and science developed in these studies has been delayed because of inadequate or overly time-consuming qualification test methods, most of which are qualitative rather than quantitative.

Conclusion (Aging Aircraft Airframes)

Understanding of aluminum alloy corrosion and mitigation was advanced by large multi-institutional efforts funded by government agencies and a need to address specific technological problems. However, changes in government priorities prevented the research successes from being fully developed into practical solutions.

Pipelines

More than 2 million miles of pipeline in the United States are used to transport natural gas, crude oil, petroleum products, and other petrochemicals economically and efficiently over long distances. These steel pipelines can be subjected to corrosive conditions both internally (from the aggressive fluids being transported) and externally (from the aggressive soil or subsea environments). The catastrophic failure of an oil or gas pipeline can result in loss of life and environmental disasters. In United States, more incidents/accidents in pipeline systems are due to human intervention, followed by external and internal corrosion.[12] The U.S. Depart-

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[12] Available at http://www.phmsa.dot.gov/.

ment of Transportation's Pipelines and Hazardous Materials Safety Administration (PMHSA) has been implementing regulations requiring new inspection methods and specific inspection intervals. These inspections, in conjunction with better coatings and cathodic protection systems, have been instrumental in preventing failures due to external corrosion. The PMHSA reported that serious incidents on pipelines have been reduced by more than 50 percent since 1989.

The demonstrated reliability of these pipelines has required the use of several different corrosion protection schemes. To reduce attacks on the outer surfaces of pipelines, improved cathodic protection systems and coating materials (fusion-bonded epoxy, which replaced coal tar systems) have been used along with better inspection programs.

For high-pressure natural gas transmission lines, the most feared hazards are two forms of external stress corrosion cracking: One is associated with failure of cathodic protection to penetrate to the base of a coating defect, and the other is associated with near-neutral water that has equilibrated with the soil. Decades of research using ever more sophisticated tools have pinpointed the stress and environment criteria for both kinds of stress corrosion cracking, leading to more efficient monitoring, protection, prediction, and, ultimately, mitigation.

What's Next for Pipelines?

Although significant strides have been made in the pipeline industry, future challenges do exist. For example, the corrosion science and engineering related to the transport and storage of biofuels (such as ethanol) are largely unknown. Another potentially important material system is supercritical carbon dioxide ($SCCO_2$) for transport in dedicated pipelines. This system will be significant if carbon capture and sequestration processes begin to replace fossil fuel for use in power plants, and it may present challenges for corrosion protection as the cost of purification/separation processes for $SCCO_2$ grows.[13] Although successful, the current approaches used in protection systems may not be sufficiently robust to support newer fuels, increasingly aggressive environments, and/or longer pipelines, and better schemes or new material compositions with fundamentally better corrosion resistance will likely be required. Internal corrosion due to hydrogen sulfide, carbon dioxide, and biological factors is still poorly understood. More recently, important spills that threatened the pristine environment in Alaska and the Gulf of Mexico are believed to have been caused by internal corrosion. Localized internal corrosion is difficult to evaluate by the use of "smart pigs," but no accurate predictive models to estimate pipeline life have yet been formulated.

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[13] See, for example, the April 2008 issue of the *MRS Bulletin* and T.F. Wall, Combustion processes for carbon capture, *Proceedings of the Combustion Institute* 31:31-47, 2007.

Technology for carbon capture, transportation (in pipelines), and storage in various types of underground geologic reservoirs is also viewed as an important for mitigating CO_2 emissions. Long-term containment of buried CO_2 is essential to the successful mitigation of CO_2 emissions. Supercritical CO_2 is injected into a reservoir, where it is contained by natural formations that are essentially impermeable to CO_2. However, leakage pathways could allow the escape of CO_2 into subsurface aquifers or to the atmosphere. Because dissolved CO_2 creates acidic conditions, drinking water systems could become contaminated by the leaching of species from host rock. Such leakage could occur principally from the injection well or from other wells that intersect the formation at various depths as the result of earlier oil and gas drilling. Injection wells are reasonably well engineered, but the earlier boreholes are not always in good condition. At present, there are hundreds of thousands of boreholes in the United States in various stages of disrepair. Predicting the long-term (hundreds to thousands of years) performance of these boreholes requires a combination of fundamental electrochemical models and experimental data. Such data in supercritical CO_2 or in multiphase liquid CO_2-aqueous environments are not easily available. Furthermore, emissions from various industries will introduce additional contaminants, even after the CO_2 has been purified in the capture processes. Some data show that these impurities can cause corrosion. The experience gained by the corrosion community in nuclear waste container life prediction could be utilized in CO_2 containment, but unique challenges remain for mitigating corrosion in high-pressure CO_2-water systems.

Conclusion (Pipelines)

Environmental protection and safety regulations have driven the need to assure pipeline integrity and have led to the introduction of new materials and coatings—including nonmetallics—and the application of corrosion protection principles. A fundamental understanding of corrosion and cathodic protection effects has had and will have an important part in assuring pipeline integrity under aggressive conditions, particularly as innovative material systems (perhaps adapted from other application areas) are used more widely and advances in tools for modeling and simulation are realized. Naturally, there are many other pipeline and storage issues to address in the future, such as water mains, sprinkler valves, gas tanks, double-walled tanks for underground gas storage, and hydrogen pipelines.

Medical Devices

In the early days of the medical device industry, there were significant problems with corrosion and the general degradation of materials in the aggressive environment of the human body. However, by leveraging materials advances in other industries—such as the corrosion-resistant materials used for aerospace—developers have been able to make good progress in this field.

For example, in pacemakers, the electronics and the power source—two of the most vulnerable components of the device—are protected inside a laser-welded, hermetically sealed titanium enclosure, which isolates them from the hostile environment. Electrical connections outside the device are made via corrosion-resistant glass or ceramic feedthroughs that are further isolated from the body by protective layers of well-adhering materials (e.g., special epoxies). This sophisticated sealing technology did not exist in the early days of the industry, when corrosion resulted when water entered the epoxy potted devices. Other implantable devices such as stents, orthopedic joints, and spinal appliances were originally made of stainless steels. Sometimes corrosion was observed in such implants, especially if the materials were not processed optimally. As with pacemakers, better materials, like superalloys, were borrowed from other industries. The use of materials and technologies designed for other applications allowed the implantation of medical devices to extend and enhance the quality of life for the individuals who received them. This trend continues as new technologies like ion implantation are borrowed and used in more wear-resistant materials such as those for orthopedic applications.

Recently, the concept of controlled corrosion has been proposed as a way to provide implantable devices that can perform a function (e.g., a stent or drug delivery vehicle) and then erode away over time and leave no permanent trace in the body. Some polymeric materials based on this concept have been turned into products, and some magnesium alloys are currently being investigated.

What's Next for Medical Devices?

The need for better materials for medical device implants is driven by a combination of factors, including (1) increased longevity and expectations of reliability, (2) the increasing complexity of demands on those materials as devices become more complicated, and (3) the need for safety in devices to be used in the human body. Regulatory agencies such as the Food and Drug Administration require that device companies demonstrate the functionality and biocompatibility of their materials and devices (see Figure 1.4). Such demonstration calls for both testing and modeling, but the human body is a complex system and can be difficult to model. Moreover, many of the fundamental questions related to accelerated testing, biokinetic modeling, and acceptance criteria have not been answered. However, if we can improve modeling and testing, and can elicit responses in a controlled and predictable manner, society will greatly benefit.

FIGURE 1.4 Femoral replacement part (T28) with stress corrosion cracking. Courtesy of Stanley A. Brown, U.S. Food and Drug Administration.

Conclusion (Medical Devices)

As advances in the understanding of medicine and technology allow for innovative devices and therapies, new and better materials will have to be developed for use in the human body. Up to now most of the materials used in implantable medical devices were developed for other applications and later applied for medical uses because they had some of the desired requirements (strength, flexibility, fatigue resistance, electrical conductance, corrosion resistance). However, the cost of developing and qualifying materials for implantation is often not very attractive for the many companies. Government funding for R&D in implantable medical devices is especially desirable in this area. Current understanding of how biology and materials interact is still quite primitive. To truly design new medical devices from first principles requires a far better understanding of the interface of materials and biology.

Nuclear Reactor Systems

Commercial and military nuclear reactors have experienced a wide range of corrosion problems over the past 55 years, and—starting in the 1960s—corrosion research has been put to good use to mitigate and solve those problems. All operating plants in the United States use ordinary light water with few impurities but have nevertheless been surprisingly susceptible to corrosion.

In boiling water reactor systems, the dominant problem had been intergranular stress corrosion cracking (SCC) in 304 austenitic stainless steel sensitized by welding, which was causing crippling levels of plant outage. This situation was transformed by the recognition that the cracking could be controlled by modifying the water chemistry and the surface condition of the wetted surfaces of the plant.

First, the impurity content of the water was reduced; then, hydrogen was introduced, at undesirably high levels, to lower the corrosion potential of the steel. Then, in a classic application of corrosion science, it was shown that the wet deposition of noble metals on the plant surfaces could achieve a similar level of protection with much lower hydrogen levels. All this practical mitigation was supported by extensive corrosion science research, including the development of in situ probes for monitoring hydrogen content, electrode potential, and crack growth rate.

In pressurized water reactors, corrosion problems have been associated mostly with steam generators, where nickel-based alloy 600 was originally used for the tubing that separated the primary reactor coolant water from the water that is boiled to drive the turbines. This proved to be a bad choice because the material was susceptible to SCC from both sides. However, remedial measures—including heat-treating the tubing material, retubing with a new alloy, and reducing the deposition of sludge arising from impurities in the feed water—prolonged the life of the steam generators.

In the process of this mitigation, superb research in support of critical issues was done in metallurgy, chemical engineering corrosion science, and even geochemistry. Now, the industry is in the position that it can—with fair confidence—predict extremely long life for its new plants as well as exceed the life extension targets for refurbished plants.

Both kinds of nuclear plants have experienced SCC problems of neutron-irradiated material in the core, and some of the most ambitious corrosion research of the past two decades has dealt with the resulting blend of material property alteration, microstructure, and SCC behavior using advances in modeling and characterization. As a result of experimentation and basic research, material life can be predicted more accurately, and recommendations exist for new alloys with enhanced resistance to this specialized form of SCC. The ultimate goal is quantitative prediction of life once the corrosion and degradation mechanisms have been fully understood.

Models and real-time information measured at the plants allow the plant life to be extended while still operating within technical specifications. This real-time information provides a deeper understanding of plant behavior and leads to improved plant performance. This multitiered approach of using modeling, sensors, and plant information allowed researchers to solve the problem of corrosion-triggered activity transport around the primary cooling circuit, leading to a buildup of radiation fields outside the core. Several models, in conjunction with plant data, are used around the world to predict the accumulation of those unwanted radiation fields.[14] The models take into account that the water chemistry of pressurized water reactors is affected by water radiolysis, chemical reactions, and convection of the injected chemicals like hydrogen gas, boron, and lithium (to maintain the proper percent hydrogen). Particle deposition is modeled around the entire primary coolant loop. Such modeling and monitoring are used to assure that exposure of plant personnel to radiation can be kept at levels that meet regulatory standards.

The "chemistry control" of primary and secondary coolant fluid has become a mature, integral part of nuclear reactor corrosion control, because water chemistry and the oxidizing power of the fluids are key factors in corrosion initiation phenomena and propagation rates. Water chemistry, potential, and redox electrode sensors have all been developed that enable the verification of key water chemistry variables and their manipulation in various ways to reduce corrosion. Moreover, damage sensors have been developed to help verify model predictions and confirm the beneficial effects of water chemistry "housekeeping" on rates if stress corrosion propagation. These advances in sensor and measurement technology have been instrumental in programs to extend reactor service life and to reduce reactor downtime. These measurements and others are crucial to the ability to predict the lifetime of existing and new nuclear power reactors and corrosion in both.

What's Next for Nuclear Reactor Systems?

New designs and new types of advanced nuclear power plants (e.g., supercritical steam) present the same need for in-depth understanding of corrosion processes and the associated means to control corrosion's detrimental effects. Indeed, for new plant concepts, knowledge gained from current R&D should be used prescriptively (rather than remedially and reactively, as in earlier generations of plants) in the design of components and control systems to avoid operational problems from

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[14] International Atomic Energy Agency, *High Temperature On-Line Monitoring of Water Chemistry and Corrosion Control in Water Cooled Power Reactors: Report of a Coordinated Research Project, 1995-1999*, IAEA-TECDOC-1303, July 2002; Nuclear Energy Education Research, *Electrochemistry of Water-Cooled Nuclear Reactors*, Nuclear Energy Education Research (NEER) Final Technical Progress Report, Grant No. DE-FG07-021D14334, August 8, 2006.

corrosion and environmental effects. Indeed, as water-cooled reactors are driven to higher efficiencies and burn-ups and stricter limits on safety performance, corrosion challenges will only multiply and the environments to which the materials will be subjected become more extreme. Then there are the formidable corrosion challenges in advanced (generation IV and beyond) reactor systems. Supercritical water poses extreme risks of stress corrosion failure, especially in pressure vessel designs (as opposed to the CANDU-like design), and water radiolysis in such conditions is not well enough understood to provide a baseline for definition of the environment. Neutron irradiation complicates such assessments even further. Developments in high-temperature gas-cooled systems will be plagued by corrosion issues due to impurities in the helium gas, and other advanced designs using liquid metals will be subject to various forms of degradation, including corrosion.[15,16]

Conclusion (Nuclear Reactor Systems)

In response to regulatory and economic pressures, some of the best and most critical successes in corrosion science and engineering have come about by solving a host of initially unanticipated problems related to the continued safe operation of nuclear plants.

Radioactive Waste

Disposal of high-level nuclear waste is a worldwide issue. The United States alone has 77,000 tons of high-level nuclear waste, equivalent to one half pound for every citizen. The Federal Nuclear Waste repository was established to isolate this waste for at least 10,000 years without radionuclide release, which will be dependent on the successful choice, fabrication, and total performance of an engineered waste barrier that is resistant, but not immune, to corrosion.

The total system relies on defense in depth through vitrification and immobilization of the nuclear waste within glass, the storage of borated stainless steel baskets, and enclosure in a modern corrosion-resistant alloy. An extraordinary effort has been under way around the world to verify acceptable performance over what had heretofore been unthinkable lifetimes. This has brought about some revolutionary new lines of thinking in the corrosion field—on, for instance, the theory, experiment, and modeling of extremely low corrosion rates; the revisitation of such issues as long-term passivity of alloys in complex environments; and

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[15] U.S. Department of Energy, Office of Basic Energy Sciences, *Basic Research Needs for Advanced Nuclear Energy Systems*, 2006.

[16] C. Cabet, J. Jang, J. Konys, and P.F. Tortorelli, Environmental degradation of materials in advanced reactors, *MRS Bulletin* 34(1):35-39, 2009.

on critical partnerships with experts in other fields who are able to bring insights from, and advances in, their fields to bear on the problem.

Conclusion (Radioactive Waste)

Unprecedented coupling between corrosion scientists, geochemists, and risk assessment experts can serve as a useful model for any high-priority thrust in corrosion. Our understanding of corrosion, welding, phase stability, and nickel-chromium-molybdenum superalloys has been advanced to levels equal to any other alloy system. While translation to practice awaits policy and political decisions, this research has led to a vast improvement in corrosion science and to technological confidence that an engineered waste barrier can be perfected to contain nuclear waste.

Protective Coatings for High-Temperature Combustion Turbines

Coatings are used in a variety of applications to protect alloys that exhibit attractive properties at high temperatures but would be too reactive in the service environment. For example, aluminum-oxide-forming bond coats provide superalloys used in the hot sections of gas turbines with oxidation resistance as part of the ongoing drive toward higher efficiencies and better performance characteristics for air-breathing propulsion and land-based power systems.

Alternatively, materials that already exhibit good high-temperature properties and corrosion resistance at the requisite temperatures are desirable. As such, ceramics and ceramic-composite materials such as silicon carbide have been the subject of study and development for a number of years. However, when such composites were targeted for use in combustion turbines, the presence of water vapor at elevated pressures revealed that silicon dioxide is unstable owing to its susceptibility to volatilization. Work at the National Aeronautics and Spaces Administration (NASA) Glenn Research Center and elsewhere conclusively demonstrated the impact of water vapor on silicon carbide recession and produced a robust model that definitively described the recession rates in terms of the important environmental parameters.[17] This work also indicated candidate materials that could be used for environmental barrier coatings[18] to protect these composites (Figure 1.5) and enabled the development of reliable accelerated testing of can-

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[17] See, for example, E.J. Opila, Oxidation and volatilization of silica formers in water vapor, *Journal of the American Ceramic Society* 86:1238-1248, 2003.

[18] See, for example, K.N. Lee, D.S. Fox, and N.P. Bansal, Rare earth silicate environmental barrier coatings for SiC/SiC composites and Si_3N_4 ceramics, *Journal of the European Ceramic Society* 25:1705-1715, 2005.

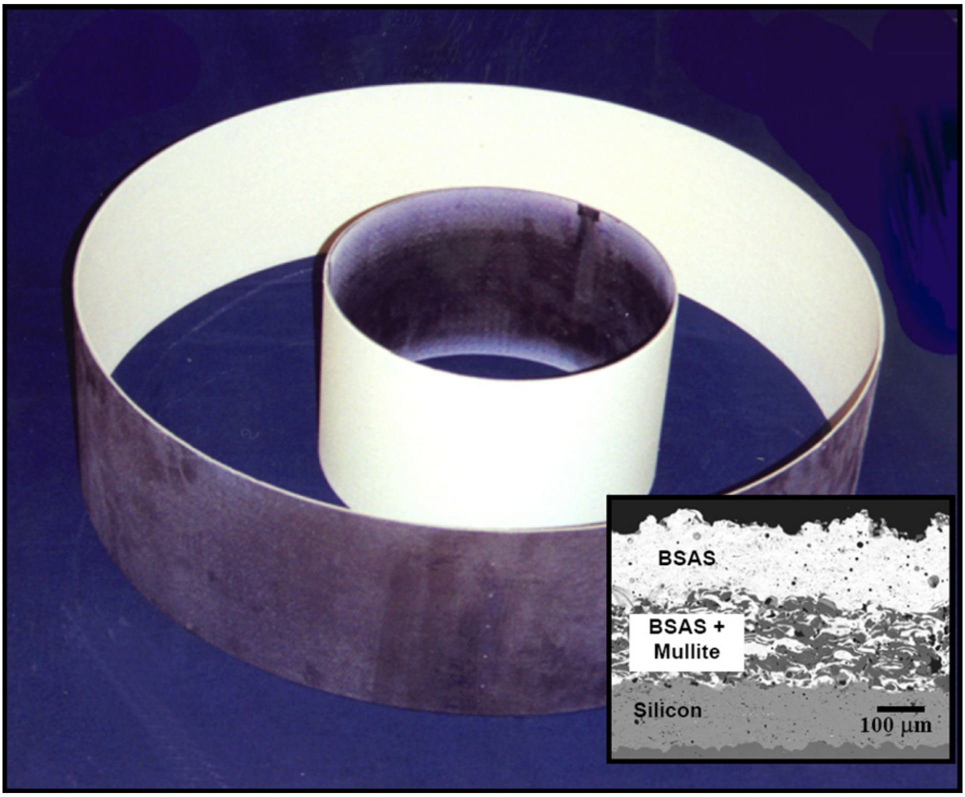

FIGURE 1.5 Combustor liner made from SiC-fiber-reinforced SiC (SiC/SiC) composite for the Solar Turbines, Inc., Centaur 50 gas turbine. An environmental barrier coating was applied to the inside circumference of the outer ring and to the outside circumference of the inner ring (the surfaces facing the combustion gas). Inset: Cross section of the coating; BSAS, barium-strontium aluminosilicate; mullite, aluminosilcate; underlying the Si layer is the SiC/SiC composite. Courtesy of Solar Turbines, Inc., and Oak Ridge National Laboratory.

didate coatings.[19] Collaborations between NASA, the national laboratories, and industrial partners have led to the development of robust processes for applying state-of-the-art coatings to SiC matrix composites.

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[19] R.C. Robinson and J.L. Smialek, SiC recession caused by SiO_2 scale volatility under combustion conditions: 1, Experimental results and empirical model, *Journal of the American Ceramic Society* 82:1817-1825, 1999; E.J. Opila, J.L. Smialek, R.C. Robinson, D.S. Fox, and N.S. Jacobson, SiC recession caused by SiO_2 scale volatility under combustion conditions: II, Thermodynamics and gaseous-diffusion model, *Journal of the American Ceramic Society* 82:1826-1834, 1999; P.F. Tortorelli and K.L. More, Use of very high water-vapor pressures to evaluate candidate compositions for environmental barrier coatings, *Proceedings of the ASME Turbo Expo 2005* 1:363-367, 2005.

What's Next for Protective Coatings?

The need for even higher engine efficiencies and performance requires materials that show extraordinary stability and resistance to degradation at environmental extremes of temperature, pressures, and reactive species.[20] Increasingly robust environmental barrier coatings will be needed, or failures as those described in Box 1.3 will continue to occur. These coatings will require the development of even more advanced mechanistic knowledge and models.

Conclusion (Protective Coatings)

Through government and industry collaborations, a fundamental understanding of the degradation mechanisms associated with high-temperature volatilization of SiC matrix composites, combined with the development of highly reliable coating processes, has paved the way for use of the high-temperature SiC matrix composites in aero propulsion and land-based combustion turbine applications. The ability to use SiC matrix composites in oxidizing environments containing water vapor and other impurities has pushed by 200°C the envelope for the temperature at which this structural material can be used, making it one of the most robust commercial materials for very high temperature applications.

SUMMARY OBSERVATIONS

There has been significant progress in the development of corrosion-resistant materials, understanding of basic mechanisms by which corrosion occurs, and the implementation of mitigation techniques. This progress has allowed for the current state of materials usage in both common and harsh environments. The primary drivers for corrosion research have been industrial and government needs. Addressing these needs has led to advances in science, as well as further practical improvements, which then provide for further scientific advances. Although there is always a possibility for doing more, the government has played a vital role in the field of corrosion research—including challenging industry with critical problems (e.g., related to access to space, nuclear power, reduced maintenance of roads and bridges, and performance of military equipment), funding and conducting research, establishing standards, and prescribing regulatory requirements for safety and health. Nevertheless, the industrial research and development base that led to many of the advances in new materials and understanding of corrosion behavior has eroded, and as such, the government agencies that have responsibilities dependent on the

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[20] U.S. Department of Energy, Office of Basic Energy Sciences, *Basic Research Needs for Materials under Extreme Environments*, report on the Workshop on Materials under Extreme Environments, June 11-13, 2007, available at http://www.er.doe.gov/bes/reports/files/MUEE_rpt.pdf.

BOX 1.3
Corrosion Challenges with Infrastructure Systems

Infrastructure systems are meant to safely serve society for long periods. Design codes provide guidance and requirements to limit the corrosion of these infrastructure systems with the objective of ensuring these longer service lives. It is generally not the objective of these codes to prevent all corrosion, but in conjunction with proper inspections to limit the risk of failure resulting from corrosion. However, these guidelines and requirements have not always resulted in long-lasting infrastructure systems. Corrosion in our infrastructure systems results in reduced structural capacities, which can lead to structural failures. Figure 1.3.1 shows the underside of a steel bridge member exhibiting significant corrosion—in this case, good inspection practices revealed the damage, thereby preventing failure. However, corrosion has led to failures (in 1967, corrosion and fatigue of an I-beam on the Silver Bridge resulted in its collapse,[1] killing 26 people who were using the bridge. More recently (2000), a pedestrian bridge in Charlotte, North Carolina, failed due to corrosion of the steel reinforcement, injuring 107 people.[2] Underground infrastructure systems also exhibit corrosion. Figure 1.3.2 shows a failed cast iron pipe. Water pipe failures throughout the United States have led to closures of subways, roads, and businesses, often temporarily crippling the local economy. In fact, the failure of large-diameter water mains has led to significant flooding and millions of dollars in

FIGURE 1.3.1 The underside of a steel bridge member exhibiting significant corrosion. Courtesy of the Texas Department of Transportation, © 2007. All rights reserved.

continued

BOX 1.3 Continued

FIGURE 1.3.2 A failed cast iron pipe. Courtesy of Mark Lewis, East Bay Municipal Utility District.

repair costs. The Pipeline and Hazardous Materials Safety Administration (PHMSA) regulates the inspection and incident reporting of pipelines carrying hazardous materials. Increased inspection requirements have led to a 40 percent reduction in serious incidents.[3] Although corrosion has resulted in and will continue to result in significant loss of economy, the implementation of sound inspection requirements have proven to reduce serious incidents and failures. With better science and engineering, a more economical solution to corrosion prevention can likely be discovered.

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[1] National Transportation Safety Board, *A Highway Accident Report, Collapse of U.S. 35 Highway Bridge*, Government Printing Office, Washington, D.C., 1971.

[2] R.P. Poston and J.S. West, Investigation of the Charlotte Motor Speedway Bridge collapse, *ASCE Conference Proceedings* 171:243, 2005.

[3] U.S. Department of Transportation Web site, http://www.phmsa.dot.gov/portal/site/PHMSA, accessed April 20, 2010.

materials used will need to consider new options. In addition, despite major differences in corrosion problems as well as solutions from industry to industry, the issue is always there. To ensure that corrosion-related issues are identified and solutions implemented, industry must be integrally involved.

Advances in corrosion research have also been facilitated over the years by developments from other fields. Major advances in materials characterization and computation and modeling in recent years make this an opportune time to address previously unsolvable corrosion problems.

New materials developments have been significant, and recent developments based on computational methodologies allow the process to occur at a much faster pace. However, corrosion resistance is not yet among the properties being optimized (see the section on integrated computational materials science and engineering in Chapter 3).

With some exceptions (see, for example, the nuclear reactor systems success story outlined above), a common element lacking in materials development and selection is the ability to predict the effects of corrosion on useful system lifetime and to use condition monitoring to detect end of life. Methodologies for accelerated testing and predictive modeling are often lacking but are nonetheless critical to the design and management of complex systems. Recent advances in data analysis and engineering practice are aimed at predicting and managing lifetime using advanced techniques of informatics, which can be of great value to knowledge discovery regarding corrosion processes and development of mitigation strategies but has, for the most part, been lacking in corrosion efforts. Hence, corrosion is not one of the properties generally considered in this new prognosis strategy. The impact of corrosion on society is very significant and affects nearly every aspect of daily life in an industrialized country. In monetary terms, degradation by corrosion causes a loss of several percent of the gross domestic product of industrialized nations every year. Other major impacts of corrosion may be challenging to estimate, such as loss of productivity, but are no less significant to society than pure monetary loss.

Although corrosion processes are inevitable, their rate of progression can be significantly curtailed by appropriate mitigation strategies. Many examples exist of how mitigation was successfully achieved after corrosion problems were observed and often became the limiting factor in the engineering lifetime of an application.

Corrosion research has been inspired by application needs, seeking to understand the specific details of the mechanisms of corrosion. Mitigation, which is a corrosion engineering activity, has been most successful when it has been guided by an understanding of the forces driving corrosion processes.

2

Corrosion Research Grand Challenges

This chapter presents the committee's thoughts about grand challenges for the broad field of corrosion science. The committee developed a working definition of a corrosion grand challenge, applied that definition to guide the identification of specific corrosion grand challenges, and then explored ways to prioritize these grand challenges. The results of the three steps—definition, identification, and prioritization—are presented in this chapter. Chapter 3 then describes representative samples of leading-edge research opportunities within each corrosion grand challenge area.

It is clear that this committee is not the first to have thought about grand challenges. Various agencies and organizations have used different approaches to the development of grand challenges, some of which are outlined in Box 2.1.

DISCOVERING THE CORROSION GRAND CHALLENGES

For the purposes of this study, the committee established the following as the criteria that a corrosion research grand challenge must meet:

- The corrosion research problem is demonstrably difficult to solve.
- The problem involves something that was not solved in the past, but may prove to be readily solvable if modern techniques are applied to the research.
- The problem requires significant contributions from multiple scientific disciplines.

BOX 2.1
Examples of Other Grand Challenges and Their Uses

In March 2009 the National Academy of Engineering organized a grand challenge summit that defined a list of 14 leading engineering challenges for the 21st century.[1] These grand challenges encompassed broad areas of human concern—sustainability, health, vulnerability, and joy of living—and encouraged the technical community to forge a better future by addressing the challenge areas. Although "corrosion" was not specifically mentioned in the resulting report, a case can be made that corrosion does affect each of the above four areas of human concern.[2]

The high-performance computing (HPC) community has effectively used grand challenge problems to define and focus resources on accomplishing "really difficult" tasks.[3] The HPC grand challenges have been in the vanguard of the supercomputing revolution.

Another example is evident in the grand challenges developed by the computational astrophysics community to stimulate interchanges among computational astrophysicists and applied mathematicians. A result has been identification of current barriers to algorithmic efficiency and accuracy, which has motivated a search for creative ways to surmount those barriers, or to decisively demonstrate that certain limitations are unavoidable.[4]

The National Science and Technology Council sponsored the report *Grand Challenges for Disaster Reduction,*[5] which provided a framework for prioritizing federal investments in science and technology with the goal of reducing the impact of disasters. If met, the resulting six grand challenges targeting America's capacity to prevent and recover from disasters would enhance the safety and economic well-being of the country.

The American Association of State Highway and Transportation Officials adopted the grand strategy approach to identify seven high-level critical problem areas for bridge engineering that, if solved, would lead to significant advances in bridge design and reduced life-cycle costs. The resultant study *Grand Challenges: A Strategic Plan for Bridge Engineering*[6] included a grand challenge, "extending service life," that highlighted the need for improved corrosion-resistant materials and coatings, and improved corrosion-mitigation methods.

The Department of Energy's Basic Energy Sciences organization has consistently used the grand challenge approach to identify difficult science problems across a range of basic research areas.[7]

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[1] National Academy of Engineering, *Grand Challenges for Engineering,* The National Academies Press, Washington, D.C., 2009.

[2] Typically, corrosion research needs are rarely explicitly identified, and when they are mentioned it is within the context of a discrete engineering goal.

[3] What are grand challenge problems?, *Inside HPC,* September 16, 2006, available at http://insidehpc.com/2006/09/16/what-are-grand-challenge-problems/.

[4] See "Grand Challenge Problems in Computational Astrophysics," available at http://www.ipam.ucla.edu/programs/pca2005/.

[5] National Science and Technology Council, *Grand Challenges for Disaster Reduction: A Report of the Subcommittee on Disaster Reduction,* June 2005, available at http://www.nehrp.gov/pdf/grandchallenges.pdf.

[6] Association of State Highway and Transportation Officials, Highway Subcommittee on Bridges and Structures, *Grand Challenges: A Strategic Plan for Bridge Engineering,* June 2005, available at http://bridges.transportation.org/Documents/2005strategicplan-websiteversion.pdf.

[7] See basic research needs reports, available at http://www.er.doe.gov/bes/reports/list.html.

- The focus is on mitigation and prevention of detrimental corrosion processes, as opposed to beneficial applications of corrosion processes.[1]
- The solution will have a significant economic and/or social impact or overcome obstacles to desirable key technology required by society such as clean water and abundant environmentally benign energy.

The committee then considered two main approaches to developing a set of corrosion grand challenges:

- *Hierarchical (top-down)*, starting with an overarching context for a grand challenge. For example:
  - —Formulate a set of societal grand challenges, and then identify corrosion research grand challenges that support these societal challenges.
  - —Identify major barriers to engineering accomplishments caused by corrosion.[2]
- *Technological (bottom-up)*, developing grand challenges based on difficult technical problems. For example:
  - —Identify the critical gaps in understanding of the various forms of corrosion, and select those that might have the most far-reaching or transformative consequences. This mechanistic approach could be divided between classical aqueous metallic corrosion, corrosion issues related to non-metallic materials, and non-aqueous metallic corrosion such as high-temperature gaseous oxidation.
  - —Determine how recent fundamental breakthroughs in the underlying enabling science might be used to solve corrosion problems that have long been considered unsolvable, or applied to advanced materials subject to extreme environments.

The committee decided to combine the hierarchical and technological approaches (see Figure 2.1). First, it identified the top national priorities or goals, which are the far-reaching societal demands that trigger future technology advancements. The committee then linked those drivers to the various U.S. federal agencies with missions in each of those areas. Applying its members' knowledge of gaps in knowledge of corrosion, the committee identified key areas for corrosion research and correlated them with the societal drivers to formulate a list of challenges for

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[1] For example, many batteries rely on anodic corrosion processes.

[2] A drawback of this approach is that a narrow focus would not necessarily lead to a comprehensive solution so that multiple applications may not benefit for the research.

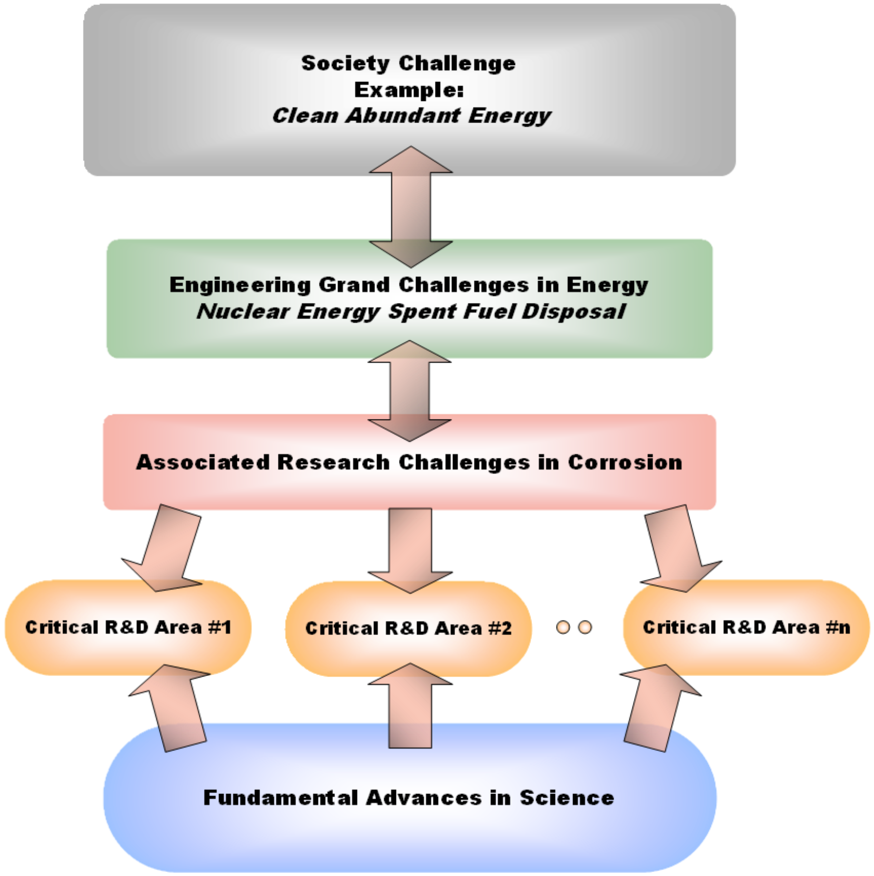

FIGURE 2.1 Corrosion grand challenges and how they lead to critical research and development areas. Courtesy of J.R. Scully, presented at NACE 2009.

future research.[3] Finally, the committee aggregated and generalized the list of challenges to avoid narrowing the range of corrosion problems. The result was a small set of corrosion grand challenges.

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[3] This approach was similar to that taken by the Department of Transportation in developing decision-making strategies for the future: a set of external forces and trends were identified and cross-matched with a set of research focus areas; see "Long Range Strategic Issues Facing the Transportation Industry—Final Research Plan Framework," prepared for National Cooperative Highway Research Program Project 20-80, Task 2, by ICF International, October 17, 2008, available at http://onlinepubs.trb.org/onlinepubs/archive/NotesDocs/NCHRP20-80(2)_FR.pdf.

LINKING TECHNICAL GRAND CHALLENGES TO SOCIETAL NEEDS

Top-level priorities for federal investment are contained within each federal agency's strategic plan, budget requests to Congress, presidential speeches, congressional hearings, and so on. It is these high-level national priorities that guided the committee in its identification of overarching societal priorities for protection against and mitigation of corrosion. The top national priorities were categorized as infrastructure, health and safety, energy, environment, national security, and education.[4]

The federal agencies and departments associated with these national priorities have distinct roles in corrosion research, as outlined in Figure 2.2. Additional details are given in Appendix E.

In broad terms, the issues in corrosion science and engineering can be subdivided into four key areas for research and development:

- Design (materials modeling tools),
- Mitigation (corrosion protection and maintenance methods, corrosion modeling tools and databases, design rules, lessons learned),
- Detection (corrosion damage assessment), and
- Prediction (life extension, prognosis).

Following the approach to analysis depicted in Figure 2.1, the committee considered critical gaps in current understanding of corrosion science that affect each of the societal drivers for the four key corrosion research areas. The committee developed a set of 11 representative corrosion challenges (Table 2.1) that, although not intended to be a comprehensive compilation of all the important challenges in corrosion research and development, does reveal many connections to the societal drivers. When coupled with Figure 2.2, the information in Table 2.1 suggests the relevance of corrosion research challenges to the intended goals of federal agencies with missions in these societal areas.

CORROSION GRAND CHALLENGES

The list of 11 challenges in Table 2.1 was sufficiently comprehensive to allow the next step of analysis—identifying the corrosion grand challenges. With the challenge "constructive uses of corrosion" eliminated as not applicable to materials

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[4] These are essentially the same priorities as those identified in National Research Council, *Assessment of Corrosion Education,* The National Academies Press, Washington, D.C., 2009, available at http://www.nap.edu/catalog.php?record_id=12560.

TABLE 2.1 Matrix of Challenges and Societal Drivers That Lead to Corrosion Research Opportunities

Challenges	Infrastructure	Health and Safety	Energy	Environment	National Security	Education
Cost-effective corrosion- and stress corrosion/hydrogen embrittlement-resistant materials	✓	✓	✓		✓	✓
Environmentally friendly materials, coatings, and inhibitors		✓		✓		
Understanding the nature of protective films and scales, including structure		✓	✓		✓	
Complete and comprehensive understanding of electrochemistry and other interfaces from the electronic to the microscale level	✓	✓	✓	✓	✓	✓
Lifetime modeling and prediction, design for specific corrosion properties, quantitative environmental corrosion intensity factor	✓	✓	✓	✓	✓	✓
Advanced coatings, including long-lasting paint and functional coatings	✓	✓		✓	✓	
Science of accelerated testing; quantitative assessment technique for corrosion rate in “difficult” electrolytes	✓	✓	✓	✓	✓	✓
Product and reaction pathways in systems with multiple environmental stresses		✓	✓		✓	
Constructive uses of corrosion (synthesis, mechanistic understanding of functional processes)		✓	✓			
Effects of stress and cracking	✓	✓		✓	✓	
Prognosis—sensors, detection, remote monitoring		✓	✓		✓	

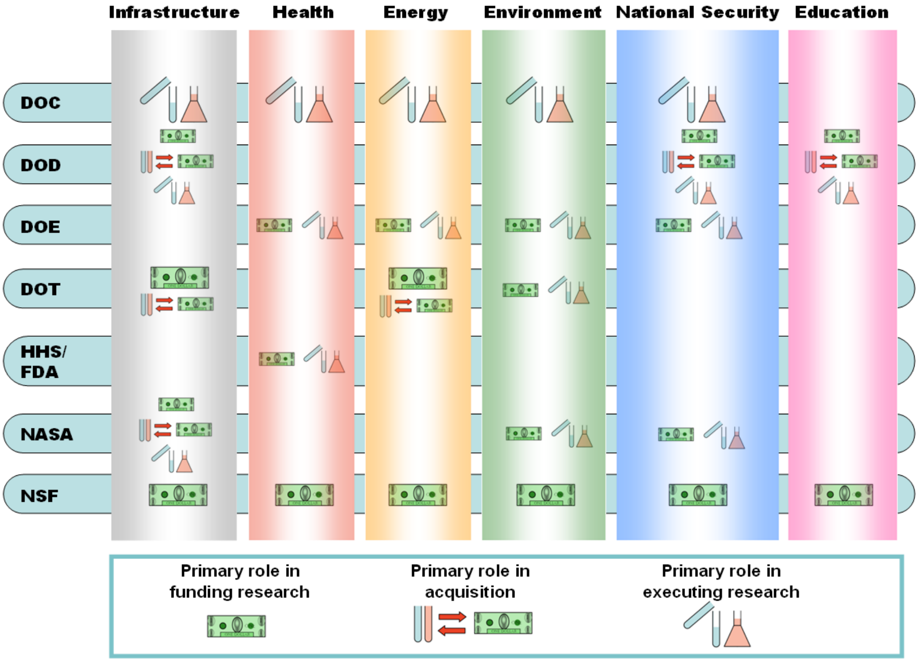

FIGURE 2.2 Principal U.S. government agencies that invest in corrosion research and their relation to the top national priorities emphasized by the committee. NOTE: Not included are three agencies critical to U.S. national priorities but not central to the subject of this report—the U.S. Department of Agriculture, the Environmental Protection Agency, and the Department of the Interior. Activities in the purview of these three depend on a capacity to protect against and mitigate corrosion, but the three are not organized to do research in these areas.

degradation, Table 2.2 indicates how the 10 remaining challenges were grouped by the committee to yield four corrosion grand challenges (CGCs):

CGC I—Development of cost-effective, environment-friendly corrosion-resistant materials and coatings;

CGC II—High-fidelity modeling for the prediction of corrosion degradation in actual service environments;

CGC III—Accelerated corrosion testing under controlled laboratory conditions that quantitatively correlates to observed long-term behavior in service environments; and

CGC IV—Accurate forecasting of remaining service time until major repair, replacement, or overhaul becomes necessary—i.e., corrosion prognosis.

TABLE 2.2 Correlation of Corrosion Challenges to Corrosion Grand Challenges

Challenge	Key Area for R&D	Grand Challenge
Cost-effective corrosion- and stress corrosion/hydrogen embrittlement-resistant materials	Design, Mitigation	CGC I Development of cost-effective, environmentally friendly corrosion-resistant materials and coatings
Environmentally friendly materials, coatings, and inhibitors	Design	
Advanced coatings, including long-lasting paint and functional coatings	Design	
Understanding the nature of protective films and scales, including structure	Prediction	CGC II High-fidelity modeling for the prediction of corrosion degradation in actual service environments
Complete and comprehensive understanding of electrochemistry and other interfaces from the electronic to the microscale level	Prediction	
Lifetime modeling and prediction, design for specific corrosion properties, quantitative environmental corrosion intensity factor	Prediction, Mitigation	
Product and reaction pathways in systems with multiple environmental stresses	Prediction	
Effects of stress and cracking	Prediction	
Science of accelerated testing; quantitative assessment technique for corrosion rate in "difficult" electrolytes	Prediction	CGC III Accelerated corrosion testing under controlled laboratory conditions that quantitatively correlates to observed long-term behavior in service environments
Prognosis—sensors, detection, remote monitoring	Detection, Prediction	CGC IV Accurate forecasting of remaining service time until major repair, replacement, or overhaul becomes necessary—i.e., corrosion prognosis

The four CGCs developed by the committee represent engineering, science, and technology challenges deemed to incorporate the drivers and guiding principles of a framework for prioritizing research and development activities. However, the committee strongly notes that addressing these challenges will demand an integrated body of cross-disciplinary and interdisciplinary scientific and engineering research targeted at specific needs and coordinated to minimize duplication and to take advantage of synergism.

As depicted in Figure 2.3—a hierarchical representation of the four corrosion grand challenges, supported, as they must be, by the body of corrosion science and engineering research—the ultimate proactive challenge is the development of materials that resist corrosion for a given application (CGC I). The remaining three corrosion grand challenges effectively address the design and in-service life cycle of functional components: (a) CGC II leads to the development of modeling tools and databases that will allow calculation of the degree of corrosion attack and the effort required to reduce its impact, for a particular application given the material of interest, sufficient knowledge of the anticipated corrosion environment, and the different corrosion processes of concern. This capability will allow quantitative consideration of the life-cycle costs for different design solutions during the acquisition phase of a system that will be subject to corrosive environments. (b) CGC III attacks the thorny issue of extrapolating, with high fidelity, expected field performance based on laboratory-scale testing. The crux of the challenge is that there is a large mismatch between the time available for laboratory testing,

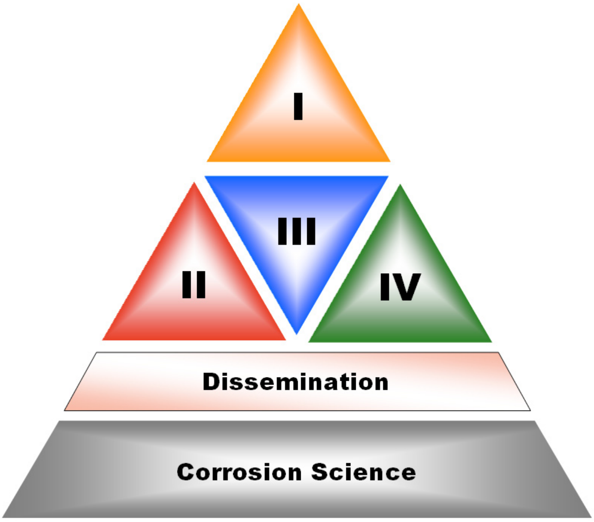

FIGURE 2.3 Hierarchy of corrosion grand challenges identified by the committee.

typically on the order of months, and the time that a structural or functional component will be in service, typically many years. Therefore, laboratory testing must be accelerated, requiring significant knowledge of the underlying corrosion mechanisms and the expected corrosive environment, including temporal variations in key environmental parameters. (c) CGC IV addresses the critical need to monitor the actual deterioration of a component once it is placed in service in a corrosive environment and then provide a reasonable forecast of the remaining time before a maintenance or replacement action is required.

Underlying all these applied issues is a strong need to resolve basic mechanistic issues that are barriers to progress in CGCs I through IV. The committee felt that addressing these mechanistic issues is essential to reducing gaps in understanding. Also essential is the dissemination of the fundamental information that will enable other grand challenges to be addressed.

ADDRESSING THE GRAND CHALLENGES: A NATIONAL CORROSION STRATEGY

Each of the four corrosion grand challenges (see Figure 2.3) addresses important societal needs. The committee recognizes that each federal agency and department must establish its own priorities for investing in corrosion research, depending on the nature and relevance of corrosion damage with respect to their individual missions and their underlying science and technology capabilities. Their diverse responsibilities may include funding and performing research as well as leveraging what is already known about corrosion control and mitigation to reduce the cost of corrosion for their mission applications. Accordingly, the committee recommends that each agency and department utilize the corrosion grand challenges proposed here and the underlying research opportunities as a framework for prioritization, based on expected benefits for its mission, and using methodologies consistent with an appropriate plan for allocating resources. Furthermore, the committee encourages development of a process that involves industry and professional and scientific societies to facilitate rapid dissemination of results. Examples are shown in Box 2.2.

The corrosion research opportunities presented in Chapter 3 of this report support the corrosion grand challenges presented above. In prioritizing these research opportunities, various factors should be taken into account, including expected societal value, degree of scientific difficulty, and the time required to attain a meaningful benefit. (See Box 2.2 for some examples.) Societal impact can be measured in different ways, such as the magnitude of the potential problem or the probability (or frequency) of its occurrence. Some corrosion problems might be solved fairly readily, and priorities could be established by identifying which research avenues are likely to yield the greatest or most rapid payoff, as measured

BOX 2.2
Examples of Corrosion Challenges and Societal Needs

Challenge: Cost-effective corrosion-resistant materials
Societal Driver: Energy
Need: Lack of cost-effective materials leads to high energy costs, including inability to fully develop energy resources.
Example: Deep offshore oil and gas wells—current piping materials suitable for harsh corrosion environments are quite expensive and can account for an appreciable fraction of the cost of developing these resources. Also, some oil and gas fields are not economical to develop as a result.
Research Opportunity: Surface modification of lower-cost materials to impart required corrosion resistance, and use of fundamental materials understanding and combinatorial methods to develop new corrosion-resistant alloys that are inherently less expensive to manufacture and field

Challenge: Remote detection and monitoring of corrosion
Societal Driver: Safety
Need: Manage aging infrastructure structures that suffer from corrosive degradation.
Example: Dams and bridges (highway and railroad)
Research Opportunity: Development of highly durable, accurate corrosion sensors suitable for remote application; development and validation of algorithms that use sensor information to determine extent of life degradation and predict when maintenance actions will be necessary

Challenge: Cutting by half the cost of materials for energy systems
Societal Driver: Energy
Need: Lack of cost-effective materials leads to high energy costs, including inability to fully develop energy resources.
Example: Solar concentrating technologies such as parabolic dish, trough, and Scheffler reflectors can provide process heat for commercial and industrial applications. However, the reflectors need to retain their surface properties and not corrode.
Research Opportunity: New production methods to produce coatings that can protect the surface of reflectors for solar concentrating technologies

Challenge: Improving the safety of the built infrastructure by 10 percent
Societal Driver: Safety
Need: Manage aging infrastructure that suffers from corrosive degradation.
Example: As infrastructure is built or rehabilitated, life-cycle cost analysis should be performed for all infrastructure systems to account for initial construction, operation, maintenance, environmental, safety, and other costs reasonably anticipated during the life of the project.
Research Opportunity: Algorithms to better predict costs of maintenance and protection against corrosion of infrastructure, which could enable effective up-front decisions about, for example, materials selection

continued

BOX 2.2 Continued

Challenge: Advanced coatings, including long-lasting paints and functional coatings
Societal Driver: Safety
Need: Lack of cost-effective materials creates maintenance problems leading to safety problems.
Example: Bridge paint is often incorrectly applied or incorrectly chosen, causing many corrosion problems, especially in areas not open to direct human inspection; underperforming corrosion-protective paint was part of the Minneapolis I-35W Bridge failure in 2007
Research Opportunity: New polymers; new application methods; new inspection methods; new coating materials (pigments, inhibitors); improved durability in the face of exposure to ultraviolet radiation

Challenge: Environmentally friendly inhibitors
Societal Driver: National security
Need: For environmental and health reasons, future military systems may be required to eliminate use of chromate inhibitors and heavy-metal coatings. Use of composite structures (e.g., polymer composites that contain carbon fibers) can exacerbate the corrosion attack of contacting metals.
Example: Advanced fighter aircraft utilize advanced carbon-reinforced composites in contact with metallic structural elements.
Research Opportunity: Design of environmentally benign barrier coatings using fundamental understanding of materials science and mechanisms of active corrosion

by the potential return on investment or savings, increased safety, or enhanced quality of life. Alternatively, priorities could be based on selecting research that is expected to be the most transformative and far-reaching.

To tackle the full range of research opportunities that address societal needs, a robust research portfolio must contain a balance of programs that provide both incremental benefits and large, transformative benefits. The matrix in Figure 2.4 shows one strategy that a federal agency could use in building a balanced corrosion research portfolio and indicates examples of research projects in each quadrant.

> **Recommendation:** Using as guidance the four corrosion grand challenges developed by the committee, each federal agency or department should identify the areas of corrosion research pertinent to its mission and draw up a road map for fulfilling its related responsibilities. In doing so, each should take a cross-organizational approach to planning and execution and should include input from industrial sectors that have experience in handling corrosion.

		Number of Occurrences in Society	
		High	Low
Impact of Corrosion Research and Development	Transformative	Difficult Technical Problem with Significant Societal Impact *Example:* Accurate prediction of corrosion damage accumulation in a highly stressed pipeline structure subject to multiple corrosion modes Develop and validate an accelerated laboratory test that quantitatively correlates to field experience	Advanced Material System Applied to Severe Environment *Example:* Silicon-carbide ceramic matrix composite airfoils in turbine engine Develop environmental barrier coating that is protective against water vapor, stable at high temperatures, and accommodates high strain induced by thermal transients.
	Incremental	Readily Solved Problem with High Return on Investment *Example:* Increase life of reinforced concrete pavement used for highway infrastructure Develop and validate long-term cost-effective protective coating for reinforcing steel.	Readily Solved Problem with High Societal Impact *Example:* Bio-compatible materials for implant devices Develop and quantify materials that exhibit high durability and efficacy in human tissue without negative biological effects.

FIGURE 2.4 Suggested strategy for developing a corrosion research portfolio.

For most federal agencies, with the exception of DOD and NASA, the committee was unable to discern a coherent, integrated top-level corrosion strategy or roadmap. In general, federal agencies play multiple roles by which they could influence the corrosion community and supporting industries: as purchasers of equipment and facilities, as sponsors of scientific research and engineering developmental work, as developers and enforcers of regulations and standards, and as sources of best-practice information for use by state governments, industries, and small businesses. For agencies that do not have a strategic plan, corrosion research appears fragmented, and funding is allocated without considering the full impact on agency activities. While each agency and department must play a role consistent with its own mission, isolated government programs can lead to duplicative efforts, reduced opportunities for synergistic progress, and difficulty in focusing interdisciplinary research teams on addressing large-impact research opportunities.

To address such issues and to establish its proposed national corrosion strategy as a multi-agency effort that must be aimed at maximizing societal benefit, the committee emphasizes the need for cross-agency coordination and policy oversight.

Recommendation: The Office of Science and Technology Policy (OSTP) should acknowledge the adverse impact of corrosion on the nation and launch a multiagency effort for high-risk, high-reward research to mitigate this impact. OSTP should set up a multiagency committee on the environmental degradation of materials. It should begin by documenting current federal expenditures on corrosion research and mitigation and then encouraging multiagency attention to issues of research, mitigation, and information dissemination. Collaboration among departments and agencies should be strengthened by collaboration with state governments, professional societies, industry consortia, and standards-making bodies.

3

Research Opportunities

Industry and government needs have been the primary drivers of corrosion research, the results of which have often led to new science, followed by further practical improvements in a continuing symbiotic cycle. Government has played many critical roles, including challenging industry with critical problems (such as the need for applications that can function well in extreme environments encountered, for example, during propulsion, and new synthetic-fuel, energy-storage, and fuel-cell concepts)[1] and also performing and sponsoring research to address critical gaps in understanding. Future corrosion research priorities should continue to be guided by societal drivers and associated technological needs (top-down drivers), but progress in this area will also benefit from advances enabled by focusing on related areas of fundamental science (bottom-up drivers). The strong interactions between engineering-oriented corrosion grand challenges and the underlying fundamental science as discussed in Chapter 2 are illustrated by the iconic triangle shown there whose foundation is corrosion science.

The impact of corrosion on everyday life is a major issue, given that corrosion and materials reliability affects public infrastructure, industrial complexes, and major areas of governmental endeavor and responsibility. The deleterious effects of corrosion and its societal impact are highlighted by growing concerns about public safety, endangerment of personnel, national security, energy security, national de-

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[1] Department of Energy, *Basic Research Needs for Materials Under Extreme Environments*, Report of the Basic Energy Sciences Workshop on Materials Under Extreme Environments, June 11-13, 2007, available at http://www.sc.doe.gov/bes/reports/files/MUEE_rpt.pdf.

fense, industrial productivity, economic competitiveness, environmental protection and sustainability, and the standard of living and quality of life. Numerous what-if scenarios suggest ways that fundamental advances in corrosion science could have a positive impact on numerous problems facing society. What if fundamental science uncovered so-called silver bullets in materials or coating designs for mitigation of corrosion that could extend the use of cost-effective materials into more extreme environments or enhance materials capabilities for energy storage? The ability to effectively address many societal and technological challenges could benefit from game-changing advances in corrosion science.

Corrosion science, a truly interdisciplinary field that includes aspects of physics, materials science, surface science, electrochemistry, and fracture mechanics, benefits directly from new developments not only in those associated fields of fundamental science, but also in others. One challenge for the corrosion science community is to pursue strategies to harvest those diverse benefits and apply them to corrosion-related problems.

The multidisciplinary nature of corrosion research requires a balanced portfolio of single investigator and collaborative group activity. Group efforts at various government laboratories have addressed corrosion problems, and some continue at this time. In academia, however, funding for group efforts is difficult to find, particularly for fundamental and applied problems. National Science Foundation (NSF) funding, with the exception of that for large centers, tends to focus on single-investigator projects. A model of what is required is the DOD Multidisciplinary University Research Initiative (MURI) program, which supports research by small teams of investigators from more than one traditional science and engineering discipline in order to accelerate both research progress and the transition of research results to applications. Most MURI efforts involve researchers from multiple academic institutions and academic departments and include support for up to 5 years.

Corrosion science remains a fertile scientific endeavor, poised for advances that will benefit society. As in the past, these advances will be enabled by progress in related fields, particularly in materials characterization and computation. Indeed, an overarching observation is that the amazing recent advances in these areas portend well for the future of corrosion science as capabilities for refining time and length scales allow modeling and experimentation to converge.

While corrosion traditionally has been observed at the macroscale, recent scientific emphasis has shifted to understanding the processes at smaller length (and time) scales. For example, many corrosion processes are now known to be controlled by molecular-, submicrometer-, and micrometer-scale phenomena. Although much has to be learned regarding the nanoscale chemistry, structure, and dynamics at individual grain boundaries or other key material features, progress is also required at the granular scale to understand how networks of boundaries and arrays of defects behave under corrosive conditions for metallic and nonmetallic materials. Thus multiscale characterization and modeling will enable progress in understanding this phenomenon.

This chapter highlights some of the research opportunities that hold great promise for corrosion mitigation, organized according to the four corrosion grand challenges (CGCs) identified by the committee:

- CGC I—Development of cost-effective, environment-friendly corrosion-resistant materials and coatings;
- CGC II—High-fidelity modeling for the prediction of corrosion degradation in actual service environments;
- CGC III—Accelerated corrosion testing under controlled laboratory conditions that quantitatively correlates to observed long-term behavior in service environments; and
- CGC IV—Accurate forecasting of remaining service time until major repair, replacement, or overhaul becomes necessary—i.e., corrosion prognosis.

As indicated in each section, high-priority fundamental science issues are at the heart of the ability to predict corrosion damage, design new materials and coatings, and sense as well as predict corrosion. The section below is not intended to be an exhaustive compilation of all corrosion research opportunities. Instead, it highlights some of the challenges in the field of corrosion science and engineering in each of the important high-priority areas identified by the committee. An underlying theme is the need for participation by multidisciplinary and cross-disciplinary teams of researchers, in addition to the individual investigator, to address the above corrosion grand challenges, as well as the need to disseminate the knowledge acquired to the greater community.

This chapter also includes a section on opportunities in instrumentation that briefly describes some of the analytical techniques that have enabled and will continue to enable ongoing advances in corrosion science and mitigation of corrosion.

OPPORTUNITIES FOR RESEARCH

CGC I: Development of Cost-Effective, Environment-Friendly Corrosion-Resistant Materials and Coatings

Development of superior corrosion-resistant materials and coatings is the ultimate proactive corrosion challenge. While this has long been a goal, it has not been realized in many applications for a number of reasons, including the strategy of using trial-and-error approaches for material development, the high cost of achieving an ultimate materials solution, the lack of fundamental knowledge about how to design a materials system expressly to resist corrosion while also meeting all the other mechanical and physical property requirements, and inadequate understanding of corrosion processes that degrade materials, including the very definition of the corrosive environment itself.

The research opportunities identified are those that address key needs in the development of:

- Corrosion-resistant materials,
- Protective coatings, and
- Materials for active corrosion protective systems.

Together with factors that impact the recyclability of materials, they suggest the type and scope of effort needed to make progress toward the goal of CGC I. Surface materials science is closely linked to corrosion behavior and should also be a focus of technologies in CGC I. Advances in corrosion mitigation will require better understanding of surface structure and properties.

Development of Corrosion-Resistant Materials

The design stage of a product or system is one of the first lines of defense against corrosion, and a designer should have the ability to prevent the onset of corrosion by choosing materials that are as intrinsically resistant to corrosion and environmental degradation as possible. By carefully considering materials choices, it is possible to affect the thermodynamic stability and/or alter the rate of corrosion kinetics, and thus appreciably impact performance of the system over time. As stated in the 2004 Defense Science Board Task Force report on corrosion,[2] "an ounce of prevention is worth a pound of cure." ICMSE will soon be possible,[3] and there is the opportunity to tailor microstructure, composition, and processing to achieve corrosion properties to meet the needs of a design if certain scientific barriers are overcome. Increasingly, environmental concerns are driving the need for engineering materials with intrinsic corrosion resistance,[4] but high-performance corrosion-resistant materials are often too expensive to use for applications where

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[2] See Defense Science Board, *Corrosion Control,* Final Report ADA428767, October 2004, available at http://www.acq.osd.mil/dsb/reports2000s.htm.

[3] National Research Council, *Integrated Computational Materials Science and Engineering: A Transformational Discipline for Improved Competitiveness and National Security,* The National Academies Press, Washington, D.C., 2008.

[4] For instance, large amounts zinc, and copper are exposed to the environment as parts of structures such as roofs, facades, and support beams; atmospheric corrosion of these structures results in unintended release of metal ions by run-off and then dispersion into the environment.

large amounts would be required.[5] Clearly one opportunity lies in creating cheaper materials with high performance. Other engineering considerations—such as joining and fabricating—also play important roles in deciding whether a particular material can be used in an application.

As described in Chapter 1, the traditional materials development process is long and drawn out, requiring multiple iterations in chemistry, microstructure, and processing methods to achieve desired material properties. In the past, optimization of corrosion properties has been achieved by trial-and-error, lessons learned, or—at best—by corrosion experts using a mix of empirical experience blended with some scientific intuition. One vision for the inclusion of corrosion in quantitative materials design is the development of focused tool-kits that can be used to optimize the development of materials, coatings, and treatments for mitigation of targeted corrosion processes—such as paint delamination, crevice corrosion, or high temperature selective alloy depletion of coatings. The lack of such a process for rapid, "intelligent" materials development in corrosion has been a major impediment to making significant improvements in the design of new products but also represents a significant opportunity to move this area forward when such tool-kits are developed. Integrated computational materials science and engineering (ICMSE) has shown the potential to optimize a new material relative to its required properties and cost through advanced computational tools and supporting databases.[6] Figure 3.1 contrasts the traditional approach with the ICMSE approach.

The ICMSE approach is based on computer modeling and simulations that have a high fidelity to physical experiments. Consequently multiple iterations equivalent to alloy development cycles can be conducted quickly, at low cost, by analysis (with selective physical experiments) compared to the traditional entirely physical materials development approach. This is revolutionizing materials development and reducing the time necessary to do so by more than 50 percent.[7] Key to the advance of this process have been advances in other engineering tools and the rapid increase in available computational power. Clearly, development of new materials using this technology is strongly dependent on the availability of good models, which

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[5] For example, many superalloys are mainly used in very high value situations such as nuclear reactors, aircraft engines, equipment handling reactive, dangerous chemicals, or implantable medical devices. Because of this, much of our infrastructure is constructed using less-sophisticated materials such as ordinary concrete with carbon steel reinforcement.

[6] National Research Council, *Integrated Computational Materials Science and Engineering: A Transformational Discipline for Improved Competitiveness and National Security,* The National Academies Press, Washington, D.C., 2008.

[7] The time to develop new high temperature single crystal nickel-based superalloys with low rhenium content was reduced by more than 50 percent (see R. Schafrik, Accelerating materials and process development, International Association of Air Breathing Engines, ISABE2009 paper ISABE-2009-1167, September 2009).

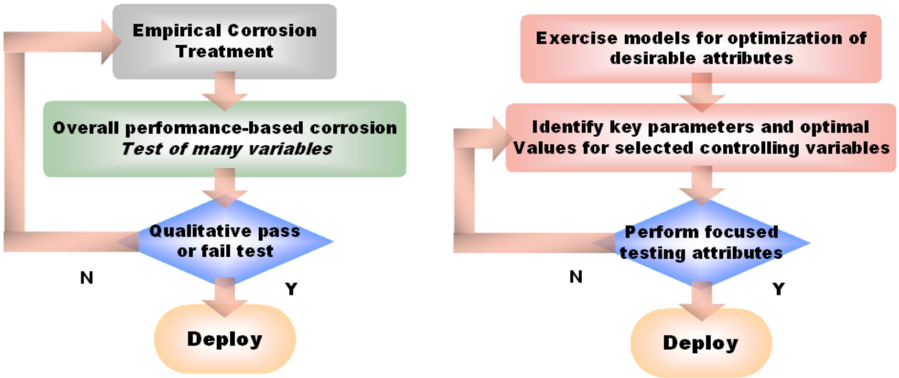

FIGURE 3.1 Comparison of existing or traditional approach (left) and desired approach (right) to the design of corrosion-resistant materials. SOURCE: John R. Scully, Department of Defense Corrosion Conference, 2009.

is discussed later in this chapter as part of CGC II. A significant opportunity for research consists of developing and integrating corrosion models (discussed under Corrosion Grand Challenge II) with other materials models so that high-fidelity predictions can be made regarding corrosion behavior for new materials and new corrosion environments. With this integration, the following types of problems are among those that could be addressed by the ICMSE approach.

- *Identifying the elements that act in synergy with other major alloying elements to enhance the intrinsic effects of corrosion mitigating elements.* For instance, additions of molybdenum and minor amounts of nitrogen to stainless steels, copper to weathering steels, and arsenic as well as tin to brass have been found to be incredibly potent strategies to improve aqueous and atmospheric corrosion resistance. The expectation is that other such combinations of elements are soon to be discovered for other materials systems.
- *Improving the properties of ultra-high-strength stainless steels that are desired for critical applications within aerospace, such as highly durable bearings, power transmission shafts, and aircraft landing gear structures.* Advanced modeling tools have the potential to guide the selection of an optimum chemistry balance in which general corrosion resistance is improved without increasing the susceptibility to at the expense of other modes of corrosion such as environmental cracking. Because of their ability to form protective chromia layers at elevated temperatures, stainless steels also proffer good high-temperature corrosion resistance—up to a point. As new applications demand higher temperatures and introduce more aggressive reactants, often for energy or process efficiency, conventional stainless steels do not

have sufficient strength or corrosion resistance. However, advances in capabilities to do accurate thermochemical modeling and prediction, combined with principles of selective oxidation of alloys and mechanistic knowledge of creep, provide new and unique pathways to producing future stainless steels with higher temperature capabilities.[8]

- *Developing corrosion-resistant materials for use in concrete reinforced structures often deteriorated by corrosion of the reinforcing steel.* Solid stainless steel and stainless steel-clad rebar materials have demonstrated the ability to extend the chloride induced corrosion initiation threshold in concrete to over 100 years when compared with plain carbon steel currently such a material change is quite costly.[9] There is a possibility to design new low cost, intrinsically corrosion-resistant reinforcing materials without resorting to the use of expensive alloying elements,[10] which will ultimately enable their use not only in concrete but in other environments. Other innovative mitigation strategies that can also be investigated, including developing concrete microstructures that have lower permeability to moisture or contain corrosion inhibitors as part of their intrinsic chemistry.[11]
- *Developing an affordable, manufacturable, high-strength pipeline steel that is highly corrosion resistant.* Pipelines for deep-water oil and gas production and recovery present severe corrosion challenges: hydrogen sulfide, carbon dioxide, oxygen, and mineral salts (especially chlorides) can lead to material degradation by hydrogen embrittlement, sulfide cracking, and localized corrosion. Even though modest progress has been made with corrosion-resistant nickel-based superalloys and supermartensitic stainless steels with Ni and Mo in limited applications the former are currently too expensive for widespread use and thus pose an excellent opportunity for research. The need for material development for pipelines for CO_2 sequestration must also be considered as this is a possible solution to excess atmospheric CO_2 in global warming control. However there is a shortage of true data and engineering knowledge, especially on potential corrosion problems in such a large undertaking.

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[8] Y. Yamamoto, M.P. Brady, Z.P. Lu, P.J. Maziasz, C.T. Liu, B.A. Pint, K.L. More, H.M. Meyer, and E.A. Payzant, Creep-resistant, Al_2O_3-forming austenitic stainless steels, *Science* 316:433-436, 2007.

[9] M.F. Hurley and J.R. Scully, Threshold chloride concentrations for localized corrosion on selected corrosion resistant rebar materials compared to carbon steel, *Corrosion Journal* 62(10):892-904, 2006.

[10] F. Presuel-Moreno, J.R Scully, and S.R Sharp, Literature review of commercially available alloys that have potential as low-cost corrosion resistant concrete reinforcement, NACE Corrosion Conference 2009, Atlanta, Georgia, Paper 09204, 2009.

[11] National Institute of Standards and Technology, *International Workshop on Fire Performance of High-Strength Concrete, NIST, Gaithersburg, MD, February 13-14, 1997, Proceedings,* NIST SP 919, September 1997.

The related "add-on" challenge is to optimize materials for conjoint failure modes when conjoint, nonlinear and coupled corrosion processes occur, including mechanically induced modes (wear, fretting, fatigue, and creep). Another need is the ability to handle or anticipate changes in solution or processes with time and transitions in corrosion modes.

The IDEAL Corrosion-Resistant Alloy for Aqueous Environments

Alloys are often designed with properties other than corrosion resistance in mind, such as mechanical strength. In the case of structural materials strength, ductility, toughness and joining issue are often dominant properties. Corrosion resistance is often secondary, although major alloying elements have been incorporated for many years to increase corrosion resistance. The question arises as to the ideal attributes of an alloy for maximizing corrosion resistance whilst keeping its originally intended properties. It should be recognized that there are trade-offs with a range of properties and that all of those below cannot likely be realized simultaneously. A corrosion-resistant alloy ideally would have the following properties:

- Form a homogeneous solid solution alloy lacking structural and chemical non-uniformities.
- Contain a critical amount of beneficial alloying elements in homogeneous solid solution that are readily enriched in the passive film, in amounts exceeding the thresholds for passivation.
- With respect to the key alloying element, be preserved by having the means to avoid interface or surface depletion. The passive films developed on the surface might function in other roles through engineering of the properties of these films (which are, in essence, semi-conducting oxide films) to suppress electron transfer reactions or create ion selective membranes. Avoidance of depassivating alloying elements would be desirable. However, if they cannot be avoided, ideally these elements would not be hydrolysable so that the pH would not be lowered at local corrosion sites.
- Embody beneficial synergy among the alloying elements listed above.
- Contain alloying elements that make the passive film a poor substrate for electron transport reactions such that reactions like oxygen reduction are suppressed.
- Have attributes for maintenance of low interfacial stresses and possess sufficient ductility to avoid cracking and spallation. Perhaps the oxide would be graded to avoid a classical interface.
- Contain elements that enable fast repassivation rate at scratches and flaws on multiple occasions.
- Lack negative impurities to the extent possible or otherwise sequester them so that they cannot be swept or collected at surfaces and interfaces (interface engineering).

- Contain other beneficial trace alloying elements such as bond promoters, passivity promoters, glass formability, or elements that serve as gettering agents to sequester harmful species.
- Exploit the full capabilities of defect engineering to avoid one-, two-, and three-dimensional defects of critical sizes, and spacings that trigger certain corrosion modes and their spreading. This is especially necessary in classes of alloys where heterogeneity is unavoidable, as in the case of precipitation age-hardened alloys.
- Exhibit avoidance of grain boundaries or incorporate clean grain boundaries with controlled application of a number of boundaries with low CSL.
- Avoid segregation or depletion of the alloying element during heating.
- Exhibit diffuse, not co-planar, plastic deformation that occurs in grain interiors and is not focused at grain boundaries.
- Have alloying elements that, once the oxide film was broken down or penetrated, would have a slow dissolution rate, resist noncongruent dissolution that is detrimental, and collect beneficial alloying elements at easy low coordination dissolution sites. The alloying element might also be engineered to alter surface diffusion rates.

Inspection of this list suggests that amorphous metallic alloys satisfy many of these criteria. This is partially true. Amorphous materials are a possible choice in some applications, and this list is growing with the advent of bulk metallic glasses. However, in many cases where conventional crystalline alloys must serve as the best available choice, they are either unavailable in the product form needed or lack some other desired properties. A slightly different set of attributes might be desired for resistance of hydrogen embrittlement.

The ideal corrosion allowance material might:

- Exploit species in the solution to make an insoluble tenacious oxide or corrosion product that slows the corrosion rate,
- Dissolve in a extremely predictable manner,
- Avoid stress buildup that can spall or crack oxide, or
- Corrode in a uniform, predictable manner.

Protective Coatings

The ICMSE approach is also applicable to the development of corrosion-resistant coatings. An advantage of coatings is that they offer the potential of a hybrid structure in which the function of the coating can be specialized for corrosion resistance while not affecting the key properties of the underlying substrate material. (However, this is a particular challenge at high temperatures, where interdiffusion puts additional requirements on the coating-substrate system.) Coatings can also provide a lower cost solution than using a higher grade substrate material. Such coatings are often solely physical and chemical protective barriers between the corrodible substrate and its environment. Barrier protection from corrosion occurs when a physical layer is constructed to prevent damaging environmental species from reaching an object or system. In the simplest sense, humans use buildings as barriers between the contents of the building and the outside environment, thus preventing weathering attack on the interior objects. This form of barrier is passive, because the barrier material does not depend on a chemical process to provide protection, but rather simply stops the passage of environmental threats—such as acid rain—to the object to be protected. Passive barriers, coatings, and barrier layers include the following:

- Electro-deposited metal layers such as gold, silver, chromium, and others that put a relatively inert material between the corrodible substrate and its environment;
- Vapor-phase-deposited metals, alloys, oxides, or other materials for protection of reactive metal substrates;
- Spray-applied layers, including flame-sprayed metals, reactive sprays, high velocity sprays, cold sprays, and plasma-deposited layers of all sorts;
- Zinc- and zinc/aluminum-based galvanized layers for steel that combine a cathodic protection layer and a barrier layer; and
- Organic coatings (paints) that insulate reactive metal surfaces from aggressive environments.

The following is a selection of areas focusing on coatings that the committee identified as high-priority opportunities:

- *Coatings possessing high adhesion, mechanical property matching, interfacial compatibility, and low interfacial impurities.* This is applicable to a wide range of films from high-temperature ones of the type used on turbine blades to those on electro-coated metal connectors. As an example, for coatings designed to proffer high temperature oxidation resistance, it is often critical to tightly control rare earth (RE) and light element (e.g., carbon and silicon) concentrations at the less than 0.1 atomic percentage level, both respectively and with respect to the RE-C and RE-S ratios.[12] These concentrations can be quite difficult to achieve without advances in understanding and controlling processing approaches. If there were

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[12] B.A. Pint, Optimization of reactive-element additions to improve oxidation performance of alumina-forming alloys, *Journal of the American Ceramic Society* 86:686-695, 2003.

new deposition monitoring tools capable of accurately determining composition, direct feedback could achieve the needed accuracy in the composition.

- *Robust, defect-free cost-effective barrier films, available for large surface areas.* Nanoscale thin films for aqueous corrosion resistance show much promise; however, the results have been based on films produced in the laboratory. Further assessing the feasibility of these barrier films' properties requires considerable process scale-up. Recently, paints containing zinc oxide powder, which have long been utilized as anticorrosive coatings for various metals and alloys, have been seen in a new light. These paints are especially effective for galvanized steel, which is difficult to protect because its reactivity with organic coatings leads to brittleness and lack of adhesion. Zinc oxide paints retain their flexibility and adherence on such surfaces for many years. Progress has been made recently[13] with ZnO highly n-type doped with Al, Ga, or In which is transparent and conductive and can be used as heat protection if applied to windows. Another exciting ongoing development is the incorporation of additives such as Mg in the zinc oxide. This Mg addition renders the oxide inactive by a change of semiconductor type from n-type to p-type for the reduction of oxygen. This inactivation of oxygen-reduction capability is a necessary step in mitigating corrosion and coating degradation. The n-type oxide is detrimental because it reduces oxygen too easily, whereas conversion to the p-type makes that process less probable and as such improves the protective capability of an already-flexible and highly adherent sacrificial coating.[14]
- *Self-sensing and self-healing films and coatings.* These smart films can be externally interrogated or can self-sense their own health and respond by either self-healing or actuating an external healing response.[15] A number of strategies that can be used to trigger healing and release.[16] However, more research is needed to determine what approaches works best. One example is a material that contains small spheres with a sealant; if a crack forms, some spheres will break open and release the sealant into the crack. This sealant can be designed so that it reacts upon release and solidifies, effectively repairing the crack.
- *Thorough understanding of corrosion protection mechanisms for nontoxic corrosion inhibitors and conversion-coating procedures.* Over the past several years, considerable effort has been spent in replacing chromate coatings, which pose a

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[13] A. Kalendová, D. Veselý, and P. Kalenda, Pigments with Ti^{4+} -Zn^{2+}, Ca^{2+}, Sr^{2+}, Mg^{2+}-based on mixed metal oxides with spinel and perovskite structures for organic coatings, *Pigment and Resin Technology* 36(1):3-17, 2007.

[14] R. Hausbrand, M. Stratmann, and M. Rohwerder, Corrosion of zinc-magnesium coatings: Mechanism of paint delamination, *Corrosion Science* 51:2107-2114, 2009.

[15] E.J. Barbero, and K.J. Ford, Characterization of self-healing fiber-reinforced polymer-matrix composite with distributed damage, *Journal of Advanced Materials* 39(4):20-27, 2007.

[16] D.Y. Wu, S. Meure, and D. Solomon, Self-healing polymeric materials: A review of recent developments, *Progress in Polymer Science* 33:479-522, 2008.

health and environmental hazard due to the chromium VI ion. This issue is especially important with respect to protecting aluminum structural materials, including those used in commercial and military aircraft. Researchers have examined a range of new potentially corrosion-inhibiting compounds as well as radically different approaches to protective coatings. None of these approaches has yet achieved the broad and effective performance of chromates. Unlike chromates, many current-generation, nonchromate inhibitors have not shown consistent performance for aluminum alloys; herein lies a very important area for additional research.

- *Taking advantage of—and exploiting—mineral scales that can naturally develop on materials' surfaces.* Limiting the corrosion of copper and copper-based alloys, for example, often depends on the formation of mineral scales (e.g., atacamite, brochantite, malachite, and other) that can increase their corrosion resistance. Magnesium offers even greater opportunities in this regard because phosphate- and carbonate-based mineral scales may significantly alter corrosion behavior. Here, clever design of materials[17] in combination with exploiting the environment can generate extremely low rates of corrosion[18] owing to the formation of corrosion-resistant compounds. This would be especially true for materials where damage to the protective film (as a result of wear, pinhole formation, and so on) would be repaired by the regeneration of new scale. The development of such scale should incorporate detailed understanding at the molecular scale in order to fine-tune properties appropriately.[19]

Corrosion Environments—Properties of the Ideal Coating for Aqueous Corrosion Resistance

An ideal coating (Figure 3.2) should have a very hydrophobic surface and should form high barriers to water and electrolytes. This property normally requires a polymer coating that is highly cross-linked and that contains silicone or fluorocarbon monomer, has reduced polar groups on the polymer, and maintains desirable thermo-mechanical properties. The ideal coating should also have controllable gradients in chemical composition to minimize interfacial discontinuities and create a covalent bonded structure from the substrate through to all of the coating layers.

In the substrate immediate interfacial region, one needs a gradient in properties from bulk to interface that maximizes the desirable mechanical and physical prop-

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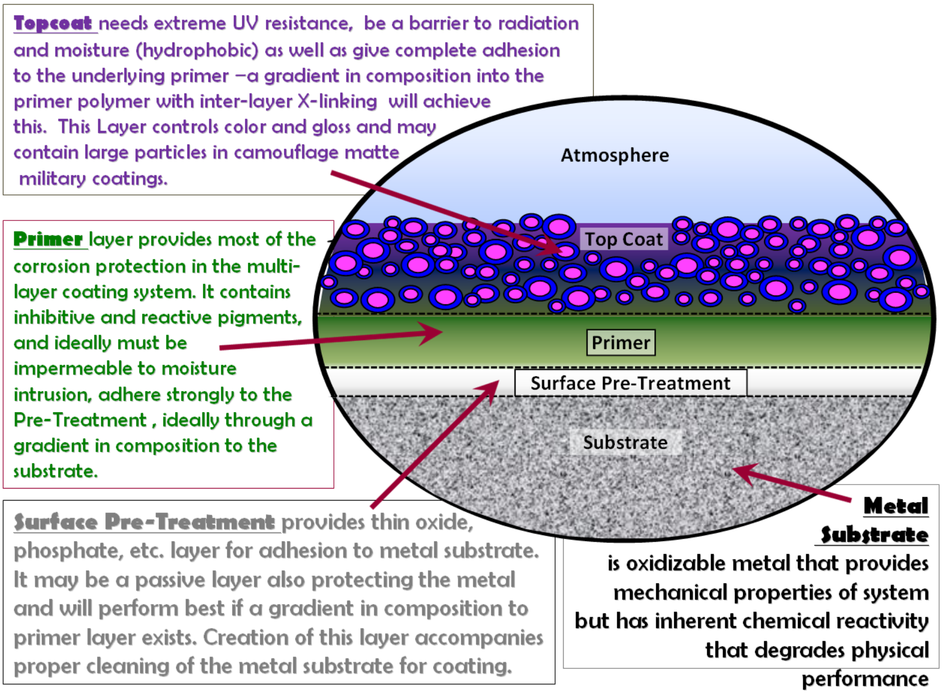
[17] B. Zberg, P. Uggowitzer, and J. Loffler, Mg-Zn-Ca glasses without clinically observable hydrogen evolution for biodegradable implants, *Nature Materials* 8:887-891, 2009.

[18] R. Rettig and S. Virtanen, Composition of corrosion layers on a magnesium-rare earth alloy in simulated body fluids, *Journal of Biomedical Materials Research Part A* 88A:359-369, 2009.

[19] C.A. Ohlin, E.M. Villa, J.R. Rustad, and W.H. Casey, Dissolution of insulating oxide materials at the molecular scale, *Nature Materials* 9:11-19, 2010.



Topcoat needs extreme UV resistance, be a barrier to radiation and moisture (hydrophobic) as well as give complete adhesion to the underlying primer –a gradient in composition into the primer polymer with inter-layer X-linking will achieve this. This Layer controls color and gloss and may contain large particles in camouflage matte military coatings.

Primer layer provides most of the corrosion protection in the multi-layer coating system. It contains inhibitive and reactive pigments, and ideally must be impermeable to moisture intrusion, adhere strongly to the Pre-Treatment , ideally through a gradient in composition to the substrate.

Surface Pre-Treatment provides thin oxide, phosphate, etc. layer for adhesion to metal substrate. It may be a passive layer also protecting the metal and will perform best if a gradient in composition to primer layer exists. Creation of this layer accompanies proper cleaning of the metal substrate for coating.

Metal Substrate is oxidizable metal that provides mechanical properties of system but has inherent chemical reactivity that degrades physical performance

FIGURE 3.2 The ideal coating system—technical issues.

erties of the substrate but minimizes its corrosion/degradation susceptibility and provides a proper composition for interaction with the protective coating system. This would be a coarse gradient on the atomic scale from bulk to several nanometers of interface. Then there should be a tightly controlled interfacial region that can be chemically matched to the coating system and provide a basis for water-resistant adhesion and mechanical property matching with the coating layer to avoid excess stress concentration in the interface and subsequent coating mechanical delamination. This may include control of surface oxide formation with residual reactivity for the matrix of the pretreatment (which may be simply oxide formation) or substrate enrichment of minor elements in an alloy substrate. If one can get cross-diffusion across an interface without creating excess chemical reactivity or mechanical stress, one gets true improvements in adhesion.

If the coating is applied as a liquid layer, no defects in the application and film formation processes are acceptable (this is why electro-deposited paints such as those used in automobiles are so excellent at corrosion protection)—this is a true ongoing challenge in quality engineering.

If it were possible to create composite structures within the films described above while still maintaining the prerequisite environmentally resistant adhesion, this would potentially improve film properties considerably, because the composite structures would offer significant improvements in layer chemical, mechanical, and barrier properties.

A multicoat system provides a higher probability of ensuring complete, uniform coverage of the corrodible substrate. Maintenance of interlayer adhesion is crucial. The multilayer structure might allow incorporation of many desirable properties in the outer coatings system, such as:

- Water resistance,
- Controlled or minimal oxygen permeability,
- Electrolyte resistance,
- Chemical resistance,
- Capability of sequestration of undesirable reactive materials permeating in the film to extend diffusion lag times by orders of magnitude, and
- Pigments with shape factors (such as platelets or needle-like shapes) that orient in the film to give desirable improve resistance of electrical connection properties.

A new emphasis in the design of coating systems that needs field demonstration to deliver its considerable promise is the so-called smart coating. Coatings in this category respond to stresses from their environments in a designed, intelligent manner. This includes triggered release of corrosion inhibitors when the possibility of corrosion occurs due to external threats, self-repair of mechanical damage, local sequestration of corrosion-inducing impurities such as chloride ions, local color or spectral changes that allow external sensing of corrosion, and even alteration in local cross-link density in polymer matrices. However, many issues remain in achieving these attributes, such as simultaneous optimization of properties and their translation into exact lifetime extensions by other than trial-and-error approaches.

Improved Materials for Active Corrosion Protection Systems

A common mode of corrosion protection under aqueous or atmospheric conditions is to actively protect a metal object by electrochemical means. Two basic types of this protection are in use: anodic and cathodic.[20] Anodic protec-

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[20] See, for example, U.K. Mudali, H.S. Khatak, and B. Raj, Anodic and cathodic protection, Chapter 5, Section 5.1 in *Encyclopedia of Electrochemistry: Volume 4, Corrosion and Oxide Films* (A. Bard, M. Stattman, and G. Frankel, eds.), Wiley-VCH, Weinheim, 2003.

tion consists of electrochemically driving a metal to a passive state it would not spontaneously achieve as an electrochemical anode.[21] This form of protection requires very good potentiostatic control and a robust, accurate reference electrode. Unfortunately, expanding the use of active protection mechanisms requires more accurate and more robust reference electrodes to ensure precise control of the anodic protection potential. Hence, research in developing a new robust, accurate reference electrode is needed in order to extend active corrosion protection to areas such high-temperature systems.[22]

Another research need for anodic protection is alloys designed to be effectively self-driven to a stable, self-healing passive state under ambient conditions. This is the current mechanism for the corrosion resistance of stainless steels in oxygenated near-neutral water. The development of alloy compositions that could achieve the same effect in more aggressive environments is a major driver for further research.

Cathodic protection, currently one of the most widely used forms of corrosion protection, includes applying an external potential to an object that might corrode, driving it to a potential where the corrosion rate will be decreased, or—for passive alloys—driving it to a potential below a critical potential for localized corrosion.[23] Some advances needed in cathodic protection include:

- *Improving methods for controlling imposed cathodic (impressed-current) protection.* Currently most modes use galvanostatic control with a strong tendency to overprotect the substrate because of uncontrollable potential fluctuations.[24] Shifting to potentiostatic control would reduce this, but no methods are commonly available to bring a reference electrode close enough to the object being protected to give accurate control of potential. The usual problem with cathodic protection is that objects are extended and cannot be controlled from one spot. Another issue is the need for self-sensing, self-correcting anodes that are on and aware of changes

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[21] This type of protection is used mainly with steel alloys for use in handling sulfuric acid ,and in similar situations.

[22] S.N. Lvov, Electrochemical techniques for studying high temperature subcritical and supercritical aqueous systems, Chapter 11, pp. 723-747 in *Encyclopedia of Electrochemistry: Volume 5, Electrochemical Engineering* (A. Bard, M. Stratmann, D.D. Macdonald, and P. Schmuki, eds.), Wiley-VCH, Weinheim, 2007.

[23] Chemically sacrificial anode(s) externally attached to an object can also provide cathodic protection by an imposed potential or current with or without a protective organic barrier coating, by a layer of metal whose potential is anodic to the substrate (such as a zinc layer over steel-galvanizing), or by an organic or inorganic binder-based coating pigmented with a metal powder more reactive than the substrate metal at volume concentrations high enough to have all of the metal particles in electrical contact with each other as well as the substrate, thus providing effective cathodic protection to the substrate (e.g., zinc-rich coatings for steel, magnesium-rich coatings for aluminum).

[24] I is the current flowing, and R is the electrical resistance of the system.

in environment or of the need for protection. These anodes could then change or adapt to the conditions in order to optimize protection of corrosion-prone materials without causing embrittlement or coating damage. They could also enhance anode lifetime if they did not operate when conditions were more benign. While tunable resistors are currently available to limit current output, there is the need for set-and-forget smart anodes requiring minimal monitoring that can self-correct themselves. There is also the need for tunability, but this requires electrochemical interface control. Clearly, additional research efforts in this area represent a good opportunity to advance active protective methods.

- *Increasing the range of metals and alloys that can be cathodically protected.* There are indications that a broader range of metals and alloys (other than steels) can benefit from this form of protection. Magnesium particles in coatings have been shown to be effective in protecting aluminum without the need for chromates. However, there is a need for additional research to determine promising materials combinations.

CGC II: High-Fidelity Modeling for the Prediction of Corrosion Degradation in Actual Service Environments

Corrosion grand challenge II entails developing a better understanding of corrosion mechanisms and morphologies, coupled with the environments in which they operate, and the fusion of the knowledge, data, models, and tools available into more accurate—and widely descriptive—models of materials and environments for all types of corrosion.

This capability will greatly accelerate the development of corrosion-resistant materials, as discussed above in connection with CGC I. Additionally, it will provide insight into the feasibility and benefits of various corrosion mitigation approaches. However, modeling has several challenges besides the usual computational limitations, including lack of fundamental mechanistic information, lack of understanding of the environment, and the large statistical distributions often seen in corrosion damage processes and metrics that represent real effects, not instrument errors, which are often limited by shortcomings in mechanistic knowledge in the corrosion field. It is often said the best models are possible when the mechanism is well understood. Two key areas for future work in this field are (1) increasing the available knowledge of fundamental aspects of corrosion the lack of which thwart modeling and (2) connecting the current islands of knowledge to provide more complete models, such as linking the governing nanoscale processes across many time and length scales to meaningful engineering-scale metrics, depicted in Figure 3.3. These needs are complementary to the larger, multifaceted modeling efforts directed at predicting materials performance as part of the integrated product development process. It is also clear that even more

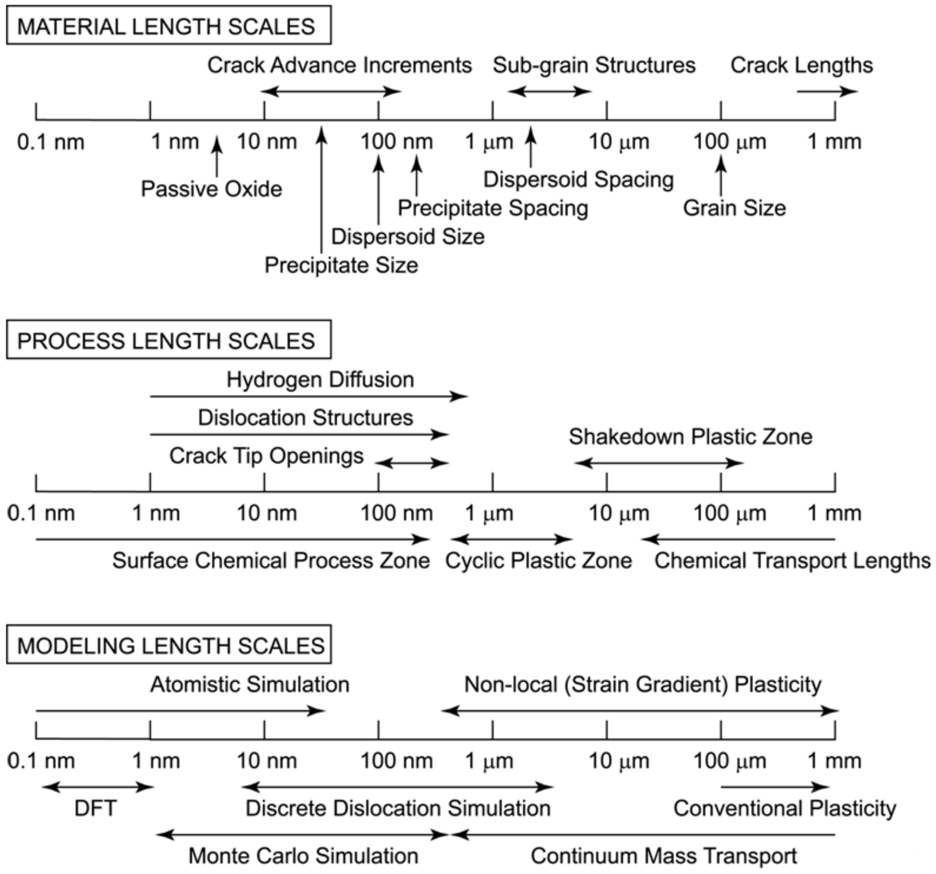

FIGURE 3.3 The wide span of different length scales with relation to the material, the processes, and the models needed to correctly predict corrosion degradation. SOURCE: University of Virginia Center for Electrochemical Science and Engineering, courtesy of Matthew R. Begley and Richard P. Gangloff.

overarching hierarchies of models might be required at three levels: (1) materials behavior (ICMSE); (2) degradation mode models; and (3) system-level models for equipment or infrastructure systems.

As discussed in relation to CGC I, advances in ICMSE are making possible the rapid development of new materials based on knowledge gained through the development of better models, as well as through continued empirical inputs. However, the emphasis to date has been on tools to optimize mechanical and physical properties within a target cost range, and corrosion resistance has rarely been directly considered in ICMSE except by extension of physical properties. Figure 3.4 shows

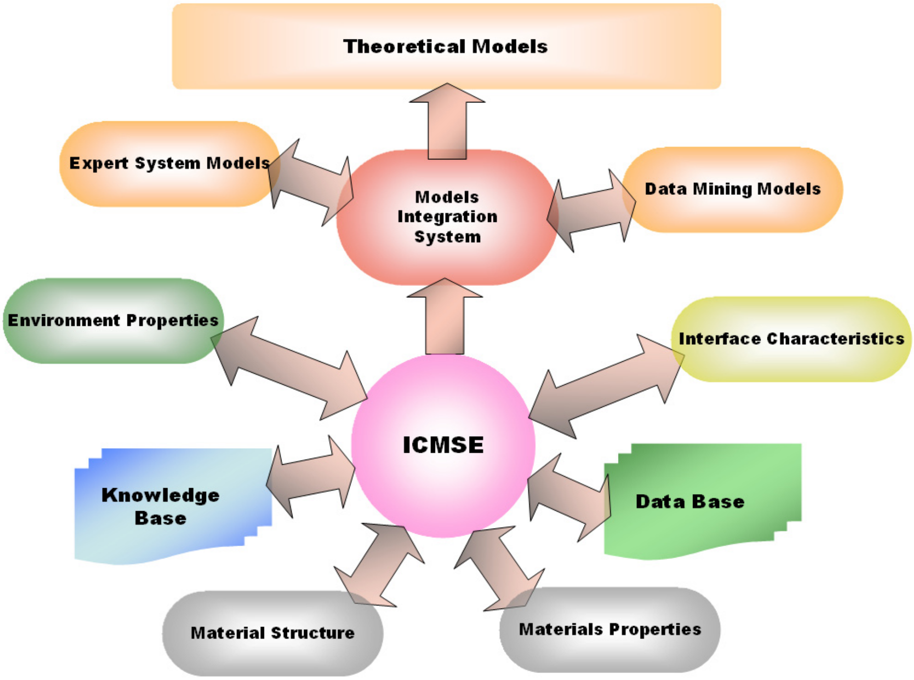

FIGURE 3.4 The flux of materials information required to achieve computational materials design.

some of the multiple databases, knowledge bases, and models that will be required to make ICMSE a reality, with model-integration a critical activity.[25]

Computational materials design tools are now emerging in physical and mechanical metallurgy but are lagging with respect to corrosion behavior. To parallel these tools for materials degradation modeling would require inputs such as details of alloy chemistry and phase formation, as well as environment definition, mechanistic behavior, potential and pH stability diagrams (for aqueous corrosion), kinetic laws, including the probability of certain events occurring or statistically distributed properties and parameters based on knowledge of the corroding system. The outputs might include initiation, propagation, and arrest of selected corrosion phenomena. Advances in computational methods and enhanced understanding of stages of corrosion processes create an opportunity for solid advancement, especially if gaps in the fundamental knowledge of corrosion are pursued. Filling

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[25] National Research Council, *Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security,* The National Academies Press, Washington, D.C., 2008.

these gaps will enable high fidelity models without guesses or assumptions. The subsections below discuss the variety of corrosion models now available.

Corrosion Modeling—General Aspects

Corrosion models incorporate knowledge gained by understanding the details of corrosion mechanisms and through experience with particular materials in specific applications and environments, along with data from corrosion testing to either predict damage or tailor materials to resist it. Prediction is accomplished by capturing the mechanism of time-dependent damage as well as physical, geometric, and environmental factors such that time steps can be accelerated faster than real time to predict damage accumulation. Another goal of modeling, already mentioned above, is computational materials design whereby a range of corrosion behaviors in addition to other materials properties (e.g., mechanical, electrical, and magnetic) can first be understood and then tailored for a given application. Resistance to corrosion can often be achieved by selecting an appropriate material or coating, and such strategies are often a worthy investment.[26] For example, empirical formulas such as the pitting resistance equivalency number can be used to predict certain critical parameters (e.g., critical pit and crevice temperatures) of the performance of corrosion-resistant materials in aqueous environments. Such prediction is now possible in a limited number of alloy systems but is in its infancy—for instance, the effects of all alloying elements are not incorporated, and broad applicability to a range of environments in uncertain. Moreover, although some progress has been made in grain boundary engineering using percolation theory and in interface engineering for single species on simple boundaries, the design of materials via tailoring of the composition of major, minor, and trace elements is not yet fully developed. The selection and control of phases and control of defects such as inclusions by interface engineering are also very much in their infancy. By contrast, thermodynamic and phase transformation models are now available to predict the types and amounts of phases in both aqueous and high-temperature, condensed-phase, and gaseous environments. These pockets of progress should be encouraged to continue to grow.

The overarching goal of corrosion modeling is to provide a reasonable estimate of expected corrosion behavior for a material in a particular application. This is inherently a complex undertaking for a number of reasons:

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[26] A June 2008 Department of Defense (DOD) report estimates the average return on investment from more than 80 recent corrosion mitigation projects at around 50:1 (DOD, Efforts to Reduce Corrosion of the Military Equipment and Infrastructure of the Department of Defense, 2008, available at http://www.corrdefense.org/CorrDefense%20Magazine/Summer%202007/PDF/2007_DOD_Corrosion_Report.pdf).

- Corrosion of even a single form or type often involves multiple stages, each of which has different elementary steps or processes across several length scales.
- Corroding systems are often multilayered and involve geometric complexities such as physical recesses, crevice, or cracks.
- Chemical, physical, electrical, electrochemical, metallurgical, and mechanical factors often affect corrosion initiation and kinetics.
- Chemical, electrical, and material-based gradients are often very steep and can occur over very small length scales.
- Real environments are often complex, uncontrolled, and incompletely delineated. The critical factors controlling the type and the rate of corrosion are often unknown.
- Some corrosion parameters are statistically distributed, and the challenge is to properly capture and represent such distributed behaviors.

Because of such complexity, there are scientific barriers to the advancement of lifetime prediction models that forecast damage accumulation, as well as barriers to computational design of materials for obtaining desired corrosion properties and to achieving, at the engineering level, a prognosis of future damage on the basis of physics at the materials science scale. These barriers present opportunities for improvement that include, but are not limited to:

- Closing the many gaps in understanding of mechanisms of corrosion for improved formulation of scientific laws governing the phenomenon of corrosion damage.
- Incorporation of environmental parameters into the complex time-dependent laws governing damage of materials. An interface can have a surface composition that may differ from that of the bulk material on both the electrolyte and material sides.
- Formulation of more corrosion-damage laws that can describe the process in three dimensions or can incorporate necessary combined spatial and temporal aspects of corrosion.
- Improved definition of the environment affecting corrosion. Corrosion-related properties are not intrinsic to a given material but instead are dependent on the details of the environment to which materials are exposed.
- Modeling at multiple length scales ranging from atom to component scales, and modeling of the damage from corrosion in three dimensions.
- Further scientific progress required to completely understand the details of corrosion mechanisms at multiple length scales. Such knowledge will ultimately be useful in engineering applications through their impact on mesoscale or engineering-scale material properties.

Advances in modeling over the last 30 years make predictions of damage evolution a realistic goal for the near future. As increased mechanistic understanding occurs, computational capabilities expand, and the corrosion field follows the progress made in modeling in materials science elsewhere, making this goal achievable. As long as each step in the degradation process can be validated, modeling should improve for use in control of corrosion. Appendix C describes the models in more detail.

Deterministic Modeling

By definition, a deterministic model assumes quantitative, physical-based knowledge of the causal laws that govern corrosion, which is a very complex phenomenon. Accordingly, strong hypotheses simplifying the problem have had to be introduced to allow causal natural laws to be applied. Some of the factors required, and thus research opportunities presented, to perform realistic deterministic modeling are the following:

- Understanding the key driving factors affecting corrosion, including knowledge of the material (chemistry, defects, processing history, mechanical and physical properties, and so on), the chemistry of the corrosive environment (general and localized), and information about the component (geometry, stress, temperature, pressure, environment, and so on);
- Accessing reliable information on the kinetic parameters of the corroding system;
- Understanding the corrosion evolutionary path from initiation through the different phases of the corrosion degradation process; and
- Understanding and accounting for any inaccuracies introduced by numerical method solutions and by computer system limitations.

Because corrosion phenomena are complex, deterministic models evolve continually as restrictive hypotheses are eased when additional, empirical knowledge is acquired. In essence, it is the scientific method that nudges a model to reality. Hybrid deterministic models have been developed in fracture and fatigue where a particular property or parameter is considered to be statistically distributed. This statistical distribution is carefully chosen for implementation to selected parameters in the deterministic model (a true deterministic model retains its probabilistic aspect as a placeholder until the statistical scatter can be replaced with true mechanistic understanding).

Empirical Modeling

Empirical models, sometimes called "database" models, exist at the other extreme of the modeling spectrum from deterministic models. Empirical (or phenomenological models) are based on the philosophy that everything that can ever be known must have been observed. Accordingly, these models are very restrictive and are not a good choice for exploring the outside limits of the data used to develop the model. For example, if an empirical model is developed based on observation of the corrosion of iron in an acidic medium, the use of that model for the corrosion of the same iron in a basic medium will give inadequate results.

Empirical corrosion models can benefit by adapting techniques from the field of artificial intelligence (AI), especially when the knowledge base is very large. Data itself is not knowledge, but knowledge can be extracted from the data with the proper tools to assist in (1) collecting, formatting, and accessing corrosion data; (2) capturing knowledge in very important research areas; and (3) unifying the best models and making the resulting algorithms readily available. AI tools of interest include:

- Methods to organize knowledge, such as expert systems;
- Tools to cluster data by similarities, such as self-organized maps;
- Tools to extract patterns, such as neural networks;
- Tools to transform dynamic data, such as wavelets; and
- Tools to perform optimization and fast search, such as genetic algorithms.

When the underlying knowledge is lacking or poorly defined, data mining is a powerful technique that automates searching for patterns in available data. Data can be ordered, transformed, and mapped and then used to predict results. Data mining also utilizes special algorithms that aid visualization of emergent patterns and trends stored and/or hidden within the data.[27] Probability inference can help to estimate the likelihood that the conclusion obtained by analyzing the data is true. Bayesian inference networks—also known as belief networks—are used to estimate the probability distribution of one or more attributes of the data.

Neural networks map variables into results using a black-box approach and can be used as components of analyses designed to build explanatory models, because they explore data sets in a search for relevant variables or groups of variables; the results of such explorations can facilitate the process of model building. Neural networks are capable of approximating any continuous function, and thus a researcher does not need to have a hypothesis about the underlying model. An important

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[27] Mark Newman stated, "Statistical methods in modern network analysis answer the question, How can I tell what this network looks like, when I can't actually look at it?" in M.E.J. Newman, The structure and function of complex networks, *SIAM Review* 45(2):167-256.

disadvantage is that it can be difficult to interpret the solution in traditional analytic terms such as those used to build theories that explain phenomena. It is clear that these approaches are not used nearly enough in corrosion, and opportunities exist to develop their effective use with dedicated research and the development of relevant corrosion data and testing approaches.

Statistical, Probabilistic, and Stochastic Models

Statistics, the science of making effective use of numerical data relating to experiments, can provide insight into the quality of the data produced experimentally. To apply statistics to a given data set, it is necessary to (1) start with the assumption that the population represented by the data set follows a pre-established behavior or (2) infer a type of population from the data set. In both cases, problems can arise when the data set is small and poorly represents the population or when the data (and the population) are in a nonsteady state or reflect an evolutionary phenomenon. For this last case, when time constants are short and the model evolves within the time record of the collected data, a stochastic approach is more correct mathematically, but it is generally much more difficult to use.

When the phenomenon is known only poorly, the collected data may contain some degree of randomness or even reflect beliefs and bias on the part of the collector. To mitigate this problem, analysts may rely on probability, which relates statistical concepts to stochastic variables by mean of large data sets. An example of the use of one statistical and probabilistic method is the use of extreme value distributions applied to cumulative distribution functions to analyze pitting corrosion as performed by Macdonald and colleagues and shown in Figure 3.5.[28]

Thus, while statistical analysis of the data is highly recommended, before applying any data mining techniques, it must be understood that the misuse of statistics and/or stochastic models can lead to incorrect predictions. Still, collected data represent a multitude of opportunities for mathematicians and data miners and for researchers dedicated to theoretical electrochemistry. The knowledge obtained from such data can be used to build new and realistic models and thereby expand knowledge of the problem. However, data produced have not always been sufficiently consolidated to reach their full potential. Models are frequently isolated constructs (local models that account for only a limited number of observations), whereas global models that account for all observations are needed and should be sought. Today there are ample opportunities for an overall effort on data consolidation and model evaluation that would greatly benefit corrosion science and engineering.

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[28] D.D. Macdonald et al., The deterministic prediction of corrosion damage, in L.L. Shreir, *Corrosion*, Elsevier, 2010.

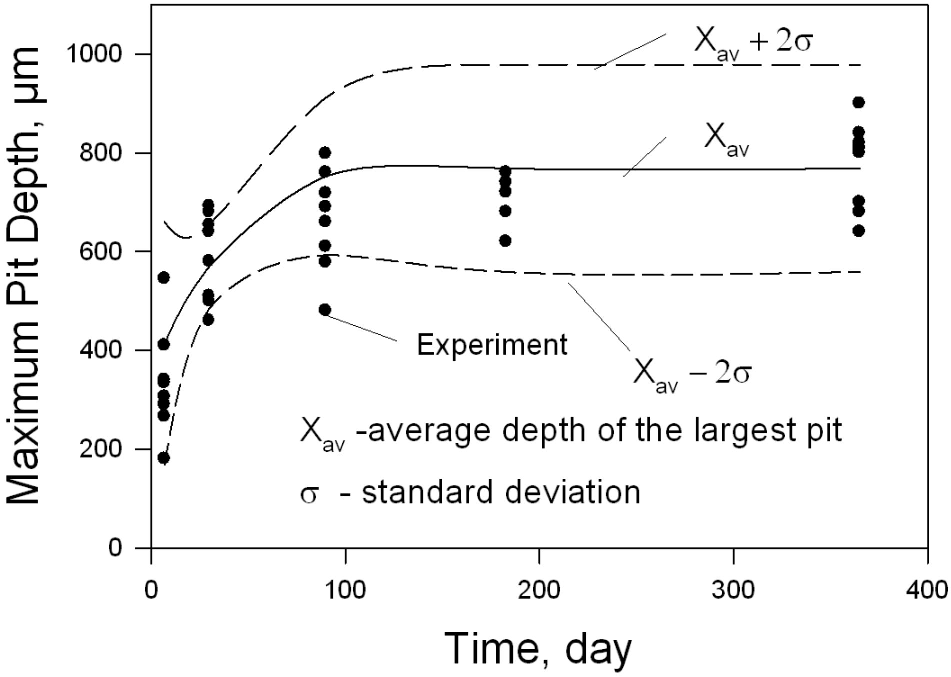

FIGURE 3.5 The mean depth of the deepest pit as a function of time. Experimental data are from Aziz et al. and are for aluminum alloy Alcan 2S-O in Kingston, Ontario, tap water. Note that no calibration was performed on short-term data.

Model Integration

Model integration and multiscale modeling are critical if modeling is to be useful in predicting the behavior of materials in specific environments. Opportunities exist to integrate models across length and time scales, and to describe each step in the corrosion evolutionary path, beginning with initiation of corrosion damage, in order to produce macroscopic predictions from nano- and microscale observations.[29] One example of model integration is mixed deterministic-statistical modeling where fundamental laws of corrosion are expressed in the model where they are known. (See deterministic modeling, above, and hybrid modeling.) A statistical spread or distribution may then be applied to a few parameters when that behavior is observed. The statistical spread is best applied when (1) it follows

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[29] J.W. Halley, P. Schelling, and Y. Duan, Simulation methods for chemically specific modeling of electrochemical interfaces, *Electrochimica Acta* 46(2-3):239-245, 2000.

observations of variability in the lab or field and (2) the modeler can justify the distribution technically but does not know enough details of what controls the statistical distribution to incorporate them deterministically in the model. Such models are attractive because they capture well-understood scientific aspects of realistic behavior but account for observed variations using statistical or probabilistic approaches, the explanations for which may be lacking. Multi-scale modeling has become a reality in other aspects of materials science. In this type of modeling, atomistic information may inform and feed selected properties or phenomena at a higher length and time scales. The notion of multiscale modeling is that not everything is modeled at the atomistic scale, but rather only selected phenomena of great importance whose input at the atomistic scale may influence properties at a coarser length scale and ultimately parameters at the engineering scale. There is no reason why this approach cannot be extended to the corrosion field to benefit both the understanding of material behavior and prognosis. Additionally, because materials degrade through processes other than corrosion, such as fatigue and creep, a complete set of modeling tools would incorporate corrosion modeling with these other degradation models.

Final Thoughts on CGC II

Considerable effort over a substantial period of time will be required to produce fully deterministic models, complete with appropriate boundary conditions. Until then, empirical models will need to be integrated with deterministic models. Mixed models may also provide some utility and become more attractive as the technical basis for statistical distributions becomes understood. Much of the research needed to develop corrosion models requires contributions from many different disciplines, including contributions from theoretical materials scientists and chemists working together on corrosion problems using data and knowledge generated by experimentalists, along with computer scientists and mathematicians, under the guiding hand of real-world corrosion engineering. Indeed, opportunities to apply models to corrosion should not be limited to a particular perspective, and models borrowed from other fields (medical, for example, or other areas, such as math and risk-reliability assessment) may prove very useful. One example is the use of level-set mathematical methods, which are adept at front tracking of corrosion, etching, deposition, or lithography or profile evolution, which can develop sharp changes in profiles and order-of-magnitude changes in speed. These types of mathematical models could be applied to corrosion.[30]

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[30] J.A. Sethian and D. Adalsteinsson, An overview of level set methods for etching, deposition, and lithography development, *IEEE Transactions on Semiconductor Manufacturing* 10(1):167-184, 1997.

CGC III: Accelerated Corrosion Testing Under Controlled Laboratory Conditions That Quantitatively Correlates to Observed Long-Term Behavior in Service Environments

Corrosion grand challenge III attacks the thorny issue of extrapolating—with high fidelity—expected field performance based on laboratory-scale testing. The crux of the challenge is that there is a large mismatch between the time available for laboratory testing, typically on the order of months, and the time that a structural or functional material will be in service, typically many years. Accelerated testing is used for a variety of purposes, including demonstration, validation, and lifetime prediction of new materials, coatings, and environments; early detection of failure mechanisms not foreseen during design; lot acceptance; as well as a tool to assess the return on investment in mitigation and robust design. Unfortunately, accelerated testing in corrosion has many shortcomings, most of which can be traced to either a lack of detailed specific environmental definition or a lack of fundamental understanding of the processes occurring during accelerated testing and field exposure, and how the two are related.

Three high-priority research needs for advancing accelerated testing are described in the subsections that follow. The list is not meant to be inclusive, but rather to indicate the type and scope of effort that must be made to achieve the goals of CGC III. Although many of the examples relate to metals, accelerated testing is also needed that yields meaningful prediction of long-term corrosion behavior for all material types (see Figure 3.6 for one example).

Corrosion Intensity Factor

A critical research gap in corrosion science is the absence of the corrosion equivalent for the stress intensity factor (K) that has been the mainstay of structural mechanics for the past several decades.[31] The stress intensity factor was developed to predict the behavior of pre-existing flaws in structural materials and the eventual life of a component under conditions in which the flaw develops into stable cracks. The power of K is in the concept of similitude: well-defined cracks and crack tips that are different in size or shape but possess the same K (as determined by geometry, loading, and the theories of linear-elastic fracture mechanics) will experience the same mechanical driving force for crack growth. Thus, similitude allows small, well-defined samples to be tested in the laboratory to determine the conditions of crack growth and fracture and the results to be quantitatively extended to more complicated real-world structures containing cracks. Virtually

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[31] The effectiveness of K is that it has its basis in thermodynamics and thus can be calculated from basic principles.

FIGURE 3.6 A ferrous based alloy exposed to the environment since 1882 (note the date on the part). With a cold and dry environment the corrosion process is very slow. SOURCE: University of Virginia Center for Electrochemical Science and Engineering, courtesy of John R. Scully and UVA MSE 3080 class participant.

all structural integrity approaches rely on similitude for their predictions of a component's mechanical performance.

Although there continues to be extensive research on K and on the limitations in the concept of similitude, the creation of the field of fracture mechanics in the 1960s was a breakthrough for the understanding and prediction of crack growth and eventual fracture. Many industries now regularly use fracture mechanics in the design and maintenance of their engineering structures. Moreover, damage-tolerant design can specify the size and shape of defects, plus load levels that can or cannot be tolerated according to a specification of critical stress intensity factors for crack growth or sudden fracture. In many ways the safety of modern air travel and of power-generating equipment such as nuclear reactors is possible only through the application of fracture mechanics in the design and maintenance of aircraft structural components and reactors. On the small end of the scale, the same is true for the conductors used in the leads that deliver electrical energy to the heart from implantable defibrillators and defibrillators in general.

The field of corrosion science could make very good use of an analogous corrosion intensity factor[32] if one could be developed to help define equivalent corrosive situations in a more quantitative manner. This would allow much needed predictions from accelerated tests toward field exposure of components as well as facilitate comparisons between one condition and another. One example is the use of an exposure factor in sulfidation, whereby the product of H_2S concentration and exposure time yields the same "corrosion intensity" or "exposure" factor. This means that the same thickness of copper sulfide film could be produced on copper exposed to H_2S at parts-per-million concentrations in a thousandth of the time needed when exposure to the same gas occurs at parts-per-billion. However, rarely is it the case in corrosion that the concentration of the corroding agent can be traded for time so simply. [33] One reason is that all the driving forces that control the rate of corrosion are not completely understood; another is that there is currently no way to equate them or even describe them in common terms. If a corrosion intensity factor could be realized, then the driving force for corrosion in a laboratory test, a field test, and a component in service could be equated or the differences quantified. Therefore, it is possible to foresee a time when an environmental or corrosion intensity factor, C_{envir}, akin to K, based on similitude would quantify the acceleration provided by test conditions and allow predicting the performance of equipment based on equivalent exposures or CIFs between field and accelerated environments. With such a tool, corrosion conditions could be manipulated to control and dial in the driving force and hence the rate of various corrosion processes as well as forces controlling transitions in corrosion mode or triggering changes in corrosion mode. A science-based parameter would allow quantitative connections between corrosion rates observed in laboratory exposures and those found in field environments and might also allow databases on materials in one environment to be translated into equivalent corrosion behavior in another environment, such as one with lower concentrations of aggressive species. The

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[32] The corrosion intensity factor describes the product of driving force and time in one parameter such that the equivalent CIF would produce the same mode and amount of damage whether exposure occurred in a laboratory test, a field test, or during component service. This capability is beyond that of an environmental severity index, which exists but falls short of this higher goal. It should also be noted that stress corrosion cracks contain a mechanical and chemical driving force and that short and long cracks may be mechanically "equal" but may not be "chemically" equal if, for instance, a long crack develops a more aggressive chemical environment.

[33] T.E. Graedel, J.P. Franey, and G.W. Kammlott, Ozone- and photon-enhanced atmospheric sulfidation of copper, *Science* 224:599-601, 1984.

scientific and technological impact of a viable environmental corrosion intensity factor would be of great significance.

However, as stated above, there are many scientific barriers to the development of an environmental corrosion intensity factor, including the complexity of many field environments, lack of accurate knowledge of many exposure environments, and the highly nonlinear nature of corrosion rates with certain environmental species attacking metals (e.g., ammonia, sulfur, and chloride). As such, even when precise environmental definitions are known, the highly negative and positive synergies created between various combinations of factors and the lack of quantitative information in many environments make this an extremely challenging goal. It should also be pointed out that a corrosion intensity factor is not a replacement for deterministic or some other form of modeling to predict behavior and performance. In fact, deterministic models of sulfidation exist, but there is still the acute need for relevant accelerated testing.

Quantitative Connections Between Laboratory Exposures and Field Environments

Another issue affecting the ability to perform accelerated testing is replication of the actual environment in crevices or local occluded sites in metals formed by complex geometries or deposits (see Figure 3.7) when that environment differs from the nominal bulk environment, whether it is submersed in liquid or exposed to the atmosphere. A classic example is that of steam generators in nuclear reactors. These structures were originally fabricated from nominally corrosion-resistant nickel-based alloys; however, crevices formed between the tubes and tube sheets used in these heat exchangers led to environments in which a variety of species were concentrated owing to the local heating and boil off of water.

Through the years, as corrosion problems have persisted, increasingly corrosion-resistant alloys and new environmental chemistries have been used. Accelerated testing clearly requires knowledge of all environments to which a structure will be exposed.

There are numerous electrochemical approaches to quantitatively assessing the corrosion resistance of bare and painted metallic materials immersed in conductive electrolytes, and they can be very sensitive and relatively easy and rapid to perform (Figure 3.8), either in the laboratory or in the field for corrosion rate monitoring. However, in some environments such as those with high-temperature gases or high-resistivity electrolytes that do not follow classic electrolyte behavior, standard electrochemical approaches either are extremely difficult or fail completely. An important research opportunity is to develop sensitive, quantitative, and accurate methods for evaluating corrosion resistance in these environments.

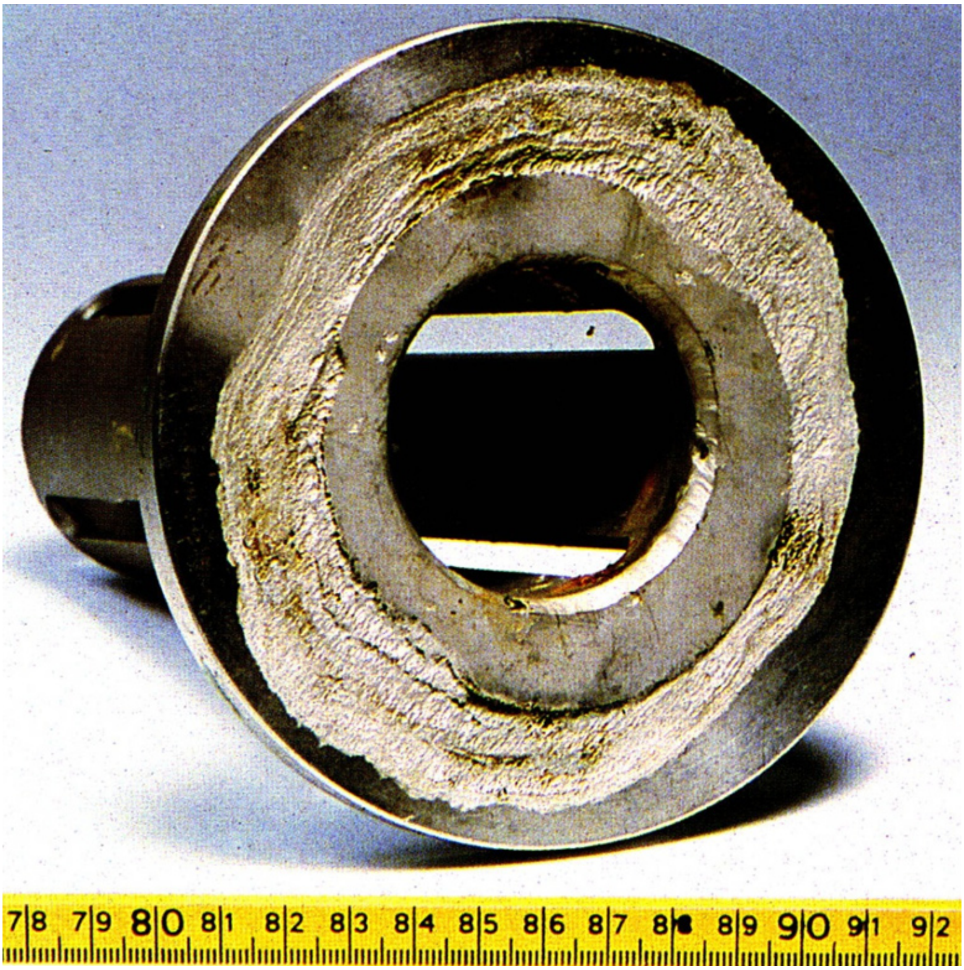

FIGURE 3.7 Crevice corrosion of a corrosion-resistant alloy flange. SOURCE: *Corrosion Atlas* (E.D.D. During, ed.) 1997, copyright 1997, Elsevier.

Understanding the Corrosion Processes That Occur During Accelerated Testing

Current accelerated testing methods are empirically correlated with field performance, and acceleration factors are often deduced from relative differences in the evolution of damage over time. However, there is often little understanding of why a given method succeeds or whether it will be effective on another coating, material, or in another environment, because the rules that determine its applicability to other situations are not understood. The uncertainty surrounding

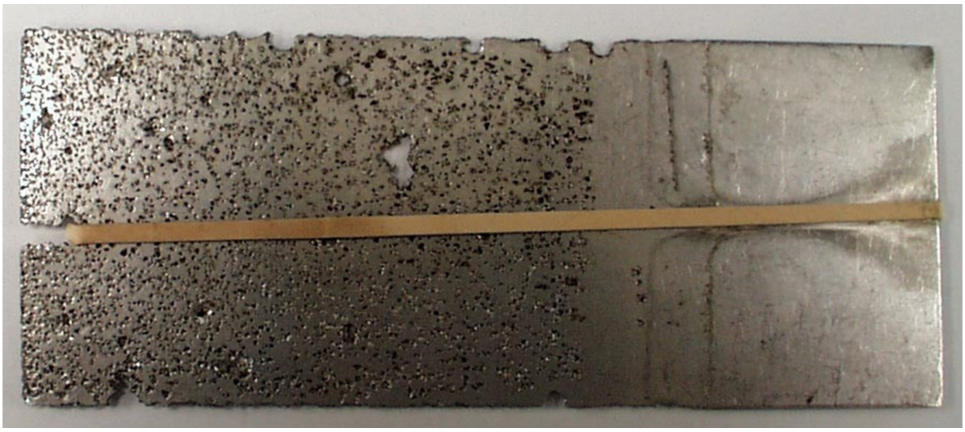

FIGURE 3.8 Acid-induced pitting and crevice corrosion of a stainless steel alloy exposed to ferric chloride (note the corrosion under the rubber band at left—left side dipped). SOURCE: University of Virginia Center for Electrochemical Science and Engineering, courtesy of John R. Scully.

accelerated testing could be reduced if research were done to better understand how to accelerate the mechanisms and modes of corrosion that prevail in the field, and how to avoid introducing spurious mechanisms that do not occur under the conditions of use. If these were better understood, it would then be possible to compare various environments as well as materials, and even coatings. Eventually this would lead to improved rules for conducting and interpreting accelerated tests. In the nuclear industry, a common concept is the material improvement factor. For example, much information has been gained about alloy-600 failures over the years, but only a few have occurred in alloy-800 and none in alloy-690. Scientists are currently working on accelerated laboratory tests that do crack these latter materials and are developing statistical methods to predict when and how they will eventually fail in service.

CGC IV: Accurate Forecasting of Remaining Service Time Until Major Repair, Replacement, or Overhaul Becomes Necessary—i.e., Corrosion Prognosis

Corrosion grand challenge IV addresses the critical need for better methods to monitor the actual deterioration of a component once it is placed in service in a corrosive environment, analyze that information, and, based on decision-making algorithms (or “reasoners”), provide a reasonable forecast of the time remaining before maintenance or replacement becomes necessary.

As noted elsewhere in this report, corrosion is ubiquitous, quite complex, and driven by a multitude of variables. Many properties of materials are directly, and most often negatively, affected by corrosion. As a consequence, much effort is expended in mitigating corrosion by providing effective protection and ensuring proper inspection, assessment, and maintenance. Monitoring is needed to verify modeling and accelerated test predictions and to provide information on corrosion occurring in high-value or critical equipment.

There are two high-priority research needs required to advance the real-time, accurate determination of the extent of in-service corrosion degradation. The technology required to address CGC IV draws heavily on the modeling work described under CGC II, which involves basic understanding of the corrosion types and of damage accumulation, as well as corrosion modeling algorithms. Two key research opportunities are highlighted below.

Improved and Automatic Sensing Devices for Quality Inspection

An essential aspect of corrosion mitigation involves inspection of engineered structures, in order to avoid costly unscheduled repairs and to ensure safe and reliable materials performance. Extensive inspection and maintenance/repair programs have been established in a multitude of sectors concerned with corrosion and its costly impact—for example, in oil transmission pipelines, bridges, naval vessels, refineries, and chemical plants. These programs typical rely on traditional inspection methods, among them visual methods using magnifying glasses, borescopes, liquid penetrants, and magnetic particle testing), and electromagnetic, ultrasonic, and radiographic techniques.

Traditional inspection methods have known limitations (such as lack of accessibility to difficult- to-reach areas), can involve personnel safety concerns, and are not always reliable (such as operational inaccuracies due to scale formation, noise, or vibration); all of these add a measure of uncertainty to the effectiveness of the inspection and raise concern about the possibility of undetected corrosion problems in areas that cannot be inspected. For a comparison of monitoring techniques, see Table 3.1.

Effective corrosion mitigation and control require appropriate action at the correct time. Since many engineered structures include multiple components and corrosion processes are cumulative, periodic inspection is often not the optimal procedure for identifying areas requiring timely action to mitigate corrosion. Thus there is an urgent need to change from time-based inspection to a more effective condition-based inspection. This change can be achieved through continuous monitoring with advanced sensor technologies that generate meaningful data, provide accurate assessment of materials condition, detect corrosion, analyze its impact, and determine the risk of further degradation. The importance of condition-based, continuous monitoring programs is being recognized in various sectors affected by corrosion, such as shipboard tanks.

Interest in sensors as reliable evaluation tools is increasing, based on expressed needs for online, nondestructive, accurate, and cost-effective evaluation of the condition of materials and the integrity of equipment. Figure 3.9 illustrates how sensors might be utilized at various stages in the lifetime of a component or device.[34]

Currently, continuous monitoring methods are aimed at generating on-demand data for determining the condition of materials and for detecting the presence of corrosion. These monitoring methods for metallic systems rely on sensors that fall into several categories:

- Sensing electrochemical measurements of instantaneous rates of corrosion of metals;
- Sensing of environmental reactivity, including upset conditions, which does not measure corrosion rates but instead indicates the propensity or risk for corrosion based on environmental severity; and
- Sensing a material's accumulated damage at some location, often using surrogate material for damage assessment but preferably based on the accumulated damage of the actual component.

Overall, the information provided by these sensor technologies tends to include:

- Mechanical data, such as strain field;
- Chemical data, such as pH, oxygen, and dissolved ions; and
- Electrochemical data for metallic systems, such as current, potential, and impedance.

Experience with monitoring methods based on generating data from samples or coupons (such as damage sensors) indicates the need to ensure relevant correlation to the condition of the system's component itself. Electrochemical methods of monitoring suffer drawbacks and limitations related to deposition of corrosion products and changes in a corrosion medium's conductivity that may affect the sensor output. Furthermore, most corrosion sensor technologies are not capable of accurately identifying localized corrosion or clearly evaluating cumulative corrosion processes.

Additional corrosion sensor issues that must be considered include probe life, sensitivity range, response time, flexibility, and detection of prior damage. Table 3.1 lists key characterizations for several corrosion sensors for monitoring

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[34] Defense Science Board, *Corrosion Control*, presented in modified form during a NACE Roundtable discussion on corrosion, March 2009.

TABLE 3.1 Comparison of Techniques for Monitoring Bridge Health

Method	Coupon	ER	AE	LPR
Response time	10 to 365 days	2 hours to days	Instant	Instant
Qualitative localized corrosion	Yes	No	No	No
Quantitative localized corrosion	Yes	No	No	No
General corrosion	Yes	Yes	No	Yes
Field monitoring use	Yes	Yes	Maybe	Yes
Measure corrosion of actual structure	No	No	Yes	Maybe if use structure used as one electrode
Sensitivity/ range	Low	Low-medium	Low	High
Stress corrosion cracking	Maybe (stressed coupon)	No	Yes	No
Expected probe life	Long (5 to 100 mil)	Short (5 to 40 mil)	Long	Short for thin film type, long for imbedded
Atmospheric	Yes	Yes	Yes	Maybe for thin film type
Paintable	Yes	Yes	n/a	No
Concrete	Yes	Maybe	Yes	Yes

NOTE: AE, activation energy; ER, electrical resistance; EIS, electrochemical impedance spectroscopy; EN, electrochemical noise; LPR, linear polarization resistance.

SOURCE: Courtesy of J.R. Scully, Evaluation of State-of-the-Art and Emerging Innovative Corrosion Rate Sensors for Monitoring Steel Bridges in Various Corrosive Environments, ERDC, 2009.

EIS	EN	Galvanic	Multi-elctrode Array	Oxidation Power
Instant	Instant	Instant	Instant	Instant
	Yes	No	Yes	No
	No	No	Yes	No
Yes	Yes	For corrosivity	Yes	For corrosivity
Yes	Yes	Yes	Yes	Yes
Maybe if use structure used as one electrode	Maybe if use structure used as one electrode	Maybe if use structure used as one electrode	No	Yes (for estimation, if coupled to structure)
	High	High	High	High
No	No	No	No	No
Long (structure as one electrode)	Can be long if imbedded	Short for thin film, long for imbedded	Long for imbedded type	Unlimited for single noble electrode type
Maybe	Yes	Yes	Yes	Yes
Yes	Yes	Yes	Yes	Yes
	Maybe	Maybe	Yes	Yes

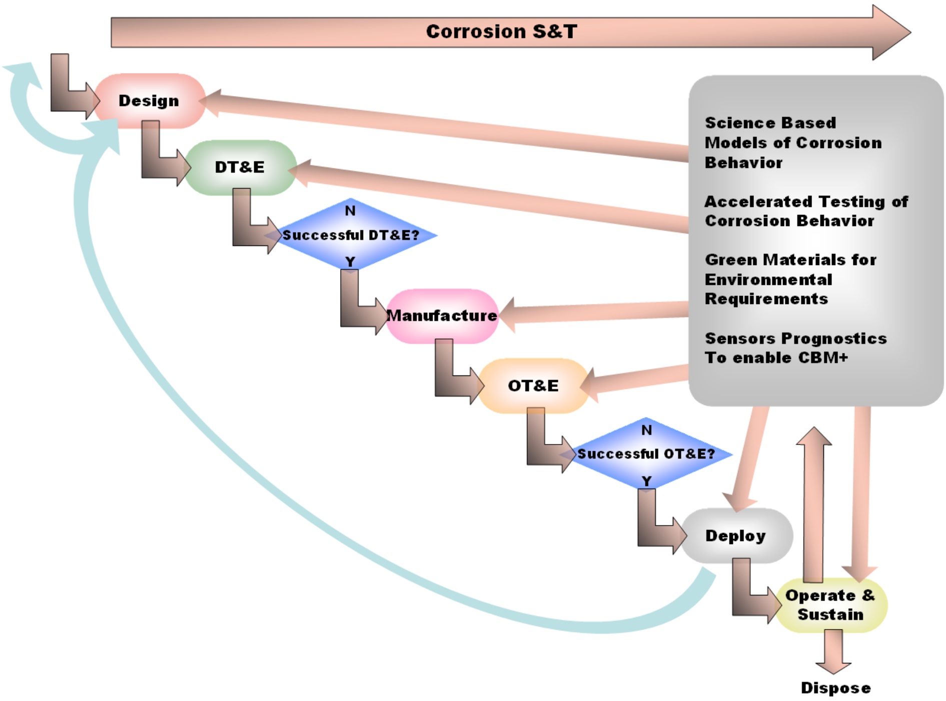

FIGURE 3.9 The cradle-to-grave development of an engineering system requiring corrosion protection and mitigation of corrosion and the impact of corrosion modeling, accelerated testing, and sensors. CBM+ is an enhanced form of condition-based maintenance that uses advanced hardware and software tools to support decision making. Adapted from Defense Science Board, *Corrosion Control,* Final Report ADA428767, October 2004, available at http://www.acq.osd.mil/dsb/reports2000s.htm, and based on information in *Ammtiac Quarterly,* Vol. 4, No. 2, 2009.

bridge health. The reader will note that each existing sensor has shortcomings and cannot be used at all with certain electrolytes or in challenging situations such as hidden corrosion and corrosion under coatings. Another strategy is the vast use of surrogate coupons or materials instead of interrogation of the actual structure or component of interest. The actual component is always preferred for analysis, and the surrogate coupon always represents a proxy that may or may not replicate the actual situation. There is an urgent need to improve these capabilities.

For corrosion in environments with high-temperature gases, the ability to detect corrosion in real time suffers from the lack of a good (sufficiently conductive) electrolyte for electrochemical measurements. However, electrochemical methods, including noise and impedance measurements, have been and are being pursued for these environments, albeit with poor or mixed results.[35] More extensive and innovative studies in this area would prove extremely valuable for real-time quality-control sensing applications as well as for condition monitoring as part of prognosis. Such measurements would have to be compared with those obtained by the traditional, cumbersome approach of probing for corrosion by inserting actual materials of construction that are removed at intervals for examination, and with measurements of corrosion rates by gravimetric or (more accurately) metallographic/ceramographic methods. Although electrochemical methods can be used reliably for measurements of corrosion rates in molten salts (hot corrosion),[36] techniques of greater sophistication, such as are used in aqueous environments, would be worth developing.

Researchers continue to make progress in corrosion monitoring and inspection. Recent developments include the use of fiber optic sensors to monitor pipeline corrosion and stress corrosion cracking, the development of both surface and penetrating sensors aimed at detecting cracks and corrosion in bridges, laser scanner systems that are being tested for evaluating urban structures' integrity and fluorescing nanomaterial coatings to reveal when and where corrosion is occurring in the substrate. Needless to say, there are many more advances that will be required in order to develop reliable sensor technologies.

Numerous challenges still face personnel engaged in inspection and monitoring, as well as those entrusted with accurate assessment of corrosion and prediction of materials performance. Opportunities include:

- Correlating data from surrogate sensors with actual performance of structural components;
- Gaining increasingly accurate of measurements, automation, and usefulness in inaccessible areas;
- Developing sensors that generate data to identify chronological and cumulative corrosion processes;
- Developing smart materials with embedded capability to indicate the onset and rates of degradation;
- Developing sensors that can sense remaining barrier properties, inhibitor or sacrificial anode capacity; and

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[35] C.J. Davis, P.J. James, L.W. Pinder, and A.K. Mehta, Effects of fuel composition and combustion parameters on furnace wall fireside corrosion in pulverized coal-fired boilers, Materials Science Forum 369-372:857-864, 2001; B.S. Covino, Jr., S.J. Bullard, G.R. Holcomb, M. Ziomek-Moroz, and D.A. Eden, Fireside corrosion probes for fossil fuel combustion, Corrosion 2006 Paper 6472, NACE International, Houston, Tex., 2006.

[36] G. Gao, F.H. Stott, J.L. Dawson, and D.M. Farreil, Electrochemical monitoring of high-temperature molten-salt corrosion, *Oxidation of Metals* 33:79-94, 1990.

- Developing sensors that interrogate, use, or consist of the actual structure or component.

Ability to Track and Monitor Corrosion Protection Systems

Currently there is no commercially available electrochemical sensor or sensor suite that has been proven to yield the corrosion rate of a metal under a protective coating. The instantaneous detection and measurement of corrosion under paint in atmospheric exposure is a challenge that has eluded a solution. Although in principle damage sensors should work under paint, they typically employ a surrogate material under a new coating. Thus, past performance and degradation of the coating up to the point of installation is challenging to match, and the rate of corrosion of the sensor surrogate material must be correlated with the corrosion rate of the structure. Work to determine atmospheric corrosion rates of metallic materials under coatings in the atmosphere is thus a high priority.

There is also the need for distributed, non-hard-wired sensor systems that assess damage modes, corrosivity, instantaneous corrosion rates, and other information. The ideal distributed sensor system of choice for many applications should provide a suite of remotely situated field sensors that can simultaneously measure instantaneous corrosion rate, corrodent concentration, time of wetness, and possibly, accumulated damage. A sensor that has the ability to characterize pre-existing coating damage is also attractive because a freshly coated sensor on a surrogate material is not representative of this situation.

Condition-monitoring technology has evolved to the point that sensors and data mining modeling research areas might be mature enough to produce a monitoring system that will be reliable, robust, and cost-effective. However, those systems are not yet widely available because of several remaining hurdles:

- Existing wireless sensor systems are not robust, or affordable, or workable for many applications.
- Existing data-mining software is not tailored to work with wireless sensors, nor can it manage the large amounts of data collected continuously by the sensors.
- Decision-making algorithms are lacking or are in their infancy and not proven in widespread systems.
- When success is achieved with sensing, the conditions under which the success can be extended to other systems without extensive reproving are unknown.

Because advances in modeling and prediction of damage will need verification, there is an urgent need to bring monitoring to the state where it can operate in a range of environments to sense corrosion, not just in the easiest environments. Moreover, sensors in the chemical process stream can be used for real-time monitoring and feedback for process control. In some cases, monitoring will be the only strategy available other than careful initial selection of materials. Finally, there is a need for further advancement of distributed sensors and sensors that can detect different corrosion modes.

The Base—Corrosion Science

Although the fundamental principles of corrosion may be fairly simple, the details of how corrosion actually occurs are complex and often are not known. The goal of fundamental research in the field of corrosion is to better understand the detailed mechanisms by which corrosion occurs. Multiple length and time scales must be considered, because information at each scale helps feed into and produce an assessment of the risk of corrosion, such as the risk of pitting as shown in the example in Figure 3.10.

These research opportunities will lead not only to better materials but also to better models of corrosion processes for a variety of materials. Another key opportunity lies is developing knowledge of the real environmental variables to which a component is subjected, as well as the actual localized corrosive environment in occluded regions such as pits, cracks, or crevices or under films or deposits of various types. Until researchers investigate these opportunities and materials scientists apply the results to design better materials with the needed corrosion resistance, it will never be possible to control or eliminate corrosion simply by selecting the right material. Theories from other fields of science and exciting new investigative tools can also have a great impact on the corrosion field, as the advances described in Box 3.1 and some of the success stories in Chapter 1 indicate.

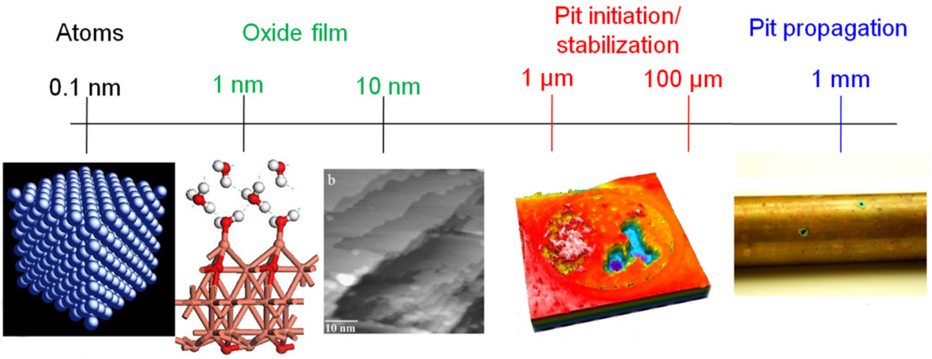

FIGURE 3.10 The length scales over which pitting corrosion is active. SOURCE: University of Virginia Center for Electrochemical Science and Engineering, courtesy of Hongbo Cong.

BOX 3.1
Advances in Science Theories and Tools in Related Fields and Subsequent Impact on the Corrosion Field

Advances in corrosion research have been facilitated over the years by theoretical developments in other fields as well as by new experimental methods. Of the numerous examples of such advances, only a few are mentioned here. For instance, when Tafel[1] observed in 1905 that electrochemical current was proportional to the exponential of electrochemical potential (where the electrochemical reaction rate is described by the current density), absolute-reaction rate theory (transition state theory) had not yet been developed. However, once developed in 1935 by Eyring and Polanyi in chemistry,[2,3] it was rapidly adapted to the corrosion field by Wagner and Traud[4] and used to explain Tafel's observation. Measurement of corrosion reaction kinetics based on these original electrochemical theories is now a mature aspect of corrosion science and engineering with a strong scientific underpinning. Field measurements of corrosion rate based on the polarization method and associated current sensing are made routinely with some accuracy using motes and telemetry; such measurements also rely on these original theories. Similarly, advances in chemical thermodynamics based on pioneering work of J.W. Gibbs[5] and others in the late 1800s rapidly spread to solid state engineered materials systems through the efforts of Darken[6] and Smith and were nearly simultaneously adapted to the subspecialties of corrosion and high-temperature oxidation. Tafel, Pourbaix, and Ellingham diagrams are examples of the routine use of a thermodynamic approach in studies of corrosion and oxidation. The state of the art is so advanced that commercial software toolkits are available to users[7] and enable thermodynamic modeling in technological applications involving corrosion and oxidation. Neither of these advances would have been possible without fundamental research in corrosion that capitalized on related scientific discoveries in thermodynamics and kinetics.

Major advances in materials characterization and in materials modeling and simulation in recent years also have provided new tools with impressive capabilities for addressing the most perplexing problems in corrosion science. For instance, there was once an ongoing debate over the very basic nature of the passivity (films versus adsorbed layer), and various theories were advanced. Development of techniques in surface science such as optical and later photoelectric and synchrotron radiation methods to characterize valence state, thicknesses, and composition produced a leap forward in the understanding of passive films.

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[1] See http://electrochem.cwru.edu/ed/dict.htm#t01.

[2] H. Eyring, The activated complex in chemical reactions, *Journal of Chemical Physics* 3:107-115, 1935.

[3] K. Laidler and C. King, Development of transition-state theory, *Journal of Physical Chemistry* 87(15):26571, 1983.

[4] C. Wagner and W. Traud, On the interpretation of corrosion processes through superposition of electrochemical partial processes and on the potential of mixed electrodes, *Z. Electrochem. Ang. Physik. Chemie* 44:391, 1938.

[5] See http://www.chemistryexplained.com/Ge-Hy/Gibbs-Josiah-Willard.html.

[6] L.S. Darken and R.W. Gurry, *Physical Chemistry of Metals,* McGraw Hill, New York, 1953.

[7] Ignasi Puigdomenech, Hydra/Medusa Chemical Equilibrium Database and Plotting Software, KTH Royal Institute of Technology, 2004.

One of the tools that is rapidly adding new knowledge is the synchrotron, as discussed in the first subsection below. A number of additional areas, beyond synchrotron work, present opportunities for pushing the frontier in corrosion science in three primary areas that are also discussed below: corrosion mechanisms, corrosion morphologies, and corrosion environments. Advances in understanding in these areas are needed to achieve the goals of all the corrosion grand challenges.

Synchrotron Radiation

An irony of the study of corrosion is how remarkably difficult it is to directly measure the rate of corrosion since it is often highly heterogeneous and takes place in cavities such as pits shielded by metal in wet environments. Electrochemical measurements cannot give spatial information. The method traditionally used is serial sectioning, but this destroys the pit, so that it is not possible to obtain time-dependent information. By far the most straightforward approach is to use highly intense X-rays (particularly those from synchrotron sources) to make microtomographic measurements that provide three-dimensional images in situ in wet environments and in real time. This approach has already been successfully pioneered to examine pits and pit-to-crack transitions in stainless steel; intergranular corrosion and pitting in Al alloys; and localized attack of Mg. The corrosion rate can be monitored by counting voxels (three-dimensional pixels) of metal that have disappeared between one frame and the next, which is the most direct method possible for quantifying corrosion.

The technology is advancing rapidly, with the time required to obtain a single tomogram (three-dimensional image) decreasing from hours to seconds in the last few years. The spatial resolution is routinely just submicron using synchrotron radiation, with developments moving in the direction of resolutions of tens of nanometers at various beamlines. Absorption contrast gives images based on the difference in electron density. For elements with characteristic absorption edges at energies appropriate for imaging, it is possible to make measurements above and below the edges to give three-dimensional elemental maps, and this could potentially be extended to discriminate between different oxidation states of the same element. Phase contrast imaging (which is easily carried out by increasing the distance between the sample and the detector) can pick up interfaces between phases of similar atomic number and is therefore effective for imaging corrosion products and water droplets. It is also possible to see the location of hydrogen bubbles. Corrosion on metal pins under microelectrochemical cells has already been achieved, so that electrochemical data can be correlated with the evolution of corrosion.

Some examples of areas where microtomography might make a valuable contribution to the understanding of corrosion include the following:

- *Search for pit initiation sites.* It is straightforward to take an image of a metal microstructure prior to pit initiation, and a further series of images as localized corrosion develops. This allows working backward in time to locate the initiation site prior to pitting.
- *Corrosion under paint films and atmospheric corrosion.* The loss of metal due to corrosion can be observed with absorption contrast, and any changes in the paint film (e.g., cracks, swelling with water) could be observed with phase contrast imaging. If suitable ions are introduced, their distribution could be tracked with energy difference imaging, described above. For atmospheric corrosion, salt droplets and crystallization of salts and corrosion products could be observed and correlated with pit development.
- *Corrosion of heavily corroded delicate objects such as archaeological artifacts or failure analysis without the need to remove corrosion products.*
- *Long-term corrosion rates—for example, metals in concrete or in clays used in nuclear waste storage.* Measurements could be carried out in sealed glass vessels to control the environment, and these samples measured at monthly or even yearly intervals. Current methods for measuring the evolution of corrosion for nuclear waste samples of this type include the indirect measurement of hydrogen evolution, which is not straightforward.
- *Crystallographic effects in stress corrosion cracking.* It is possible to use microdiffraction to obtain the crystallographic orientation of individual grains in a tomography sample.[37] This could be correlated with discontinuous advances in stress corrosion cracks.

One of the current limitations of tomography is that, for reasons connected with image processing, the sample size is limited to 2000 times the resolution required. However, "region-of-interest" imaging is under development, so that an entire object can be imaged at low resolution and the resulting tomogram used to reconstruct a region of interest that is subsequently imaged at high resolution.

While three-dimensional imaging is likely to have the most dramatic impact, there are opportunities to carry out fast radiography to image two-dimensional processes in thin foils at submillisecond rates. Such imaging can also be correlated with chemical information, including X-ray fluorescence maps, X-ray absorption spectroscopy, microdiffraction, and small-angle scattering. The spatial distribution of different chemical species is important for the development of robust corrosion

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[37] A. King, G. Johnson, D. Engelberg, W. Ludwig, and J. Marrow, Observations of intergranular stress corrosion cracking in a grain-mapped polycrystal, *Science* 321:382-385, 2008.

propagation models, and the ability to carry this out in a time-dependent fashion under electrochemical control gives a route for direct measurement of diffusion and electromigration coefficients in realistic environments. This can be done on localized corrosion sites themselves and also to evaluate the distribution of corrosion products surrounding corrosion objects. For example, two groups are currently working on the distribution of metal ions and corrosion products in human tissue around failed implants.

There is vigorous development in the technology of beamlines in synchrotrons around the world (one example is the NSLS, shown in Figure 3.11), and so possibilities are continually opening up to characterize corrosion processes more rapidly, at higher resolution, and in more hostile environments. X-rays can easily pass through diamond windows, and many synchrotron measurements are currently made at elevated temperatures and pressures, making the prospect of future opportunities extremely exciting.

Synchrotrons are only one example of how advanced tools can be used effectively in corrosion science. Other tools with great potential include, but are not limited to, neutron scattering, advanced scanning transmission electron microscopy (particularly in situ efforts), scanning probe techniques, and low-voltage electron microscopy. Advances in first-principles theory, modeling approaches, and simulation provide new opportunities to generate needed understanding over important time and length scales consistent with those being accessed experimentally. Not only do individual tools have great promise, but the fusion of tool output data or tool output integrated both spatially and temporally also promises significant impact. Tool fusion involves taking and considering the output of several tools that interrogate a material or its corrosion processes simultaneously using several different approaches. In this manner it would be desirable to map, for instance, electrochemical, electronic oxide properties, physical damage, and crystallographic texture simultaneously. This kind of unprecedented information gathering would help identify what about a given grain boundary makes it prone to corrosion initiation and propagation. This has already been done with respect to microdeformation and IGSCC, but additional information would provide a rather complete picture of the corrosion process.

Corrosion Mechanisms—Fundamental Advances in Micro- and Nanoelectrochemical Theory and Methods

In the past, electrochemical measurements of corrosion as well as processes in batteries or other electrochemical processes were averaged over many atoms and molecules. Atomic details of electron- and ion-transfer reactions associated with dissolution and passivation are now ripe for further progress given nanoscale experimental and computational advances. Recent advances such as scanning electro-

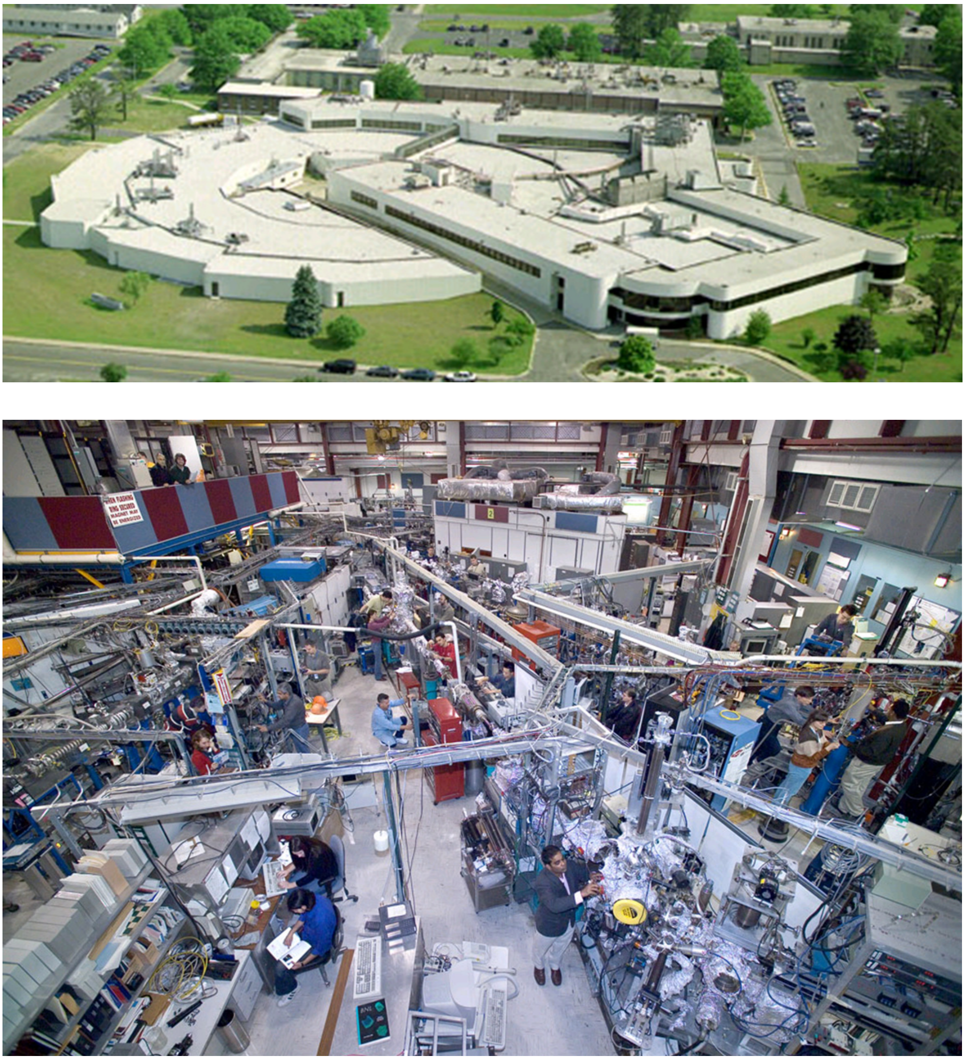

FIGURE 3.11 Aerial view of the National Synchrotron Light Source (top) and the vacuum ultraviolet, 200-10 nm, floor (bottom). SOURCE: Courtesy of NSLS, Brookhaven National Laboratory, available at http://www.nsls.bnl.gov/about/imagelibrary/.

chemical microscopy; electrochemical capillary probe microscopy; and electrochemistry mapping combined with other techniques such as micro-Raman and atomic force microscopy, scanning Kelvin probe, or scanning tunneling microscopy will allow understanding beyond that enabled by global electrochemical methods traditionally used. Societies such as the Electrochemical Society and the International Society of Electrochemistry regularly conduct symposia on these topics. Even spatial radiotracer methods (chemical interrogation) combined with electrochemistry may be possible.[38] Micro- or nanoscale electrochemistry in combination with other methods will advance the field toward new discoveries in both corrosion and electrochemical research. Two key factors are increased spatial resolution and concurrent combinations of mapping.

Corrosion Mechanisms—The Chemistry at a Variety of Occluded Sites

As mentioned above, progress in understanding localized corrosion under aqueous conditions could be gained through further understanding of the chemistry at occluded sites (e.g., pits, crevices, cracks, and delaminated sites under blisters in coatings) in three dimensions. Although there has been substantial progress in rigorously defining the chemical compositions and electrochemical conditions in pits and crevices, there are a number of opportunities for further research in areas such as ionic and transport properties of films, precipitates, and corrosion product as well as their colloidal properties. There is a need to understand conductivity and transport in concentrated solutions at low water contents as well as other aspects of physical chemistry such as activity coefficients and pH, how to make measurements in concentrated solutions, and how measurements change with concentration and other such variables.

The properties needed to either verify, or serve as inputs to, existing models remain elusive, and because of their dimensions and steep chemical concentration gradients, experimental probes of crack tips are challenging. Hence, reliable predictions, even for well-behaved materials, can be difficult to produce without the use of hypothesized, estimated, or reverse-engineered parameters.

Moreover, lack of understanding of processing and heat-to-heat variations or the effects of trace alloying elements further limits the predictability of the onset or growth of stress corrosion cracks. Similar considerations can apply to environmental effects on high-temperature crack growth in gaseous environments.

Corrosion Mechanisms—Forms of Localized Corrosion Controlled by Defects

There is a lack of atomistic-scale understanding of the role of various specific chemical species in the initiation of corrosion processes. For example, the role of ions on the precise atomic scale in processes such as pitting or cracking represents one opportunity for research. Moreover, the hierarchy of important defects across the length scales has been established only in a rudimentary way, and understand-

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[38] C.A. Ohlin, E.M. Villa, J.R. Rustad, and W.H. Casey, Dissolution of insulating oxide materials at the molecular scale, *Nature Materials* 9:11-19, 2010.

ing of the effects of arrays or distributions of defects on corrosion is in its infancy (Figure 3.12). Consequently, defect engineering[39] or damage-tolerant approaches as championed in fracture mechanics is almost totally lacking in the study of corrosion but could easily be developed. In contrast, much progress has been made in understanding the role(s) of micrometer-scale defects, propagation and stabilization. The field is well positioned for much additional progress in this area given the development of a number of imaging tools now available.

There is also a need to understand water absorption, passivity, dissolution, and cathodic reaction rates at the nanolength scale such as on nanoscale materials, where the Gibbs-Thompson effect may be large, quantum size effects may occur, and a greater percentage of atoms are on the surface and outnumber the bulk atoms, and also where the number of nearest neighbors is low and there are profound effects of strain and defects. Nanoparticles produce conditions where concentration gradients, the double layer, and ohmic voltage fields all exist on the same length scale. An additional opportunity exists to improve understanding of the reactivity of patterned surfaces, including superlattices and piezoelectric oxide supported metal.[40] Hence, nanoscale material applications may require new fundamental understandings of surface and electrochemical phenomena at the nanometer and subnanometer scales. This affects a range of applications, from catalysts to nanoelectronics. Tools such as scanning tunneling microscopy and atomic force microscopy as well as first-principles modeling methods make progress in this area possible.

Corrosion Mechanisms—Stress and Strain Effects

There is a lack of fundamental understanding of the effect of elastic tensile stress or strain and plastic strain on dissolution by either thermodynamic or kinetic interpretations. The roles of stress and/or strain in aqueous corrosion reactions occurring at the atomistic level close to room temperature have been modeled for micrometer-scale descriptions of stress corrosion cracking (SCC) and hydrogen

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[39] The concept of "defect engineering" follows along the lines of damage-tolerant design with regard to cracks, where methods exists to assess the risk of cracking given pre-existing flaws or cracks of a given size or even assumed flaws at the detection limits of the inspection tool. Similarly, the concept of grain boundary engineering has been applied to degradation phenomena that occur on one type of defect (e.g., grain boundaries). The notion is to consider the need for "safe" or benign grain boundaries to interrupt cracking or conversely the percolation of cracks along connected paths of "bad" or susceptible boundaries. The concept of defect engineering could consider any corrosion defect that might have a critical size, spacing, or property that makes the material susceptible to some mode of corrosion.

[40] Symposium D of the MRS: New Advances in Material Predictions; November 30-December 3, 1999.

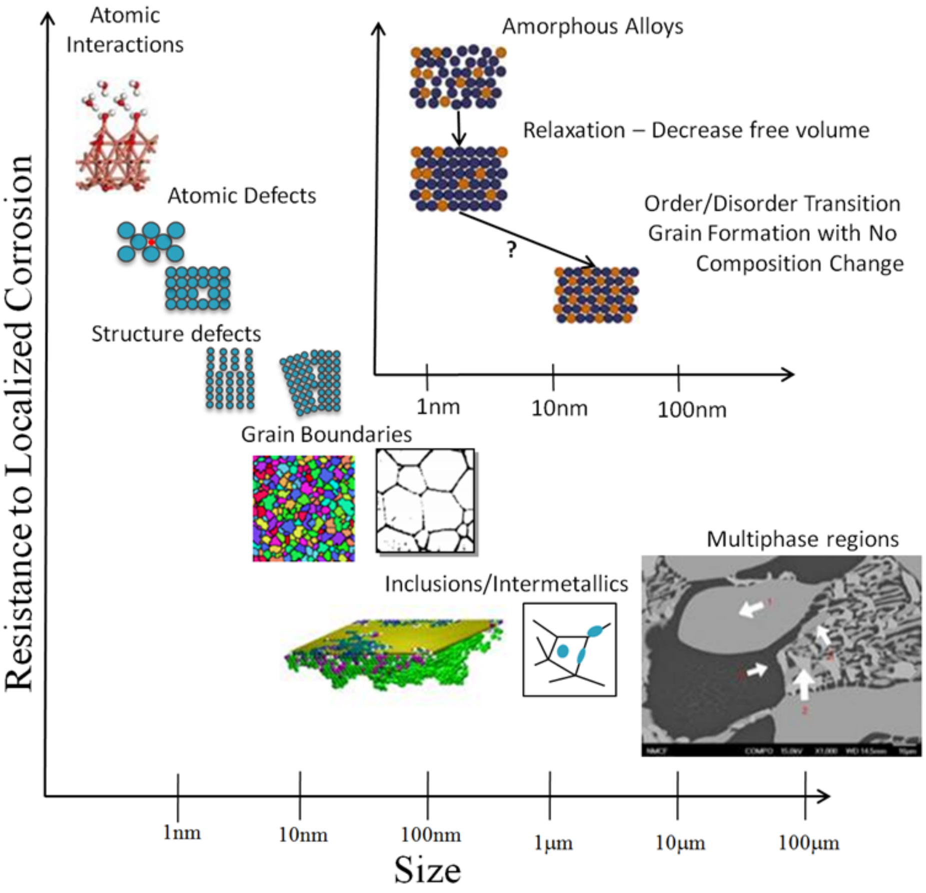

FIGURE 3.12 Hypothetical variation in resistance to localized corrosion with the type of defect and its approximate size (size on the x-axis denotes the defect size). SOURCE: University of Virginia Center for Electrochemical Science and Engineering, courtesy of Derek Horton.

embrittlement for both short and long cracks. However, this has been accomplished only for a limited number of cases, and an atomistic- or molecular-level understanding of these phenomena is still lacking.

In particular, there is no quantified understanding of how stress affects some well-known anodic dissolution SCC mechanisms, such as for pre-existing, active-path corrosion. For example, the distinction between stress-assisted intergranular corrosion and intergranular stress corrosion cracking (IGSCC) with a mix of mechanical and electrochemical driving forces versus intergranular corrosion (IGC) by purely electrochemical driving forces, is blurred (Figure 3.13). The effects of tensile stresses may involve the aggravation of IGC by opening the fissures that

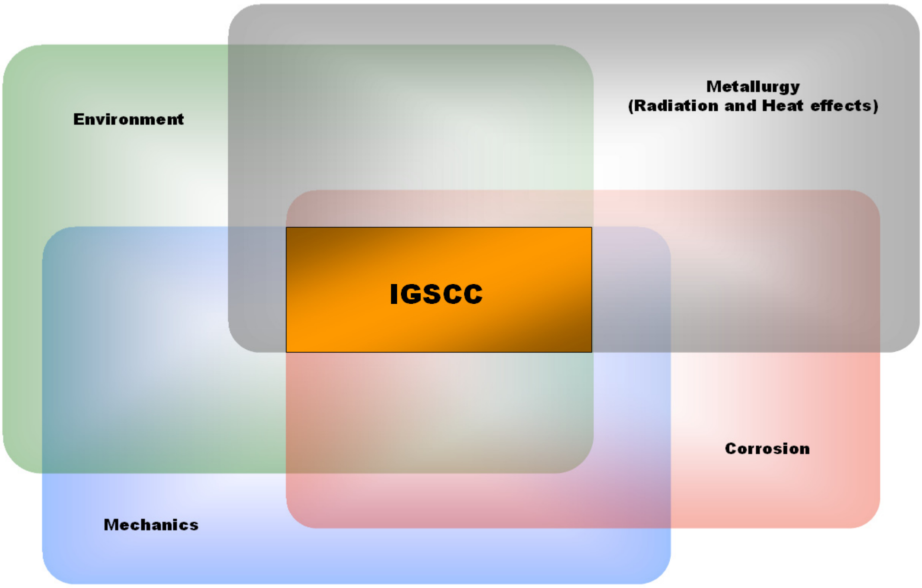

FIGURE 3.13 Areas that are related in intergranular stress corrosion cracking (IGSCC).

develop along grain boundaries facilitating diffusion and electrochemical current flow within the fissures.

The specific role of stress and strain in hydrogen embrittlement and cracking mechanisms has been established in the case of only a few models such as hydrogen-induced decohesion (HIDE) and hydrogen-induced local plasticity (HELP).

Stress also plays a role in localized corrosion owing to its connection with elastic-plastic incompatibilities between particles and matrices. For example, it has been proposed that stress or strain creates a crevice between a hard particle and a soft matrix where a special chemistry may subsequently develop. Stress effects are more complicated in many observed cases of SCC emanating from pits in complex alloys where the oxide film has already been ruptured. Because these driving forces are not well understood, the concept of accumulation of damage under stressed conditions cannot be used as a basis for quantitative life prediction.

Another area that is not well understood is the role played by dynamic plastic strain in the case of hydrogen embrittlement that occurs during hydrogen production taking place in either aqueous or gaseous hydrogen environments. Many engineering alloys are susceptible to this form of attack, yet the role of dynamic strain is unresolved. Many intermediate- and low-strength alloy systems exhibit relative immunity to this form of degradation under purely static loading but become susceptible to environmentally assisted cracking when subjected over time to slowly rising temperature (dK/dt) or to ripple, cyclic, or slow-strain-rate loading.

Although this phenomenon has been studied for years, cracking susceptibility, hydrogen interactions, and deformation substructures have rarely been systematically studied in pre-strained, actively strained, or under film-free or plastic straining conditions. The alloy systems of interest are those with oxide films that can be ruptured to produce clean surfaces prone to hydrogen entry and consequently prone to hydrogen effects such as cleavage, interface cracking, and/or hydriding, Other factors that contribute to a metal's susceptibility deserve further attention, such as dynamic trap state creation within highly deformed crack or notch structures, enhanced surface uptake on atomically clean surfaces, and dislocation transport. Finally, tight cracks and atomically sharp crack tips require additional investigation. Progress is possible given techniques, theories, and modeling. For instance tomographic transmission electron microscopy methods offer the possibility of mapping dislocation structures at crack tips, and diffraction contrast tomography and three-dimensional atom probe methods can help to advance understanding of cracking phenomena inside materials.

Corrosion Mechanisms—Self-stress in the Breakdown of Passive Films and Protective Scales

Although externally applied stresses are certainly important, many corrosion processes generate in situ local stresses. The role that this self-stress or "electrostriction" plays in the breakdown of passive films has often been discussed but is still not understood. In particular, corrosion product formation of films, and passive films, may generate either tensile or compressive stresses—for example magnetite films formed on steel in hot water or steam are in strong compression, resulting in tensile stresses in the underlying steel. Because many of these effects are not well understood, the concept of damage accumulation under stressed conditions cannot be used as a basis for quantitative life prediction.

While some of the effects of, and issues with, stress under aqueous corrosion conditions are fairly well recognized, those associated with high temperatures have received less attention. However, these stress effects play a critical role in determining whether a scale is truly protective with respect to the substrate on which it has grown.

Stress development in oxide scales has been the subject of study, both fundamentally and in terms of its consequences (spallation and its effect in accelerating corrosion) for many years.[41] By far the greatest contribution to stress arises from

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[41] See, for example, J.V. Cathcart, ed., *Stress Effects and the Oxidation of Metals*, Metallurgical Society of AIME, New York, 1975.

the cooling down from the reaction temperature that occurs because of the differences in the respective coefficients of thermal expansion between the reaction product and the material on which it is grown. These stresses can be on the order of gigapascals for certain oxides on metals and as a consequence dominate the ultimate rate of degradation.[42] While the source of thermal stress is predictable, its consequences, in terms of mechanisms of damage accumulation and cracking in the scale and along its interface with the substrate, are still being debated. These mechanisms are quite important because often the rate of spallation ultimately determines corrosion-limited lifetimes.[43] Unlike thermal stresses, the mechanism(s) underlying the source(s) of growth stresses in scales (those that arise during isothermal exposure) are still a subject of great contention. Although debates about mechanisms of growth stresses have been ongoing for decades,[44] interest in this and related issues has been reinvigorated by the relatively recent introduction of synchrotron sources to capture the earliest stages of their development via in situ experiments.[45] While steady-state growth stresses are just a small fraction of thermally generated ones, they can be much higher initially and thus can influence subsequent development of the scale (defect structure and associated transport rates across it). Indeed, the effects of stress (both transient and steady-state) on reaction kinetics, and vice-versa, constitute an understudied area in high-temperature corrosion and offer a presumably fascinating route to better understanding of the atomistic and structural/chemical factors associated with reaction dynamics.

Corrosion Mechanisms—Cracks

An understanding of the chemistry at crack tips and crack surfaces and in the fracture process zone remains elusive. Although there has been substantial progress in rigorously defining the chemical compositions and electrochemical conditions of crack tip solutions, there are a number of opportunities for further development of the model, including a lack of understanding of the exact mechanical properties of passive films at crack tips, uncertainty over bare area created by straining, and the inability to properly inventory bare surface dissolution rates once the

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[42] M. Schütze, *Protective Oxide Scales and Their Breakdown*, Wiley, West Sussex, England, 1997.

[43] M. Schütze, W.J. Quadakkers, and J.R. Nicholls, eds., *Lifetime Modelling of High Temperature Corrosion Processes*, Maney Publishing, Leeds, U.K., 2001.

[44] J. Stringer, Stress generation and relief in growing oxide films, *Corrosion Science* 10:513-543, 1970; F.H. Stott and A. Atkinson, The modelling of growth stresses during high-temperature oxidation, *Materials at High Temperatures* 12:195-207, 1994.

[45] B.W. Veal, A.P. Paulikas, and P.Y. Hou, Tensile stress and creep in thermally grown oxide, Nature Materials 5:349-351, 2006; P.F. Tortorelli, K.L. More, E.D. Specht, B.A. Pint, and P. Zschack, Growth stress-microstructure relationships for alumina scales, *Materials at High Temperatures* 20:303-309, 2003.

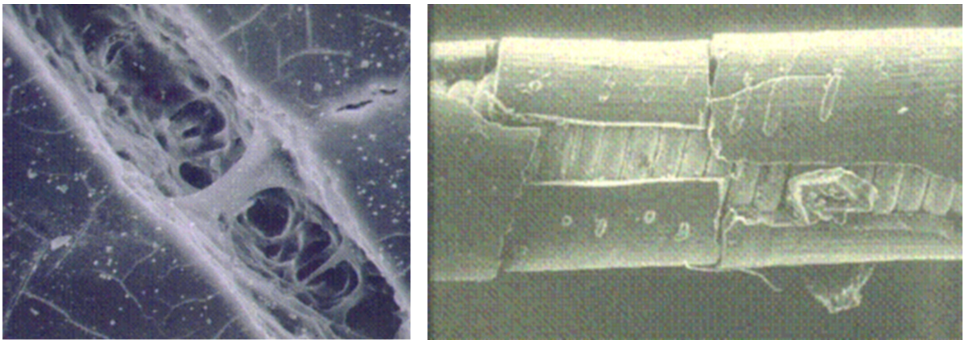

FIGURE 3.14 Large magnification of environmental stress cracking from biological stress cracking of sample under mechanical stress (left) and metal ion oxidation on inner insulation of pacing lead (right). Note impression from outer coils on polymer. SOURCE: Courtesy of Medtronic.

passive film is ruptured. See Figure 3.14 for an example. Another research opportunity lies in the fact that specific effects of trace alloying elements on hydrogen embrittlement in a variety of alloying systems cannot be anticipated or predicted, and that emerging quantitative models of hydrogen embrittlement can only loosely predict material behavior, or must be calibrated by limited experiments to define damage parameters. As with stress corrosion cracking, the effects of heat-to-heat variations cannot be predicted. Consequently, there are no quantitative models or fundamental knowledge to guide the design of high-performance engineering alloys with good fracture toughness and slow crack growth rates for use in extreme environments. Finally, the effects of reactive agents on high-temperature cracking are not as well documented as those associated with aqueous environments and as such represent an additional opportunity for research. An example of this is the processes by which high-temperature corrosion results in preferential reactions along grain boundaries and other extended microstructural features that then serve as paths for cracking and failure. Of greater interest, but less frequently studied, is the direct role of oxygen and other elements in high-temperature crack growth, as exemplified by the seminal work of Woodford and others on nickel-based alloys.[46] Issues that are in some ways similar to the competition between passivity and film breakdown at the crack tip have been discussed,[47] but they have not been studied in any detail, particularly compared to what has been done under aqueous conditions. This is clearly an area for further study given the potentially catastrophic

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[46] D.A. Woodford, Gas phase embrittlement and time dependent cracking of nickel based superalloys, *Energy Materials* 1:59-79, 2006.

[47] See, for example, C.A. Hippsley and J.H. DeVan, Study of high temperature crack growth in nickel-aluminide, *Acta Metallurgica* 37:1485-1496, 1989.

nature of such cracking, the obvious role of stress, the important scientific issues at play, and recent advancements in both modeling and simulation and experimental techniques that can be used to analyze the phenomena.

Corrosion Morphologies—Passivity and Protective Films

A metal in contact with an environment can develop—or not develop—a protective passive film comprising a defective barrier layer and a precipitated, porous outer layer of an oxide, hydroxide, or oxyhydroxide, or even a metal compound containing an anion present in the solution (e.g., siderite in the case of iron corrosion in carbon dioxide-acidified brine). Both films, if present, play important roles in determining the extent of metal passivity and hence metal resistance to corrosion. Passivity breakdown (when passivity exists) is the origin of localized corrosion. Several models exist to explain passivity. Those models based on fundamental principles are still under continual development; i.e., they often contain strong hypotheses, in order to simplify the complexity of passivity. The models evolve by relaxing the underlying assumptions and hypotheses, one at a time, as new information on the mechanism becomes available. The roles of oxide structure, disorder, devitrification, defects, dehydration, adsorbate and water adsorption, and other phenomena must be studied at the molecular scale. As elsewhere, computational and experimental methods are emerging to help produce significant advances in this area.

One model approach is that of examining other alloy systems for transitions in passivity with alloy composition analogous to those seen in stainless steel, but that approach will not lead to breakthroughs in terms of the amount of alloying element required, and there seems to be a fundamental percolation-like law that dictates the need for at least 10 to 12 percent of the beneficial element(s).

A key property of a passive film that may be manipulated in the future is its semiconductive nature in the context of the cathodic reaction that necessarily occurs on top of the film. It is not always appreciated that chromium oxide is a very good electrical insulator, so that in theory one could enrich chromium to such an extent that the reduction of oxygen on top of the passive film on stainless steel would cease, thus eliminating localized corrosion in salt water. In practice, not much iron content is required to make the film rather conductive, but still, manipulation of cathodic reaction kinetics on passive films has to be considered an important challenge for the future. Many tools and theoretical underpinnings are available for further progress in this area, including a variety of in situ probes, surface-science tools, and classical electrochemistry methods.

There is also a lack of understanding concerning nonpassivating, but protective, films, as well as gaps in knowledge concerning how these form and what controls their degree of protection. This is really a complex microscopic chemical engineering system with reaction, transport, pH change, and precipitation of metastable and stable phases. Wetting and drying, as in atmospheric corrosion, add another level of complexity. The length scale of the porosity, for a good protective film, approaches the atomic scale, leading to a whole range of poorly understood transport phenomena, and the physics of such processes are a major challenge in corrosion science. Magnesium and magnesium-aluminum would be a good basis for a systematic study, with an easier metal, such as zinc, as a possible model system.

Corrosion Morphologies—Protective Layers Formed at High Temperature

The key to achieving high-temperature corrosion resistance is the development of a continuous, protective surface layer. (See Box 3.2.) Many of the fundamental mechanisms underlying the phenomena of passive and active oxidation and corrosion at high temperature are quite different from those in low-temperature, aqueous environments, because atoms are more mobile, substrate processes are intimately involved, and gaseous products may form. Rate-limiting mechanisms may include gaseous diffusion through a static gas boundary layer, surface chemical reactions, solid-state diffusion through a surface film or substrate, or dissolution of a subsurface phase. Methods to interrogate buried interfaces and subsurface

BOX 3.2
High-Temperature Protective Scales

The formation and maintenance of protective scales at high temperatures involve the interplay of reactive subsurface diffusive processes influenced by both materials (composition, microstructure) and environmental factors. Once a layer of this type is established, the substrate's access to the environment is effectively isolated, and henceforth controlled by the transport properties and stability of the surface scale as long as its integrity is maintained.[1] A number of possible mechanisms can limit or control the rate of corrosion of a material undergoing a reaction with a fluid, and, consequently, the ability to produce this protective scale. Assume, for example, that a metal (e.g., chromium) reacts with dry oxygen to form a protective scale, chromia, to form a "surface film." In loose analogy with aqueous corrosion, this scale can be considered a passivation layer, but it is much more dynamic than the passive film formed at low temperatures in aqueous environments in that it has a finite but, by definition of a protective layer, low growth rate. Under conditions of very low oxygen partial pressure, a surface oxide may be absent and instead a gaseous, volatile oxide may form, resulting in so-called "active" oxidation. Passive and active oxidation may also occur in parallel. This leads to the formation of a film that grows to a steady state thickness.[2]

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[1] The role of stress in damaging and disrupting this scale is an intense area of study—see discussion elsewhere in this chapter.

[2] B.E. Deal and A.S. Grove, General relationship for the thermal oxidation of silicon, *Journal of Applied Physics* 36:3770-3778, 1965.

structural changes in situ are therefore of great and particular interest to the study of high-temperature corrosion phenomena and complement information gleaned from surface analytical techniques.

Wider study using sensitive in situ and ex situ probes of protective scale breakdown and subsurface processes, especially for multiphase materials and under multireactant conditions, is needed to develop a comprehensive, generic understanding of factors controlling terminal protective scale breakdown in order to predict corrosion lifetimes and to guide mitigation strategies related to materials/coating design for extended component life.

The effects of water vapor on high-temperature oxidation have always been of scientific interest for many of the reasons described earlier in this section. However, within the past 10 to 15 years, this area of study has received increasingly greater attention because many important applications (e.g., gas turbines, steam generation systems, and solid-oxide fuel cells) involve environments with relatively high levels of water that scale, in many cases, with efforts to enhance efficiency (e.g., ultrasupercritical steam or higher-turbine-pressure ratios). The presence of water vapor in the environment often promotes higher oxidation rates—particularly for chromia- or silica-formers where water can dramatically enhance oxide volatization; impact oxide structure, stability, and/or solid-state transport properties in a negative way; and decrease corrosion lifetimes.[48] While there has been substantial progress in finding alloys that are more resistant to water vapor or coatings to protect silicon-bearing ceramics in water-bearing environments,[49] there is still much to be learned about effects on protective scale stability and the underlying defect mechanisms controlling transport, particularly for the more extreme environments envisioned for future technologies.[50]

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[48] E.J. Opila, N.S. Jacobson, D.L. Myers, and E.H. Copland, Predicting oxide stability in high-temperature water vapor, *Journal of the Minerals, Metals, and Materials Society* 58:22-28, 2006; I. Kvernes, M. Oliveira, and P. Kofstad, High temperature oxidation of Fe–13Cr–xAl alloys in air/water vapor mixtures, *Corrosion Science* 17:237-52, 1977; H. Asteman, J.-E. Svensson, M. Norrell, and L.-G. Johansson, Influence of water vapor and flow rate on the high-temperature oxidation of 304L: Effect of chromium oxide hydroxide evaporation, *Oxidation of Metals* 54:11-26, 2000; J.M. Rakowski and B.A. Pint, Observations on the effect of water vapor on the elevated temperature oxidation of austenitic stainless steel foil, Proceedings of Corrosion 2000, NACE Paper 00-517, NACE International, Houston, Texas, 2000; E. Essuman, G.H. Meier, J. Zurek, M. Hänsel, and W.J. Quadakkers, The effect of water vapor on selective oxidation of Fe–Cr Alloys, *Oxidation of Metals* 69:143-162, 2008; E.J. Opila, Oxidation and volatilization of silica formers in water vapor, *Journal of the American Ceramic Society* 86(8):1238-1248, 2003.

[49] See, for example, K.N. Lee, D..S. Fox, and N.P. Bansal, Rare earth silicate environmental barrier coatings for SiC/SiC composites and Si3N4 ceramics, *Journal of the European Ceramic Society* 25:1705-1715, 2005.

[50] Department of Energy, *Basic Research Needs for Materials Under Extreme Environments*, Report of the Basic Energy Sciences Workshop on Materials Under Extreme Environments, June 11-13, 2007, available at http://www.sc.doe.gov/bes/reports/files/MUEE_rpt.pdf.

Even seemingly simple, well-studied, high-temperature corrosion and oxidation phenomena continue to offer research challenges, mainly related to the clear advantages of making direct observations of atomic-level processes at high temperatures and studying product and phase evolution, reaction kinetics, and other developments (such as stress and morphology) in real time. To date, most mechanistic studies have required the analysis of many pieces of data, which are typically derived from indirect measurements of atomic-level processes—for example, measurements of weight change, film thickness, or characterization of microstructural features. Emerging capabilities to probe atomic- and molecular-level phenomena in situ and with high time, spatial, and chemical resolution—and to model such over equivalent time and length scales—offer great opportunities to make substantial progress in high-temperature corrosion science over the next few years.

Corrosion Morphologies—Phase/Phase Morphologies and Microstructural Defects

Defect engineering is a concept that has been relegated primarily to serendipity and is not yet well developed; however, defect engineering involving control via manipulation of surface defects (e.g., undesirable intermetallic compounds that serve as pit initiation sites) is a possible cost-effective and novel strategy. Analogous to damage tolerant design in the fracture community, defect engineering incorporates flaw (crack) size and shape into fracture mechanics analysis, as well as mechanical load and global geometry. The purpose is to assess the risk of cracking. Thus corrosion damage is already incorporated on a very limited basis in defect engineering, which is also referred to as grain boundary and interface engineering. Types of defect engineering include changing the intrinsic properties of susceptible pit-forming defects or replacing them with more benign defects, changing the critical spacing of such defects, and changing the size or other attributes of critical defects. Defect engineering of grain boundaries is also possible where the distribution and percentage of corrosion-prone grain boundaries (i.e., highly misoriented grain boundaries) are controlled. Models for defect engineering may be expanded to include the effects of defect size, spacing, and intrinsic defect properties or extended to the case of grain boundaries where the most corrosion-prone boundaries, their distribution, connectivity, and grain shape can all be explored computationally and experimentally to optimize resistance to intergranular corrosion. Materials design and processing can be guided by these insights.

Corrosion Environments—Predicting Corrosion Properties of Materials in a Wide Range of Environments

There is often a great deal of corrosion data on a number of engineered materials. However, much of the available data is clustered in a limited number of environments, particularly full immersion environments. This has a number of implications, including the inability to create a meaningful national database of corrosion data useful to industry, government, and academia. Not only is there the issue of full immersion, atmospheric, and alternate immersion aqueous environments, but there are also radically different environments such as nonaqueous and high-temperature environments.

Ethanol is an example of the sort of environment for which a better ability to predict its influence on various forms of corrosion is paramount, because planned widespread use of ethanol will require an efficient and reliable transport system. Steel pipelines are by far the most cost-effective means of transporting large quantities of fuel over long distances. However, it is critical to assure that pipelines transporting ethanol are reliable and safe. Recently, SCC in the presence of fuel-grade ethanol (FGE) has been recognized and identified as a phenomenon in end-user storage and blending facilities. Investigation of the mechanisms of corrosion and cracking of steel in biofuels is still in the early stages, and the electrochemical techniques that have been applied successfully to evaluate SCC in aqueous systems are a challenge in the high-resistivity FGE environment. Bioethanol derived from sugar cane is used extensively in Brazil. Brazilian ethanol is hydrous, containing about 6 percent water (compared to the bioethanol used in the United States, which has <1 percent), which does not cause SCC. Other nonaqueous environments of interest in corrosion include a wide range of environments in batteries and fuel cells as well as a variety of biological environments. In general, environments with low water content produce different behavior, especially when an insufficient level of water is available for passivation.

Corrosion Environments—Connection Between Nominal Environmental Conditions and the Actual Chemistry of the Environment

A critical but poorly understood factor related to atmospheric exposure is the connection between nominal environmental conditions (e.g., humidity, ultraviolet radiation, pollution, atmospheric particles, and so on) and the actual chemistry of the environment on the material's surface. Time-of-wetness is known to be an important parameter in outdoor exposure, given that water associated with precipitation or condensation is critical to the corrosion processes. However, accurate prediction of corrosion rates depends on knowing how the water on the surface affects the concentration of all the important corrosive species.

TECHNIQUES AND TOOLS FOR RESEARCH

The committee highlights below some of the analytical techniques that have enabled, and will continue to enable, ongoing advances in corrosion science and in mitigation of corrosion. Steady progress in improving sensitivity, area and volume sampled, acquisition speed, and quantification makes it worthwhile to look not only toward new research efforts but also back at questions previously examined. A smaller probe size might finally enable insights about the evolution of a particular material's degradation, or the enhanced discrimination of species might shed light on the chemical environment around a corrosion pit. Steady improvement in capabilities is occurring across a wide breadth of techniques, only a few of which are highlighted below to indicate the current exciting possibilities. The committee felt strongly that it should not try to indicate which techniques and approaches hold the greatest potential for addressing the corrosion grand challenges, not only because of its inability to cover every one of the vast array of experimental and computational advances, but also, and more importantly, because the research community has historically proved adept at taking advantage of such advances when and where scientifically and technically appropriate.

Examples of Relevant Techniques and Tools

Atom Probe Tomography

Atom probe tomography and its ability to reveal the three-dimensional atomic structure of materials has become a very powerful tool in modern materials science.[51] However, its application to corrosion science has been quite limited despite the ability to finely resolve phenomena such as elemental segregation that can play such an important role in sensitization and associated stress corrosion cracking or in internal oxidation. Furthermore, until the recent advent of the laser-induced local-electrode atom probe (LEAP) technique,[52] ceramics materials could not be analyzed because of the inability of such brittle materials to withstand the high fields necessary to release atoms for subsequent mass analysis. However, using a laser-LEAP, it has been recently demonstrated that bulk alumina can be imaged with quantitative concentration determinations.[53] This opens up the possibility for detailed examination of protective oxide scales, such as alumina, to probe the disposition of minor species, which can profoundly influence how effective such surface oxides are at proffering oxidation at high temperatures. For corrosion effects at more moderate temperatures, a recent study has used the laser-LEAP to

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[51] T.F. Kelly and M.K. Miller, Atom probe tomography, *Review of Scientific Instruments* 78: 031101, 2007.

[52] D.J. Larson, R.L. Alvis, D.F. Lawrence, T.J. Prosa, R.M. Ulfig, D.A. Reinhard, P.H. Clifton, S.S.A. Gerstl, J.H. Bunton, D.R. Lenz, T.F. Kelly, and K. Stiller, Analysis of bulk dielectrics with atom probe tomography, *Microscopy and Microanalysis* 14(Suppl 2):1254-1255, 2008.

[53] E.A. Marquis, N.A. Yahia, D.J. Larson, M.K. Miller, and R. Todd, Probing the improbable: Imaging carbon atoms in alumina, submitted to *Materials Today*, May 2010.

resolve fine microstructural and compositional details of an oxide film on stainless steel formed under pressurized-water-reactor conditions (see Figure 3.15).[54] Such findings indicate the potential of state-of-the-art atom probe techniques to advance basic corrosion science knowledge and help understand origins of failures due to environmental degradation.

Time-of-Flight SIMS

Secondary ion mass spectrometry (SIMS) has had an important role in corrosion science (as shown, for example, in the work of Bishop et al. [55] and Marriott et al.[56]). For high-temperature oxidation, it has been particularly powerful in determining transport mechanisms in protective oxide scales grown on metallic specimens using O^{18} exposures.[57] Recently, time-of-flight SIMS has been used to generate detailed images through sections of protective oxide scales, revealing details of the distribution of various alloying elements/phases (Figure 3.16).[58] Further application of this technique to corrosion science and engineering seems well justified.

Advanced Electron Microscopy

For many years, transmission electron microscopy has been of great benefit to corrosion science and engineering by revealing the relationships among microstructure (and, now, nanostructure), composition, and different corrosion behaviors (dissolution, crack growth, scaling, and so on)—see, for example, Przybylski et al.[59] and Gertsman and Bruemmer.[60] Advances in analytical election microscopy for high-resolution chemical analysis and focused ion beam techniques to provide high-quality thinned sections of oxidized material from precise areas of a corroded specimen (for example, Haynes[61]) have truly made electron microscopy an essential

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[54] S. Lozano-Perez, D.W. Saxey, T. Yamada, and T. Terachi, Atom-probe tomography characterization of the oxidation of stainless steel, *Scripta Materialia* 62:855-858, 2010.

[55] H.E. Bishop, D.P. Moon, P. Marriott, and P.R. Chalker, Applications of a high spatial resolution combined AES/SIMS instrument, *Vacuum* 39:929-939, 1989.

[56] P. Marriott, S.B. Couling, and P.R. Chalker, High spatial resolution SIMS investigation of oxides formed on stainless steel under PWR conditions, *Applied Surface Science* 37:217-232, 1989.

[57] J. Jedlinski and G. Borchardt, On the oxidation mechanism of alumina formers, *Oxidation of Metals* 36:317-337, 1991.

[58] D.B. Hovis and A.H. Heuer, unpublished data.

[59] K. Przybylski, A.J. Garratt-Reed, and G.J. Yurek, Grain boundary segregation of yttrium in chromia scales, *Journal of the Electrochemical Society* 135:509, 1988.

[60] V.Y. Gertsman and S.M. Bruemmer, Study of grain boundary character along intergranular stress corrosion crack paths in austenitic alloys, *Acta Materialia* 49:1589-1598, 2001.

[61] J.A. Haynes, B.A. Pint, K.L. More, Y. Zhang, and I.G. Wright, Influence of sulfur, platinum, and hafnium on the oxidation behavior of CVD NiAl bond coatings, *Oxidation of Metals* 58:513, 2002.

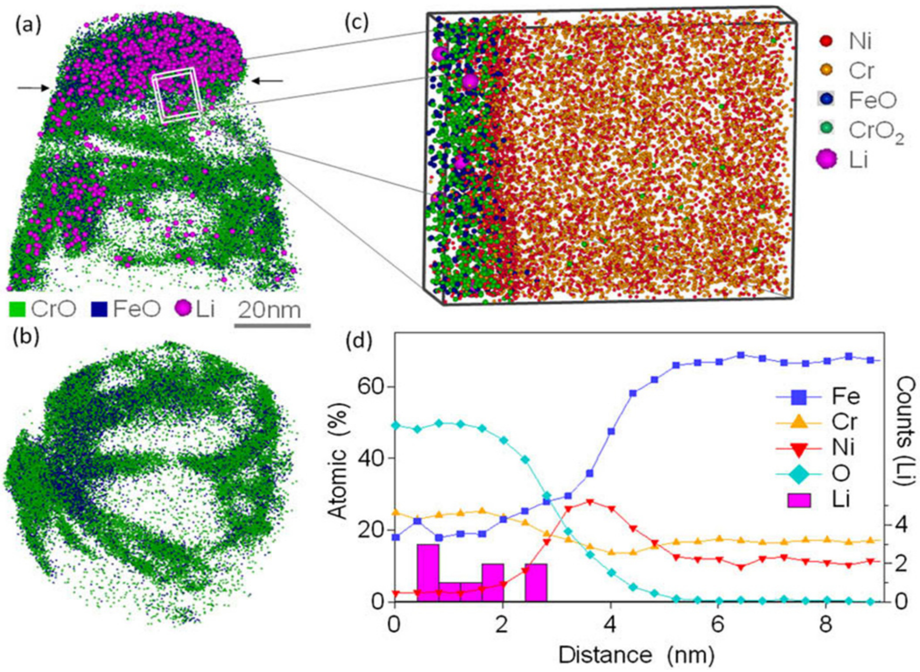

FIGURE 3.15 (a) Atom probe tomography reconstruction showing the presence of Li atoms within the cap and sub-interface oxides. The arrows indicate the location of the cap-oxide-to-metal interface. The Li atom distribution is superimposed on the oxide atom maps. (b) Top view of the sub-interface region showing the distribution of oxides (cap oxide removed). The oxide regions beneath the cap are interconnected. (c) Sub-volume (5 × 15 × 18 nm; ~40,000 detected atoms) taken from the cap-oxide-to-metal interface showing selected species. (d) Concentration profile across the oxide–metal interface generated using the proxigram technique. The presence of Li is represented by an atom count because its concentration is very low. Uncertainties in the data points are comparable to the marker size. SOURCE: Reproduced from S. Lozano-Perez, D.W. Saxey, T. Yamada, and T. Terachi, Atom-probe tomography characterization of the oxidation of stainless steel, *Scripta Materialia* 62:855-858, 2010.

part of corrosion research and development and failure analysis. Currently, there are numerous efforts to develop ways to conduct in situ experiments inside the columns of high-resolution electron microscopes, including the introduction of liquids (see Figure 3.17).[62] Such developments have obvious relevance to advancing the state of fundamental knowledge about corrosion processes and how such processes are controlled by structure and composition.

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[62] N. de Jonge, D.B. Peckys, G.J. Kremers, and D.W. Piston, Electron microscopy of whole cells in liquid with nanometer resolution, *Proceedings of the National Academy of Sciences* 106:2159-2164, 2009.

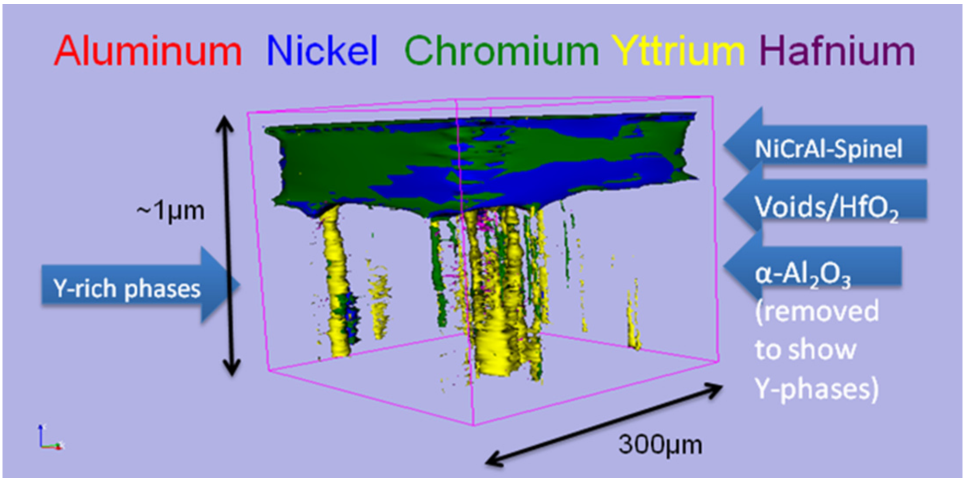

FIGURE 3.16 Cross-sectional view of multilayer scale formed on an oxidized NICrAl (YHf) alloy (spinel overlaying α-alumina). The α-alumina data have been removed to show the morphology of the embedded Y-rich oxide phases. SOURCE: D.B. Hovis and A.H. Heuer, unpublished data.

Neutron Scattering

Neutron scattering has not found wide applicability in corrosion science but is proving scientifically powerful in unraveling the structure and dynamics of oxide-H_2O interfacial regions of relevance to geochemistry and the fundamental science of aqueous solutions in contact with solids.[63,64] The greater penetrating power of neutrons, compared to other energetic beams used for analysis, can allow subsurface (or undercoating) structures and processes to be probed and could prove to be of particular value for in situ experiments. Defect distributions, structural fluctuations, and film growth can be monitored as a function of depth into a solid using various neutron scattering techniques, and the sensitivity of neutrons to protonic species is of particular relevance to many corrosion processes.

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[63] E. Mamontov, L. Vlcek, D.J. Wesolowski, P.T. Cummings, W. Wang, L.M. Anovitz, J. Rosenqvist, C.M. Brown, and V. Garcia Sakai, Dynamics and structure of hydration water on rutile and cassiterite nanopowders studied by quasielastic neutron scattering and molecular dynamics simulations, *Journal of Physical Chemistry C* 111:4328, 2007.

[64] E. Mamontov, D.J. Wesolowski, L. Vlcek, P.T. Cummings, J. Rosenqvist, W. Wang, and D.R. Cole, Dynamics of hydration water on rutile studied by backscattering neutron spectroscopy and molecular dynamics simulations, *Journal of Physical Chemistry C* 112:12334, 2008.

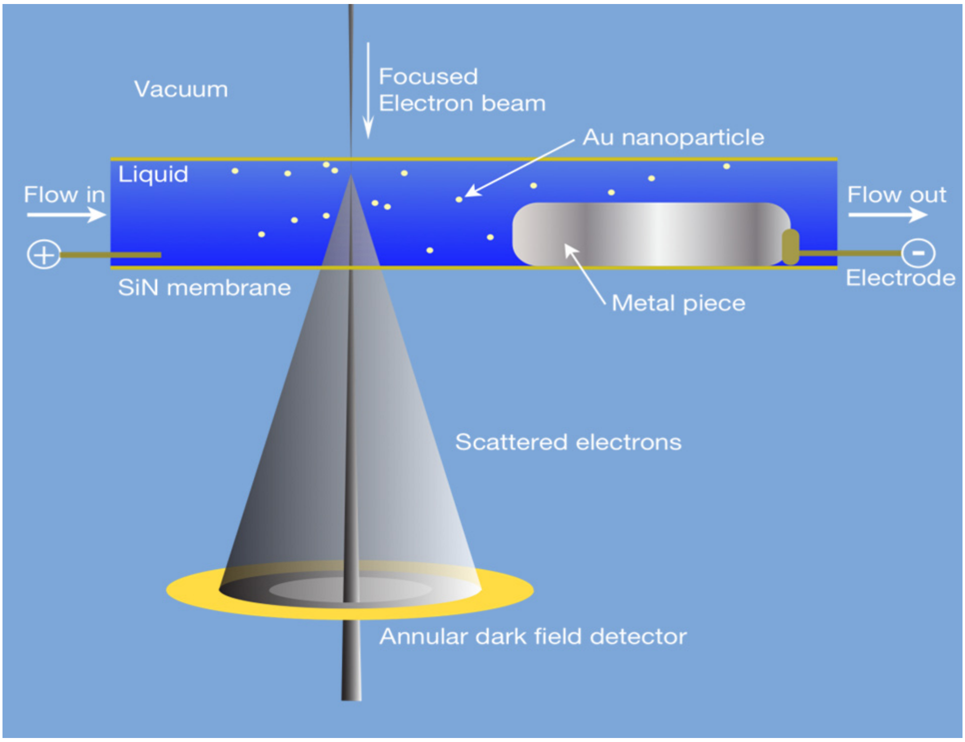

FIGURE 3.17 Schematic of scanning transmission electron imaging of metallic nanoparticles in a liquid. SOURCE: Reproduced from N. de Jonge, D.B. Peckys, G.J. Kremers, and D.W. Piston, Electron microscopy of whole cells in liquid with nanometer resolution, *Proceedings of the National Academy of Sciences* 106:2159-2164, 2009.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface analytical approach that provides detailed chemical information from the top 1 to 10 nm of a sample surface. The surface is irradiated with an x-ray beam and the kinetic energy of the emitted electrons is analyzed. This technique is well established in the corrosion field because it has great utility to measure thin protective films and corrosion product layers. The latest technical developments in XPS instrumentation enhance the usefulness of the technique. One trend is a decreasing x-ray beam size. X-ray beams are much more difficult to focus than electron beams, which are used in many other analytical techniques. As a result, XPS has relatively poor lateral resolution. However, XPS tools now provide x-ray beams less than 10 micrometers in diameter, which allows for the analysis of surfaces on small microstructural features such as second phases and inclusions. Another development in XPS technology involves the ion beams used to sputter samples for depth profiling. Standard ion beams such as Ar ion beams can damage samples, particularly organic samples such as paint coatings, which is relevant to corrosion. In recent years beams of large ion clusters have been offered for use in sample sputtering. Ions of C_{60}, so-called buckyballs, allow for gentler sputtering. The large ions impact the surface with a lower speed so that there is much less penetration and much less damage compared to beams of single ions. Very recent reports have shown that large gas cluster ions caused very little damage during sputtering of polyimide, which is very sensitive to ion irradiation damage.[65] In this work the gas cluster ion gun generated an Ar ion cluster distribution centered at Ar2500. The polyimide XPS spectra before and after sputtering with this beam exhibited very little change.

Electron Backscatter Diffraction

Although the fundamentals of the technique can be traced back to the work of Kikuchi in the late 1920s, electron backscatter diffraction (EBSD) emerged in the early 1980s as a method for analysis of local crystallographic texture in materials.[66] Automation and computerization of the analysis of backscattered electron diffraction patterns led by Adams and co-workers in the 1990s further led to the development of commercial software and hardware that has enabled EBSD to become a relatively mature technique today for characterizing microtexture.[67] It is well known that the crystallographic texture of a material influences its thermophysical properties. Manipulating texture through heat treatment or forming techniques such as rolling or pilgering may lead to improvements in corrosion resistance or resistance to environmentally influenced cracking if applied properly.

A few groups have used EBSD to inspect growth processes at crack tips during stress corrosion cracking and other crack-growth processes in structural alloys[68]

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[65] T. Miyayama, N. Sanada, M. Suzuki, J.S. Hammond, S.-Q.D. Si, and A. Takahara, X-ray photoelectron spectroscopy study of polyimide thin films with Ar cluster ion depth profiling, *Journal of Vacuum Science and Technology A* 28:L1, 2010, doi: 10.1116/1.3336242.

[66] A.J. Schwartz, M. Kumar, and B.L. Adams, *Electron Backscatter Diffraction in Materials Science*, Kluwer Academic/Plenum Publishers, New York, 2000.

[67] B.L. Adams, S.I. Wright, and K. Kunze, Orientation imaging: The emergence of a new microscopy, *Metallurgical and Materials Transactions A* 24A(4):819-831, 1993.

[68] A.F. Gourgues, Electron backscatter diffraction and cracking, *Materials Science and Technology* 18:119-133, 2002; G.S. Rohrer, D.M. Saylor, B.E. Dasher, B.L. Adams, A.D. Rollett, and P. Wynblatt, The distribution of internal interfaces in polycrystals, *International Journal of Materials Research* 95:197-214, 2004; A. King, G. Johnson, D. Engelberg, W. Ludwig, and J. Marrow, Observations of intergranular stress corrosion cracking in a grain-mapped polycrystal, *Science* 321:382-385, 2008; J. Burns, "High Temperature Fatigue Crack Growth Behavior and Microstructural Evolution in Alloy 230," M.S. thesis, Boise State University, 2010.

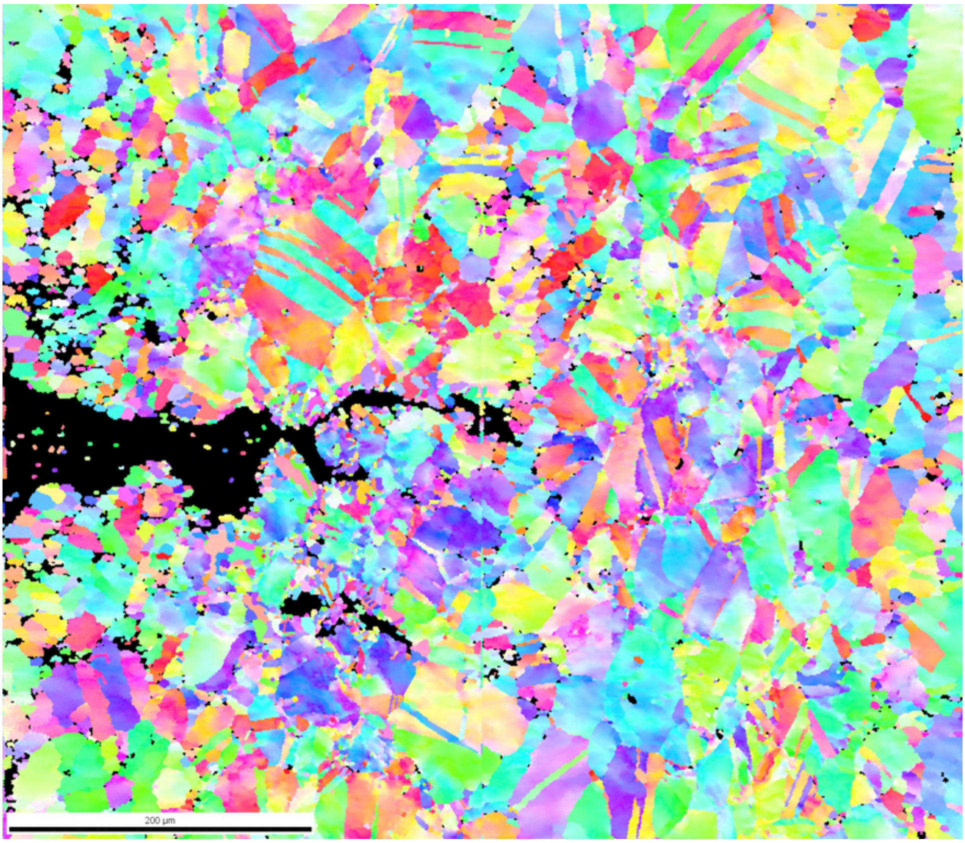

FIGURE 3.18 Electron backscatter diffraction image of a fatigue crack in alloy X. Bar is 200 µm. Colors represent specific crystal orientations. SOURCE: Courtesy of J. Burns and M. Frary, Boise State University, from J. Burns, "High Temperature Fatigue Crack Growth Behavior and Microstructural Evolution in Alloy 230," M.S. thesis, Boise State University, 2010.

(see Figure 3.18). Although only a small number of materials have been analyzed under a narrow range of conditions, studies suggest that the propensity for environmentally induced crack growth can be strongly affected by changes in the orientation from one grain to another. For example, Arafin and Szpunar found that low-angle and special coincident site lattice boundaries in API X-65 pipeline steel were more resistant to crack propagation compared to high-angle boundaries.[69] The use of EBSD, particularly when combined with other tools such as FIB and

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[69] M.A. Arafin and J.A. Szpunar, A new understanding of intergranular stress corrosion cracking resistance of pipeline steel through grain boundary character and crystallographic texture studies, *Corrosion Science* 51:119-128, 2009.

microstructural modeling, may lead to the discovery of textured, low-cost materials resistant to SCC and other environmentally induced crack processes.

Terahertz Acoustical and Electromagnetic Spectroscopy

One of the real measurement issues facing the corrosion scientist and engineer involves detecting and characterizing "hidden" corrosion, which ranges from corrosion in structures underlying the tiles on the space shuttle and corrosion of the steel reinforcement bars used in concrete bridges, roads and structures, to corrosion and blistering under paints and other types of protective and decorative coatings. An approach whose use has been growing recently is the use of both electromagnetic (EM) methods in the terahertz frequency (often between 300 GHz and 3 THz) range and acoustic spectroscopy/microscopy in related frequency ranges, as well as mixed-mode methods sometimes identified as pulsed laser acoustics or photoacoustic near-infrared spectroscopy. Reviewed in several references,[70] the EM methods occupy a niche in EM nondestructive evaluation (NDE) used in studies of corrosion under tiles in the space shuttle.[71] Acoustic methods, often described under acoustic microscopy,[72] have been used recently in studies of corrosion-related blistering in organic coatings.[73] Laser-induced acoustics to study corrosion at interfaces has also been developing quite rapidly.[74] All of these methods seek to identify hidden sites of corrosion, characterize the events and processes occurring at these hidden interfaces, and provide images, numerical characterization, or mechanistic interpretation of results. Blistering, adhesion loss, and degradation of protective coatings have been studied in detail by these methods.

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[70] D.L. Woolard, R. Brown, M. Pepper, and M. Kemp, Terahertz frequency sensing and imaging: A time of reckoning future applications, *Proceedings of the IEEE* 93:1722-1743, 2005; M.C. Martin, U. Schade, P. Lerch, and P. Dumas, Recent applications and current trends in analytical chemistry using synchrotron-based Fourier transform infrared microspectroscopy, *Trends in Analytical Chemistry* 29:453-463, 2010.

[71] E.J. Madras et al., Application of terahertz radiation to the detection of corrosion under the shuttles thermal protection system, pp. 421-428 in *Review of Progress in Quantitative Nondestructive Evaluation,* Volume 27, 2008.

[72] A. Briggs, *Acoustic Microscopy,* Clarendon Press, Oxford, U.K., 1992.

[73] M. Doughtery and J.M. Sykes, A quantitative study of blister growth on lacquered food cans by scanning acoustic microscopy, *Corrosion Science* 50:2755-2772, 2008; I. Alig, S. Tadjbach, P. Krüger, H. Oehler, and D. Lellinger, Characterization of coatings systems by scanning acoustic microscopy: Debonding, blistering and surface topology, *Progress in Organic Coatings* 64:112-119, 2009.

[74] J. Vollmann, D.M. Profunser, A.H. Meier, M. Döbeli, and J. Dual, Pulse laser acoustics for the characterization of inhomogeneities at interfaces of microstructures, *Ultrasonics* 42:657-663, 2004; A. Blouin, C. Neron, and L.P. Lefebvre, Nondestructive structure characterization by laser-ultrasonics, pp. 441-444 in *MetFoam 2007—Proceedings of the 5th International Conference on Porous Metals and Metallic Foams,* DEStech Publications, Inc., Lancaster, Pa., 2008.

Combined Techniques and Tools

One of the great hurdles in the study of corrosion is how remarkably difficult it is to make direct measurements of the rate of corrosion. Direct measurement is especially problematic because corrosion is often highly heterogeneous and sometimes takes place in cavities such as pits shielded by metal in wet environments. Electrochemical measurements cannot give spatial information: the traditional method is serial sectioning, but this causes the pit or intergranular corrosion site to cease to exist, so that it is not possible to obtain time-dependent information. The second greatest need beyond the need for information on aspects of hidden corrosion is the acute need to acquire information linking the electrochemical properties and other damage-related phenomena—such as cracking, pitting, locally dissolving, dealloying, and even hydriding—to the chemical and structural characteristics of the metallic alloy in question with spatial resolution. Traditionally this has been done with separate yet similar sites or separate specimens analyzed using separate techniques. In other words, no one corrosion site can be simultaneously subjected to multiple characterization probes. Another way to state this need is that there is an acute need for several types or channels of information (structural, chemical, electrochemical, hydrogen, and information from electrical and chemical spectroscopy) at the same time and at the same location on a surface with nanometer-scale resolution in situ. Connected to this need is the desire to look at more than one corrosion site, such as several grain boundaries, so that results from one isolated boundary or crack tip are not accidentally taken to represent the average or most prevalent behavior in the entire material. This has been a traditional shortcoming of STEM work capable of structural and chemical characterization of a slice of a crack tip. The effort expended is enormous to section and characterize just a few crack tips.

Recent advances in three-dimensional microtomography as discussed below present the opportunity to map hidden damage in three dimensions and in real time.[75] Advances in the three-dimensional atom probe tomography, three-dimensional secondary ion mass spectroscopy, and three-dimensional techniques focused ion beam sectioning are all helpful, but the need exists to combine these approaches into a supertool than can raster over large areas and then focus on sites of interests with high resolution.

Electrochemical Impedance

In the last several decades there has been an explosion of techniques that can probe instantaneous corrosion rates, including electrochemical impedance, har-

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[75] S. Lozano-Perez, D.W. Saxey, T. Yamada, and T. Terachi, Atom-probe tomography characterization of the oxidation of stainless steel, *Scripta Materialia* 62:855-858, 2010.

monic and electrochemical frequency modulation methods, and electrochemical noise methods. One approach to determining rates of corrosion and gaining mechanistic insight about corrosion of a metal involves the electrochemical impedance (sometimes known as AC impedance) method. Over the past 30 years this method has received much attention in corrosion and has shed a good deal of additional light on corrosive processes. It also has applicability to corrosion sensors. In this technique, typically a small-amplitude sinusoidal potential perturbation is applied to the subject alloy at a number of discrete frequencies, ω. At each one of these frequencies, the resulting current waveform will exhibit a sinusoidal response that is out of phase with the applied potential signal by a certain amount (Φ) and has a current-amplitude that is inversely proportional to the impedance of the interface. The electrochemical impedance, $Z(\omega)$, is the frequency-dependent proportionality factor that acts as a transfer function by establishing a relationship between the excitation voltage signal and the current response of the system. The electrochemical impedance is a fundamental characteristic of the electrochemical system it describes and contains information on the resistance to charge transfer, mass transfer, and ohmic resistive processes. Knowledge of the frequency dependence of impedance for a corroding system allows a determination of an appropriate equivalent electrical circuit describing that system. The method has application to organic coatings, bare metals, passive films, and other corrosion-related applications. Challenges still remain, however, such as determination of corrosion rates under coatings and at defects.

Both harmonic and electrochemical frequency modulation (EFM) methods takes advantage of nonlinearity in the E-I response of electrochemical interfaces to determine corrosion rate. A special application of harmonic methods involves harmonic impedance spectroscopy. The EFM method uses one or more AC voltage perturbations in order to extract corrosion rate. In the most often used EFM method, a potential perturbation by two sine waves of different frequency is applied across a corroding metal interface. The E-I behavior of corroding interfaces is typically nonlinear such that such a potential perturbation in the form of a sine wave at one or more frequencies can result in a current response at the same and at other frequencies. The result of such a potential perturbation is various AC current responses at various frequencies such as zero, harmonic, and intermodulation. The magnitude of these current responses can be used to extract information on the corrosion rate of the electrochemical interface or conversely the reduction-oxidation rate of an interface dominated by redox reactions, as well as the Tafel parameters. This is an advantage over polarization resistance and electrochemical impedance spectroscopy (EIS) methods. A special extension of the method involves harmonic impedance spectroscopy whereby the harmonic currents are converted to harmonic impedance values at various frequencies through knowledge of the magnitude of the AC perturbation. Electrochemical noise analysis can provide a parameter called the electrochemical noise resistance, Rn. It is desirable to utilize this parameter in an analogous fashion as the polarization resistance or EIS. This method also has application in sensors, but interpretation is often controversial. The future direction in these techniques is to extend them to heterogeneous corrosion processes on smaller length scales, and in combination with other spectroscopies such as local atom and molecular spectroscopies in such a way that spatial and temporal information is given from the same surface at once. Still, hidden corrosion remains a challenge, as do sensor interpretation and subsequent decision-making algorithms.

Near-Field Scanning Optical Microscopy[76]

Near-field scanning optical microscopy (NSOM) is a technique for nanostructure investigation that breaks the far-field resolution limit by exploiting the properties of evanescent waves. This is done by placing the detector very close (at a distance much smaller than wavelength λ) to the specimen surface, thus allowing for inspection of the surface with high spatial, spectral, and temporal resolving power. With this technique, the resolution of the image is limited by the size of the detector aperture and not by the wavelength of the illuminating light in the traditional wave optic limit. In particular, lateral resolution of 20 nm and vertical resolution of 2 to 5 nm have been demonstrated. As in optical microscopy, the contrast mechanism can be easily adapted to study different properties, such as refractive index, chemical structure, and local stress. Dynamic properties can also be studied at a subwavelength scale using this technique.

It is possible to take advantage of the various contrast techniques available to optical microscopy through NSOM but with much higher resolution. By using the change in the polarization of light or the intensity of light as a function of the incident wavelength, it is possible to make use of contrast-enhancing techniques such as staining, fluorescence, phase contrast, and differential interference contrast. Staining and fluorescence have large applications in corrosion, especially if the staining or fluorescence indicates key chemicals that are significant to corrosion reactions. These methods have been applied to corrosion already but seldom are coupled to an array of methods. It is also possible to provide contrast using the change in refractive index, reflectivity, local stress, and magnetic properties, among others.

Instead of performing imaging of a surface, various near-field spectroscopy methods can be applied to the study of corrosion, such as micro-Raman and surface-enhanced micro-Raman or other atomic and molecular microscopy techniques.

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[76] Paragraphs one and two reproduced from http://en.wikipedia.org/wiki/Near-field_scanning_optical_microscope.

Scanning Probe Microscopy

Scanning probe microscopy (SPM) makes it possible to form images of surfaces using a physical probe that scans the specimen. An image of the surface is obtained by mechanically moving the probe in a raster scan of the specimen, line by line, and recording the probe-surface interaction as a function of position. SPM began with the invention of the scanning tunneling microscope in 1981. Many scanning probe microscopy techniques can image several interactions simultaneously. The manner of using these interactions to obtain an image is generally called a mode. The resolution varies somewhat from technique to technique, but some probe techniques reach a rather impressive atomic resolution, owing largely to the ability of piezoelectric actuators to execute motions with a precision and accuracy at the atomic level or better on electronic command. One could rightly call this family of techniques "piezoelectric techniques." The other common denominator is that the data are typically obtained as a two-dimensional grid of data points, visualized in false color as a computer image.[77]

A number of methods have applications in studies of corrosion, such as Kelvin probe atomic force and chemical force and scanning tunneling methods. Of these techniques, atomic force microscopy and scanning tunneling microscopy are the most commonly used for roughness measurements. NSOM and SNOM are scanning probe methods used to obtain optical imaging or some form of contrast.

Summary Observations on Instrumentation

Some of the techniques and tools outlined above have been used in corrosion research over the past 20 years. The future direction for these techniques is extension to heterogeneous corrosion processes on smaller and smaller length scales, and combination with other spectroscopies such as local atom and molecular spectroscopies in ways such that spatial and temporal information is given from the same surfaces at once. Hidden corrosion remains a challenge, as do sensor interpretation and subsequent decision-making algorithms. Pan and Leygraf[78] have combined atomic force microscopy with scanning electrochemical methods to obtain a coordinated x-y surface view of metrology and electrochemical reactivity. The future for instrumentation is to expand the number of channels of information and to ensure sufficient dynamic range to sample large enough areas so as to obtain a clear picture about corrosion in complex materials.

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[77] Paragraph reproduced from http://en.wikipedia.org/wiki/Scanning_probe_microscopy.

[78] A. Davoodi, J. Pan, C. Leygraf, and S. Norgren, Integrated AFM and SECM for in situ studies of localized corrosion of Al alloys, *Electrochimica Acta* 52(27):7697-7705, 2007.

4

Dissemination of the Outcomes of Corrosion Research

The topic of dissemination has been located on this report's iconic pyramid between corrosion science and the four corrosion grand challenges (CGCs) for convenience only. In fact dissemination of research results from each area of the pyramid to all of the others and to the application community is critical to the success of this endeavor.

Corrosion science, carried out most often in universities and research laboratories, must be transmitted to scientists and engineers working in all of the CGCs, most commonly through the traditional means of publication and oral presentations. Materials scientists and engineers working on developing computational modeling in CGC II must learn of new developments in the underlying corrosion science, incorporate them into models, and transmit those models to scientists in CGC I developing new materials through the International Conference on Science and Engineering (ICMSE) as well as those working in CGC III on accelerated testing and CGC IV on prognosis. New materials, once developed, are moved into actual use through a dissemination process that involves suppliers and designers. Also, new sensors and strategies for testing—once stimulated by the introduction of new science, accelerated testing, and prognosis strategies—must pass through the process of acceptance by standards bodies and become regular practice for designers and manufacturers, which is another facet of dissemination.

Rather than attempt to trace all of these interconnected dissemination paths for each element of the corrosion pyramid, this chapter is organized by dissemination methodology. Each dissemination operation is identified and discussed as it pertains to the corrosion research discussed elsewhere in this report.

Effective dissemination of meaningful corrosion research results is a multifaceted challenge for the scientific and engineering communities. Communication across multicultural disciplines is difficult, as is educating and informing engineering practitioners with prioritized, useful results. Furthermore, the engineering community is often not able to accept research results that may not have been fully validated for the problem at hand, nor is it ready for implementation due to scale-up issues, the lack of supporting supplier infrastructure, instrumentation, proven track record of in-service performance and durability, and so on.

CULTURAL CHALLENGES

In corrosion research and the application of its results, the engineering practitioners are often separated from the researchers by background, philosophy, interest, and educational level. Anecdotal examples of these differences are evident in the major national conferences held several times each year. Many of the technical symposia at the annual conference of the National Association of Corrosion Engineers (NACE) are devoted to corrosion protection and are attended by individuals who are not directly connected with research activities. Also included in the conference, however, is a research-in-progress symposium at which the latest research results are presented; the audience for these sessions generally numbers fewer than 100, and many of these are presenters or individuals at the cutting edge of research. Few in that audience are individuals who practice corrosion mitigation. The Electrochemical Society (ECS) has an active corrosion division that holds biannual research symposia devoted to both aqueous and elevated temperature corrosion processes. However, few corrosion mitigation practitioners attend the ECS meetings.

The separation of researchers and practitioners is apparent at the many topical research symposia held worldwide. However, it should be noted that a 1-day symposium on a focused topic, the Research Technical Symposium, is held each year at the NACE international annual conference in an effort to bring together researchers and practitioners. The topic is intentionally a relatively mature subject. The presentations are by invitation only and are longer than usual, allowing considerable detail of the applications to be presented. These symposia typically attract hundreds of attendees. Unfortunately, one such symposium per year allows for only limited coverage of the technical topics. For example, research data in the elevated temperature corrosion area are presented at national materials meetings, such as the annual Materials Science and Technology meeting. But the attendance at corrosion-specific sessions within this large conference is generally limited.

Cutting-edge research results are also communicated via publication in scientific journals. However, these journals are either not readily accessible to or not widely read by many corrosion mitigation practitioners. Consequently, crossfertilization between researchers pursuing fundamental studies and those who can apply the results of research is limited.

On the other hand, many university faculty members specializing in corrosion have an interest in practical applications of corrosion science and are available to industry as consultants. Problem solving by corrosion experts is also offered by several consulting and contract R&D firms specializing in corrosion. Nonetheless, many engineering practitioners are unaware of available solutions and resources, let alone advances in research, that might impact their business.

A further complication is that corrosion is, by definition, an interdisciplinary subject.[1] Yet only a minimal effort is made to exchange the results of corrosion research with researchers in other fields.

Thus, in the present cultural environment, the results of fundamental corrosion research are nominally exchanged between experts in their own fields. There is at present no effective national or international venue for the dissemination of corrosion research results to researchers or to practitioners who are outside the currently linked communities that are organized within the technical societies.

There are several consequences of the current environment. Certainly not all corrosion research is immediately relevant to corrosion mitigation, and thus practitioners would find little interest in dissemination of in-depth results.[2] Corrosion scientists must make a special effort to learn about developments and new instrumentation techniques that are outside the corrosion field. This process is dependent on individual professional contacts and relationships that often occur within a given institution, by serendipity, or by proactively seeking out particular research data in a related scientific discipline. Currently for corrosion-related research there are no counterparts to the National Science Foundation (NSF) Engineering Research Centers to focus large multidisciplinary teams (e.g., teams that include materials scientists, chemists, physicists, systems analysts, computer modeling specialists, various engineering disciplines, etc.) on tackling hard corrosion problems. Large-scale collaboration has occurred in only a few nationally significant projects, such as nuclear reactor design and permanent storage of radioactive materials, in which concern about corrosion motivated a portion of the research but was not the dominant driver for the program.

As noted, another consequence of the current environment is poor dissemination of information from researchers to practitioners. Thus many corrosion

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[1] See, for example, P.A. Sorensen, S. Kiil, K. Dam-Johansen, and C.E. Weinell, Anticorrosive coatings: a review, *Journal of Coatings Technology and Research* 6(2):135-176, 2009.

[2] For example, fundamental studies of the specific mechanisms of corrosion processes or the structure and composition of passive films would likely not interest a practicing engineer facing corrosion problems. However, these studies are invaluable because they lead to understanding that could eventually have a positive impact on corrosion mitigation through the development of more corrosion-resistant alloys, new environmentally friendly inhibitors, and novel coatings.

problems that, taken together, cause a large consumption of societal resources could be mitigated by the application of known and accepted corrosion prevention principles, best practices, and materials. The gap arises when engineers who deal with new designs fail to appropriately anticipate corrosion problems, and when those who must address corrosion problems in the field do not apply the best-known solutions.

Based on the time periods typically required for developing and implementing new materials for aerospace applications,[3] it is expected that 10 to 20 years might be needed for incorporating new corrosion mitigation technology into mainstream practice. This long transition period can be significantly shortened through the use of several proactive information dissemination strategies.

DISSEMINATION STRATEGIES FOR CORROSION ENGINEERING

The technical community would benefit from improved dissemination of corrosion research. Studies that focus on corrosion mitigation, such as those on new environmentally friendly corrosion inhibitors and protective coating systems and the behavior of new corrosion-resistant alloys, can often be applied directly to solving current problems. However, many who need help solving fundamental problems do not need the results of new research and can instead be assisted by exposure to well-established corrosion engineering practices.

Thus there are two important aspects of dissemination of corrosion research results: (1) application of accepted corrosion prevention principles and best practices and (2) transfer of specific corrosion R&D accomplishments into practice. Strategies for accomplishing these goals are summarized in Table 4.1, and each strategy is discussed below.

Education

Many corrosion problems could be solved by the application of accepted corrosion prevention principles and known best practices. However, many engineers involved in design activities lack understanding of the issues associated with corrosion. The NRC report *Assessment of Corrosion Education* (ACE; see Box 4.1)[4] describes the current status of corrosion education. Corrosion receives very little attention in the curricula of typical engineering programs. Often, engineering

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[3] National Research Council, *Accelerating Technology Transition: Bridging the Valley of Death for Materials and Processes in Defense Systems*, The National Academies Press, Washington, D.C., 2004, p. 16.

[4] National Research Council, *Assessment of Corrosion Education*, The National Academies Press, Washington, D.C., 2009.

TABLE 4.1 Dissemination Strategies

Field	Principles and Best Practices	Transfer of Recent R&D Accomplishments into Practice
Engineering education	✓	
Continuing education		✓
Engineering design tools—models and databases	✓	✓
New products		✓
Specifications and standards	✓	
Technology transfer service	✓	✓

BOX 4.1
Some Recommendations from the NRC Report *Assessment of Corrosion Education*[1]

- Develop a foundational corps of corrosion faculty by supporting research and development in the field of corrosion science and engineering.
- Provide incentives to the universities, such as endowed chairs in corrosion control, to promote the hiring of corrosion experts.
- Enable the setting and periodic updating of learning outcomes for corrosion courses by publishing and publicizing skills sets for corrosion technologists and engineers.
- Fund the development of educational modules for corrosion courses.
- Support faculty development, offering corrosion-related internships and sabbatical opportunities, and supporting cooperative programs between universities and government laboratories to facilitate the graduate student research experience.
- Increase support for the participation of their engineers in short courses when specific skills shortages are identified and are required to be filled in the short term.

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[1] National Research Council, *Assessment of Corrosion Education,* The National Academies Press, Washington, D.C., 2009, pp. 5-6.

students' exposure to corrosion issues is limited to a single lecture in corrosion in an introductory materials science class. In many cases, lectures on corrosion are not offered because of time constraints and the demands of other topics. At many universities, even students majoring in materials science and engineering (MSE), who should be trained in materials selection, receive limited exposure to the topic of corrosion because only a fraction of MSE departments have even a single course on corrosion in their curriculum. According to the ACE report, it is generally recognized by the MSE community that corrosion is an important topic, but the curriculum is overcrowded by other topics, and faculty capable of teaching corrosion courses are scarce, even in MSE departments.

The ACE report also describes how corrosion problems are handled in industry. In some industries with critical corrosion issues and focused activities, such as the automotive industry, new engineers are given on-the-job training by senior colleagues with experience in the field. To preserve corporate knowledge, background in and understanding of corrosion issues are transferred to new employees, but only slowly. This is an inefficient means of training and can lead to problems when there is a paradigm shift whereby corporate historical knowledge does not apply to new problems, and the depth of understanding of the staff is limited. Many corporations have no expertise in corrosion and seek out experts and consultants when problems arise. The problem is exacerbated in small companies that have limited engineering staffs. In many cases there is little awareness or understanding of corrosion problems, even though corrosion is a cross-cutting issue present in many industries.

The ACE report makes a strong case for improving all engineers' background in corrosion, and in particular that of materials engineers. It is critical for design engineers to have a sufficient background to "know what they don't know" and to know when to seek assistance. The ACE report also recommends that MSE students, as future experts in materials selection, should know more about corrosion than what is provided in most curricula today. Corrosion research is an important part of this educational process in training faculty who are qualified to teach the subject. Faculty members must have strong research programs to survive in the academic world. Corrosion research programs in universities also train graduate students who will develop into corrosion experts, staffing companies needing or providing corrosion expertise. Formal corrosion education, supported by viable research activities, is critical for limiting or mitigating corrosion damage.

The ACE report concluded that "the current level and effectiveness of engineering curricula in corrosion, offered through university-based and on-the-job training, will not provide a sufficient framework to allow the country to reduce substantially the national cost of corrosion or to increase the safety and reliability of the national infrastructure" (p. 5). A series of recommendations to educational, government, and community institutions interested in increasing corrosion education and awareness was presented in the ACE report. The committee strongly endorses these recommendations, some of which are repeated, in whole or in part, in Box 4.1.

Two longer-term strategic recommendations were included in the ACE report: (1) institute an education and research council to plan for corrosion education and to identify resources to execute the plan and (2) encourage the corrosion research community to reach out to the larger science and engineering community and communicate the challenges it faces.

It is critical for the corrosion community to motivate outstanding students and professionals to enter the field. ASM International has been very successful in attracting students to the field of materials science through summer camps for high school students and teachers. NACE International has joined in this effort and has developed a module on corrosion in each camp. The module gives every high-school teacher participating in the camp a box containing information and materials for corrosion experiments. These activities are strongly endorsed and should be expanded. A dissemination venue dedicated to linking fundamental research results to specific/applied corrosion mitigation technologies would help to bridge the gaps between cutting-edge research and engineering practices for controlling corrosion.

A model program for attracting students to an underrepresented engineering discipline is the University Network of Excellence in Nuclear Engineering (UNENE) in Canada. The main purpose of UNENE is to ensure a sustainable supply of qualified nuclear engineers and scientists to meet the current and future needs of the Canadian nuclear industry through university education, university-based training and by encouraging young people to choose nuclear careers.[5] In addition to this effort, the Canadian Nuclear Association focuses on high school curricula and public outreach. NACE International has expressed some of the same goals, but with less emphasis on public information.

Continuing Education

Given that most engineering students receive so little education in corrosion, it is critical that practicing engineers be able to gain needed knowledge in that area. A number of short courses exist that facilitate on-the-job training of engineers in corrosion. Appendix D in the ACE report lists some of these. However, such programs serve only a small fraction of the engineers who need such education and information. Continuing education of engineers in corrosion and other critical technologies should be encouraged by industry and professional societies.

Engineering Design Tools and Products

An effective means of incorporating corrosion knowledge is through validated corrosion modeling tools and associated databases. The ideal models would be based on fundamental laws and first principles since analyses could be performed over a wide range of conditions with some degree of confidence. But corrosion mechanisms are not yet understood well enough for purely first-principles mechanistic models to be useful, although this is a goal for future research.

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[5] See http://www.unene.ca.

Heuristic, empirical models can be useful for disseminating the results of corrosion research, as long as the applications are within the range of the data and boundary conditions that the model is built on. These approaches include expert systems[6] and data mining modeling (including semi-empirical, statistical, pattern recognition, neural networks, etc.) models.

Models with simplified geometries embodying descriptions of corrosion phenomena based on first principles, as well as existing measured and calculated data for corrosion parameters, are commercially available.[7] Some codes incorporate mixed potential models that are used for the prediction of corrosion potential and current density. Fundamental concepts are used but calibration with experimental data is frequently required in order to estimate values for poorly known model parameters.

A considerable amount of corrosion data exists for different metals and materials in a range of environments. However, in many cases, these data are not readily accessible as they are often contained in highly technical and obscure academic treatises or proprietary databases. If all of the available corrosion data were accessible, it would be a tremendous asset to the field. A notable effort in this regard is ASSET (Alloy Selection System for Elevated Temperatures),[8] an information system that combines an assessed experimental database and thermochemical computations for a given alloy and high-temperature gaseous environment to predict the extent of corrosion as a function of time and temperature (up to 1150°C in some cases). This tool can be used not only for alloy selection and lifetime prediction, but also for defining the type and fidelity of corrosion data needed for its effective utilization. In molecular biology, databases, algorithms, and computational and statistical techniques have been developed to handle the large amounts of data generated in projects such as characterization of the human genome. A similar widespread effort in corrosion science and technology is now possible and would revolutionize the field.

An open consortium of institutions and companies interested in corrosion engineering could be set up to collect corrosion data in a data warehouse, make

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[6] The 1987 NRC report *Agenda for Advancing Electrochemical Corrosion Science and Technology* focused on the development of expert systems to provide solutions to organizations with corrosion problems. The presumption was that improvements in computer technology would allow the capture of knowledge in a way that would make it easily accessible to users (National Academy Press, Washington, D.C., 1987).

[7] OLI Systems, HSC Chemistry, and numerous noncommercial geochemical codes incorporate complete speciation using thermodynamic databases and advanced solution chemistry fundamentals to generate stability diagrams.

[8] R.C. John, A.D. Pelton, A.L. Young, W.T. Thomnson, and I.G. Wright, The ASSET Project—A corrosion engineering information system for metals in hot corrosive gases, pp. 398-430 in *Lifetime Modelling of High Temperature Corrosion Processes* (M. Schütze, W.J. Quadakkers, and J.R. Nicholls, eds.), European Federation of Corrosion Publications Number 34, Maney Publishing, London, 2001.

the data easily accessible, maintain appropriate database tools, and help members to interrogate the data. Such a consortium could be organized as or under a government entity or a technical society. Consortium members would pay an annual fee—a flat fee, or one based on a set of member characteristics, such as usage, size of the member institution, and so on—to the consortium manager, Membership would not be exclusive. NIST played a similar role in collecting phase diagram data when casting modeling and simulation tools were being developed 20 years ago.

New Products

The development of new corrosion-resistant materials, corrosion inhibitors, corrosion protection coatings, and corrosion mitigation technologies is important to reducing the costs of corrosion. However, the transition of research into products requires that the gap between researchers and practitioners be bridged. Programs designed to bridge this gap include the Small Business Innovation Research (SBIR) program and the Small Business Technology Transfer (STTR) program,[9] which are administered separately at all federal agencies that fund R&D activities. A key goals is to increase the commercialization of technology developed through federal R&D funding. SBIR and STTR projects have three phases: feasibility (6-12 months), prototype development (2 years), and commercialization (funded outside the program). These programs could transition new corrosion technology into a viable end product or service such as improved corrosion-monitoring capabilities or new protective coatings.

At least once a year, each federal agency publishes a list of SBIR and STTR topics for which proposals can be submitted. In line with the recommendation in Chapter 2 concerning an OSTP-led multiagency committee on environmental degradation of materials, departments and agencies could collaborate in defining these topics and could share the results. However, the committee points out that the time frame of SBIR and STTR projects is not conducive to conducting fundamental research or to supporting students in a university graduate program. To address gaps in knowledge, fundamental research should first be conducted in a separate research program that provides for appropriate staffing of researchers to work on projects, followed by a SBIR or STTR that can commercialize the results. Paired in this way, an individual-investigator-led program or Multidisciplinary University Research Initiative team effort followed by an SBIR or STTR might be a good way to ensure a transition from research into a product useful for corrosion-related applications.

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[9] STTR is similar in structure to SBIR, but it funds cooperative R&D projects involving small business and research institutions such as universities, federally funded R&D centers, and nonprofit research institutions.

Corrosion-Related Specifications and Standards

Specifications and standards have long been an excellent means of disseminating best practices. A key driving force for specifications and standards typically has been the establishment of a common baseline for best practices, as well as alignment of the supporting industrial infrastructure to minimal requirements. Thus standardization presents an opportunity to promulgate the latest validated corrosion best practices across an industrial application area.

As described in Box 4.2, standards related to offshore gas and petroleum pipelines exemplify the use of this approach and provide a template for a proactive strategy:

- Establish requirements, beginning at a high-level.
- Assess current capability and develop a road map to achieve the required capability, taking into account the latest technological advancements.
- Develop research ideas and disseminate results.

BOX 4.2
Example—Offshore Pipeline Standards

Oil and gas field exploration and development continue to move farther offshore and into deeper water, and farther north into arctic environments. In the Gulf of Mexico, exploration wells are being drilled at depths greater than 10,000 feet, and production systems are being installed below 7,000 feet. As reserves are discovered and deepwater facilities installed, pipeline networks for gas and oil transport must follow, overcoming new challenges posed by the need for state-of-the art riser systems; longer pipeline distances underwater; and difficult corrosive conditions. The business climate is demanding innovative pipeline design, installation, and repair options; reductions in the weight and cost of risers systems; and satisfaction of high expectations that virtually no oil will be lost to spillage in the environment.

In response to growing concern about the integrity of pipelines in offshore waters, including the susceptibility of pipelines to corrosion, the Minerals and Management Service (MMS) in the Department of the Interior is developing a methodology for assessing the safety of existing pipelines and for designing and installing future pipeline systems. The end result will be new and revised pipeline standards and guidelines. To accomplish this, MMS is pursuing a multipronged approach that includes (1) involving pipeline standards writing organizations such as the American Petroleum Institute, American Society of Mechanical Engineers, and the International Organization for Standardization in forums, workshops, meetings, and selective projects to gain insight and provide direction for existing and new standards; (2) developing research ideas and disseminating the results through pipeline R&D forums and workshops; and (3) encouraging greater communication with industry and the public to gain perspectives that can aid industry-wide R&D efforts, as well as educating the public and other offshore partners about MMS activities and how technology is used to advance safety and environmental safeguards.

- Involve appropriate standards-writing organizations to draft new and updated standards.
- Participate in relevant international standards activities.
- Communicate strategy and objectives with industry, users and the supporting industrial base, and the public

Technology Transfer Organizations

Successful results of corrosion research usually find their way into applications, albeit too often at a glacial pace, a decade or more. The reasons for this are many. Rarely are the exact conditions under which research was conducted duplicated by a particular new application, and so some judgment is needed, and perhaps additional validation. Smaller companies do not typically have the resources to stay current on developments, and the time need to develop supporting infrastructure, such as suppliers gearing up to provide new products, can be lengthy, especially if the market is slow to develop. Finally, it may not be obvious that the benefit of a new technology is worth the added cost once the entire effort to qualify and incorporate the new technology is fully priced.

The federal government funds applied corrosion research for the public benefit and could increase the benefit by taking a proactive role in promoting dissemination of the research results. Two examples of a proactive approach that supports corrosion research and assists in the transfer of technology from research to practice are the Strategic Environmental Research & Development Program (SERDP)[10] and the related Environmental Security Technology Certification Program (ESTCP).[11] These programs focus on environmental issues, but they also fund related corrosion work, transferring technology from research to implementation in manufacturing, on the shop floor, or in the government's maintenance depot. Their efforts now focus on transferring technology developed with federal funding to applications in the federal agencies. The approach would be generally applicable, however, even if the end user were outside the federal government. The two programs:

- Work with the first implementer in a real-world environment regarding the costs of testing and demonstration, which includes performance and cost analyses.

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[10] SERDP is DOD's environmental science and technology program, planned and executed in full partnership with the DOE and EPA with participation by numerous other federal and nonfederal organizations. SERDP focuses on cross-service requirements and pursues high-risk/high-payoff solutions to the DOD's most intractable environmental problems.

[11] ESTCP is a DOD program that promotes innovative, cost-effective environmental technologies through demonstration and validation at DOD sites.

- Identify the application space for the new technology, together with benefits and limitations.
- Serve as consultants to other users who have an interest in evaluating the new technology.

This approach is similar to that taken by NIST's Hollings Manufacturing Extension Partnership (MEP), which focuses on increasing the competitiveness of the U.S. industrial base by bridging the productivity gap for manufacturers, identifying opportunities for growth, and encouraging technology deployment.[12] MEP currently facilitates advanced technology adoption for businesses of any size and helps to disseminate technology from universities and federal laboratories to companies. It also attempts to identify small company technology needs and bring those needs to the research community. MEP's role could be expanded to include dissemination of corrosion best practices. In any event, a MEP-like program in the area of corrosion would improve the transfer of knowledge in corrosion to those that need solutions. It is clear that each agency and department should accept as part of its responsibility not only the funding of corrosion research, but also its dissemination.

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[12] MEP is a collection of 59 centers in all 50 states with about 1,600 (nonfederal) employees. It is managed by the National Institute of Standards and Technology (NIST) and funded one-third by NIST and two-thirds by state funds, regional partners, and other sources of revenue.

5

A National Strategy for Corrosion Research

Corrosion is a natural phenomenon affecting all materials in structures important to our economic and national security and to our well-being as a whole. Research on many aspects of this phenomenon over the past century has led to the development of mitigation techniques that help to enable our current standard of living. Better materials (slower corrosion rates), better protection (coatings), increased awareness (detection of the early stages of corrosion), and better organized and executed plans for combating corrosion or replacing corroded parts have led to dramatic improvements that would not have been possible without such research.

Chapter 1 describes a number of successful technology advances made possible by corrosion research. Particularly notable is the impact on the nation's energy independence afforded by advances in corrosion research needed for the successful deployment of nuclear energy. Endemic in both boiling water and pressurized water reactors in the 1970s and early 1980s, stress corrosion cracking, threatened to derail the entire nuclear energy program. But corrosion research performed at universities and by industry and government laboratories resulted in the development of new alloys and the control of chemomechanical parameters, effectively allowing the current fleet of reactors to greatly exceed their expected useful lifetimes. Nevertheless, further research is clearly called for as new designs push the envelope and expose materials to ever harsher environments. As the nation continues to move toward the use of advanced nuclear, wind, solar, geothermal, and still-to-be-identified and increasingly green technologies, the limitations of current materials will become increasingly apparent. The need for new materials, protection of current materials from deterioration, and prediction of lifetimes for both new and current materials are important national priorities. In addition, raw materials from emerging nations will be increasingly in demand, placing severe limitations on their availability.

The attendant needs can be met through greater understanding and improved tools for prediction, sensing, and mitigation of inevitable corrosion, but only if we apply and advance our current knowledge of science and engineering.

The cost of corrosion to the United States should be incentive enough for serious government attention to the issue. Another pressing issue is the need for new information in support of initiatives already identified by the federal government and those still in the planning stage. For example, within the Department of Energy's (DOE's) purview are a broad array of materials challenges associated with the transition from a carbon-based economy to one based on alternative forms of energy, each of which calls for materials that can withstand exposure to complex new environments. It is unlikely, however, that current DOE plans for corrosion identification and mitigation can on their own provide solutions for ensuring the longevity of the nation's emerging energy technologies.

Current issues and opportunities related to corrosion demand increased efforts by government agencies in addition to DOE, but there is generally no evidence that future requirements for advanced technologies and conservation of national resources are seriously understood. Many government research programs receive less financial support than they once did. Perhaps only in the Department of Defense (DOD) and NASA is it possible to readily find comprehensive, centrally located and monitored plans for addressing corrosion-related challenges. Although the program in DOD is relatively new and its full impact on the several diverse elements of DOD is not yet evident, it nevertheless might serve as a model for what should be sought in other large government organizations. Even more desirable would be government-wide recognition of the scope of the corrosion problem and the encouragement of urgently needed organizational structures and communication networks to optimize an overall federal effort to address it.

The use of current advanced analytical tools, the rapid development of new tools and techniques, expanded computational capabilities and strategies, and, increasingly, systems-oriented approaches for development of materials can open new ways to solve previously intractable corrosion problems. The results of materials modeling and simulation R&D activities can be applied to mitigate corrosion challenges. Such efforts will greatly shorten the time required to successfully address corrosion in advanced materials systems for critical applications, eliminate long years of testing in less demanding service applications, enable new applications in severe environments that are of great interest to society, and encourage innovative approaches to renewing and extending the life of critical, costly elements of the nation's infrastructure.

FEDERAL AGENCY CORROSION ROAD MAPS

Conclusion: Although much has been learned about the causes of corrosion and many strategies for mitigation exist and have been implemented, much important corrosion R&D remains to be done. Increased demands on systems to address societal needs will require new materials capable of withstanding increasingly aggressive environments. A strong link between fundamental research at the atomistic level and at the engineering level still needs to be established in order to advance new innovative strategies in mitigating the ravages of corrosion damage on the nation's infrastructure. Research designed to address these national needs will require significant investment by several federal agencies and departments in collaboration with universities, national laboratories, and private sector research organizations. The committee concluded that these research demands can be conveniently expressed in the following four grand challenges for corrosion:

- Development of cost-effective, environment-friendly, corrosion-resistant materials and coatings;
- High-fidelity modeling for the prediction of corrosion degradation in actual service environments;
- Accelerated corrosion testing under controlled laboratory conditions that quantitatively correlates to long-term behavior observed in service environments; and
- Accurate forecasting of remaining service time until major repair, replacement, or overhaul becomes necessary—i.e., corrosion prognosis.

Addressing these challenges will demand an integrated body of scientific and engineering research targeted at specific agency needs but coordinated to minimize duplication of effort and to take advantage of synergism.

While government has a major role in supporting corrosion science, the ultimate goal must be the development of corrosion engineering practices that will be introduced into military and civilian design and maintenance of critical infrastructure. In establishing priorities for their research road maps, agencies and departments should therefore develop processes for cooperating with organized representatives of those entities relevant to their missions.

Recommendation: Using as guidance the four corrosion grand challenges developed by the committee, each federal agency or department should identify the areas of corrosion research pertinent to its mission and draw up a road map for fulfilling its responsibilities. In doing so, each should take a cross-organizational approach to planning and execution and should include input from industrial sectors that have experience in handling corrosion.

In assessing needs related to corrosion, it will be important to engage other major branches of science and technology. Modern instrumentation facilities have been developed by the physics, chemistry, and mathematical sciences communities that can be brought to bear on corrosion science and engineering problems. Significant advances in the science and engineering of environmental degradation of engineered systems will require concerted cross-disciplinary collaboration.

APPLICATION-FOCUSED CORROSION RESEARCH

Conclusion: Corrosion studies in single-investigator laboratories have long been the norm in this field. A few of these have led to important, multi-investigator, multi-institutional involvement and large-scale testing and deployment of new mitigation techniques. However, many of the new opportunities in corrosion research are identified at the interfaces between the traditional workers in this field and workers in measurement and information science. New modes of collaboration are required, and federal agencies should respond accordingly with opportunities for such research. Links between scientific understanding and engineering applications should be encouraged through creative collaborative programs rather than simply expected to happen as information diffuses from the laboratories of individual scientists to the engineering research environs of their counterparts down the hall or across the globe. Progress in attacking the corrosion grand challenges will require a balanced effort by traditional single-investigator programs and multi-investigator, cross-disciplinary programs to build collaborative systems, including advanced measurement techniques and modern analytical and computational tools.

Recommendation: Funding agencies should design programs to stimulate single-investigator and collaborative team efforts and underwrite the costs of realistic test laboratories open to the corrosion community and its collaborators, including industry researchers. These programs should address the four corrosion grand challenges identified by the committee; provide a balance between single- and multi-investigator groups; develop collaborative interactions between corrosion, measurement, and computational experts; and be driven by both science and engineering applications.

ESTABLISHMENT OF INDUSTRY, UNIVERSITY, AND NATIONAL LABORATORY CONSORTIA

> **Conclusion:** Corrosion-resistant alloys began to be developed in the last half century by metals producers and benefited from a balance of mechanical and physical properties. The development of these alloys has had huge economic, environmental, and safety impacts. Many of the success stories highlighted in Chapter 1 of this report were the result of industrial developments responding to well-understood needs. However, the leadership of corrosion materials research has declined in recent years owing to the high cost of sustaining such an effort, the uncertainty of finding a successful product application as materials and product sophistication increase, and the move to offshore development and production of engineering materials. The idea of a materials enterprise inventing an improved material and then working with end users to qualify it and scale it up (technology "push") has fallen by the wayside owing to the lengthy development time, high cost, and application risk for early adopters.

A new development model, known as the technology "pull" paradigm, requires the engagement of multiple stakeholders, including researchers, applications engineers, design engineers, and material producers. Their efforts can reach fruition much faster if the technology needs are known in advance, allowing the research to focus on the critical issues. The other stakeholders are those who design the application for the new material and those who produce it in volume. This development model is undertaken by a consortium that engages interested, knowledgeable participants from conception to implementation. One such successful approach is that of the Semiconductor Research Corporation. In this collaborative model, large semiconductor companies have joined to fund university efforts that provide research to all of the participants and a dedicated and well-educated workforce for the industries.

Federal departments such as the DOD and the DOE currently support materials R&D in areas aligned with core mission requirements. Increasingly, these developments involve industry early in the planning process since materials developments are targeted for specific end applications.

> **Recommendation:** Federal agencies should facilitate the formation of consortia of industry, university, and as appropriate, government laboratories chartered to address significant areas of opportunity in corrosion science and engineering. In consonance with best practices, industry should be involved at the earliest practical time in the structuring of these programs so that technology pull can realistically shorten the time between development and reduction to practice. Also, early involvement by industries will facilitate their active participation as consortium members.

DISSEMINATION OF THE OUTCOMES OF CORROSION RESEARCH

Conclusion: Many of the present impacts of corrosion could be reduced through incorporation of current best practices derived from years of research and development. The path from sources of new knowledge flows through the scientific literature, professional society meetings, standards adoption, education in formal and informal settings, and, eventually, to the ultimate users of that knowledge, the designers and maintainers of systems. Large companies staffed with a broad range of engineering talent are usually plugged in to this information transfer system. Small companies, typically lacking breadth in engineering talent, are often slower to become aware of and respond to new information. While this process is more or less effective, it is not optimal or even very efficient. In many agencies, the process of dissemination is actively pursued, whereas in others dissemination is not addressed at all. New mechanisms for disseminating current knowledge and new results to small and mid-size companies can bring about considerable savings.

There are corrosion data for different metals and materials in a range of environments. In many cases, however, these data are not readily accessible because they are contained in obscure, highly technical academic treatises or proprietary databases. If all of the available corrosion data were accessible, it would be a tremendous asset to the field.[1] In molecular biology, databases, algorithms, and computational and statistical techniques have been developed to handle large amounts of data from different biological areas such as the human genome. A similar widespread effort in corrosion science and engineering is now possible and would revolutionize the field.

Recommendation: Each agency and department should assume responsibility not only for supporting corrosion research but also for disseminating the results of the research.

Dissemination of the results of corrosion research should reach beyond an agency itself and connect with, for example, other agencies that have an interest in corrosion mitigation but lack the means to conduct their own effort in corrosion research. Given that a great deal of data on corrosion already exist and that more such data are being generated every year but are not widely available to interested researchers and corrosion specialists, an open central repository for collecting corrosion data and metadata is recommended. This central repository would make

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[1] For example, Alloy Selection System for Elevated Temperature (ASSET) is an information system that combines an assessed experimental database and thermochemical computations for a given alloy and high-temperature gaseous environment to predict corrosion as a function of time and temperature.

the data easily accessible and maintain it using appropriate database tools. It could be supported by institutions and companies interested in corrosion science and engineering, organized under a government entity or a technical society. Such data warehousing is currently being pursued in Europe and should serve as a model for a U.S. system.

NATIONAL MULTIAGENCY COMMITTEE ON ENVIRONMENTAL DEGRADATION

> **Conclusion:** Corrosion affects all aspects of society, in particular, the areas where the federal government is investing: education, infrastructure, health, public safety, energy, the environment, and national security. Inevitably a thermodynamically driven process, corrosion can, however, be mitigated substantially by retarding the rate of degradation. The government has several roles to play: as purchaser of equipment and facilities, as sponsor of scientific research and engineering developmental work, and as a source of best-practice information for use by state and local governments, industries, and small businesses. Although each agency and department must play a role consistent with its mission, isolated government programs tend to lead to duplicative efforts and reduce opportunities for synergistic progress. To address such issues and to emphasize that the proposed national strategy is intended to be a multiagency effort, the committee calls for cross-agency oversight.
>
> **Recommendation:** The Office of Science and Technology Policy (OSTP) should acknowledge the adverse impact of corrosion on the nation and launch a multiagency effort for high-risk, high-reward research to mitigate this impact. OSTP should set up a multiagency committee on the environmental degradation of materials. It should begin by documenting current federal expenditures on corrosion research and mitigation and then encouraging multiagency attention to issues of research, mitigation, and information dissemination. Collaboration among departments and agencies should be strengthened by collaboration with state governments, professional societies, industry consortia, and standards-making bodies.

SUMMARY

The overarching vision of the committee is that corrosion research will be advanced further and faster when corrosion behavior is included along with other materials properties in modern science and engineering practice, as exemplified by programs such as Integrated Computational Materials Science and Engineering and Prognosis, i.e., when corrosion issues are addressed proactively rather than reactively.

The committee believes that this report, with its conclusions and recommendations, will provide a useful framework for structuring corrosion research opportunities and that it will occasion a renewed critical interest in corrosion research by federal agencies, unquestionably resulting in significant benefit for the nation once the results of the research have been implemented. Revitalization of the governmental and industrial corrosion research infrastructures will play an important role in reducing the costs of corrosion and better controlling it.

Appendixes

A

Statement of Task

BACKGROUND

As documented in the report *Corrosion Costs and Preventive Strategies in the United States*[1] the direct costs of corrosion to the U.S. economy represent 3.2 percent of the U.S. gross domestic product, and the total costs to society can be twice that or greater. Beyond that are the costs of human health, national economic sustainability, and national defense readiness, which can be affected by deteriorating infrastructure, equipment and machinery. Opportunities for savings through improved materials selection and corrosion control are possible in every economic sector. While improved, cost-effective corrosion management could significantly extend the service life of existing systems, and reduce maintenance costs and replacement requirements, the value of these preventive strategies has often not been recognized and the strategies remain unapplied. Two major barriers to realizing significant savings are a broad lack of awareness of corrosion costs and the potential savings, and a widely held misconception that nothing can be done about corrosion. An essential element to tackling the second of these barriers is a better basic understanding of materials corrosion, broadly defined as the deterioration of a material in its operating environment.

In 2002 the U.S. Congress mandated the establishment (10 USC 2228) of a Department of Defense (DOD) Office of Corrosion Policy and Oversight in the

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[1] For further information see http://www.corrosioncost.com/home.html.

Office of the Undersecretary of Defense for Acquisition, Technology, and Logistics.[2] In addition, the Office of the Secretary of Defense developed a corrosion strategy and, in 2005, began funding technology transition and implementation projects that had been set up by all branches of the services. It is becoming increasingly obvious to DOD with each year's projects, that significant new technology is needed to meet the DOD goal of predicting and managing corrosion, in contrast to the current approach of simply finding corrosion and fixing it.

While many corrosion inhibition processes have been discovered and implemented, there is often little understanding of why they work. This lack of understanding prevents the advancement of these processes and research on alternatives. Accelerated corrosion tests in aggressive environments are used to assess corrosion resistance, but in many cases they do not correlate to real-world exposures because of a lack of fundamental understanding of the role of important parameters. Predictive capabilities cannot be developed where corrosion processes or their rates are not understood. The corrosion processes of concern occur in the air, on land, and at sea; in organic and inorganic materials; and under a host of conditions with impacts that are measurable but not adequately understood. A basic understanding of materials and their degradation is necessary to all industries and is especially critical to the nation's defense, transportation, nuclear, and medical industries.

Some of the outstanding issues for fundamental research include the following:

- What is the mechanism of pit initiation?
- What are the next important processes in corrosion to better understand and model?
- What is the true chemistry inside localized corrosion sites, and how does it affect corrosion processes?
- Corrosion at the nanoscale: What is really of interest?
- What is the nature of the bond between an organic molecule and an oxide or oxi-hydroxide-covered metal surface?
- What are the new techniques available for corrosion research, and what capabilities can they bring?

These and similar questions are the foundation of a potentially compelling fundamental research program. It is timely therefore for a study to identify the compelling opportunities in research to improve the basic understanding of materials degradation and related sciences. Such a study could provide prioritized recommendations for fundamental research and development necessary to gain

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[2] For a copy of the relevant legislation (10 USC 2228) see http://www.corrdefense.org/Key%20Documents/10%20U.S.C.%202228.pdf.

the critical understanding of materials degradation and mitigating technologies essential to the national interest.

STATEMENT OF TASK

The National Research Council will convene a committee to:

- Identify opportunities and advance scientific and engineering understanding of the mechanisms of corrosion processes, environmental materials degradation, and their mitigation.
- Identify and prioritize a set of research grand challenges to fill identified scientific and engineering gaps, as well as emerging issues.
- Make recommendations on a national strategy in fundamental corrosion research with the goal of gaining critical understanding of (1) environmental materials degradation and (2) mitigating technologies. The strategy should also include recommendations on how to maximize the dissemination of the outcomes of corrosion research to maximize their incorporation into corrosion mitigation.

B

Results of the Committee's Corrosion Mitigation Questionnaire

The committee's questionnaire on mitigation of corrosion was released on March 10, 2009, for community input. Invitations were sent to key personnel at DOD, MTI, and LMI to distribute a link to the questionnaire. On April 1, 2009, the NACE Technical and Research Activities committee distributed the link to all members of NACE technical committees and the NACE Research committee. As of April 23, 2009, 172 respondents had started the survey, and 79 of them (45.9 percent) had completed the entire survey. The data gathered are summarized below.[1]

RESPONDENT INFORMATION

Respondents described themselves as end users (39 percent), research and development personnel (31 percent), contractors (20 percent), and manufacturers (15 percent). Twenty-five percent of respondents described themselves as "other," most of whom termed themselves "consultants."

The majority of respondents had been involved in corrosion mitigation for quite some time (67 percent for more than 15 years and 22 percent for 5 to 15 years) in diverse sectors including utilities, transportation, infrastructure, production and manufacturing, government, and health care. Sixty-seven percent valued their equipment or structures at greater than $10 million. The respondents indicated

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[1] As of October 21, 2009, 189 respondents had started the survey, and 90 (47.6 percent) had completed it. These new results are not included in the summary presented below. The data are available in the public access file at the National Academies.

that they were responsible equipment in the following sectors: oil and gas exploration and production, transmission in pipelines, petroleum refining, chemical/petrochemical/pharmaceutical production, gas distribution, drinking water and sewer systems, and electric utilities.

CORROSION ISSUES

The questionnaire asked which forms of corrosion were of greatest importance or concern to the respondents. All forms of corrosion presented on the questionnaire as choices—general, pitting, crevice, microbially influenced corrosion, galvanic, erosion, and environmental cracking—were described as "sometimes an issue." Pitting corrosion was most frequently described as "my biggest issues," with general corrosion coming in second. Microbially influenced corrosion was most frequently described as "not an issue."

The consequence that most concerned the respondents was safety. Loss of production, environmental issues, and loss of use of the equipment were roughly tied for second place. Legal consequences were less frequently cited. Of those who cited "other," "cost" was most frequently identified as the primary consequence.

MITIGATION SYSTEMS

This section of the questionnaire explored the types of mitigation systems currently being used by respondents. The most frequently selected options are shown in Table B.1 (respondents were allowed to select more than one).

Respondents were also asked to say how frequently they used each technique. In other words, a respondent might have indicated that he or she used coupons (monitoring), external CP with coatings (electrochemical), and inhibitors such as those in water. In this question respondents were asked to say what percentage of their mitigation effort relied on a particular technique. Overall, external CP with coatings had the highest rate of use (35 percent), followed by materials selection based on environmental application (23 percent), organic barrier coatings (19 percent), corrosion inhibitors such as those used in water (19 percent), materials selection based on cost (18 percent), design of materials based on cost (16 percent), and sacrificial anodes (13 percent).

Seventy-two percent of respondents said that they spent more than $200,000 per year on corrosion mitigation. An additional 13.5 percent spent between $50,000 and $200,000 per year.

TABLE B.1 Types of Mitigation Systems Currently Being Used by Respondents

Mitigation Technique	General Type	Total Number of Responses	Most Frequently Cited Specific Techniques	Number of Responses
Monitoring	Passive	108	Inspection	54
			Coupons	18
Material selection	Passive	103	Based on lifetime cost analysis	62
			Based on environmental application	36
Electrochemical	Active	91	External CP with coatings	57
			Sacrificial anodes	18
Organic coatings	Passive	79	Barrier	47
			Combination	16
Inhibitors	Passive	72	Those in water	47
Metallic coatings	Passive	70	Flame sprayed	22
			Sacrificial or barrier	15
Inorganic coatings	Passive	63	High temperature	24
			Low temperature	21

EFFECTIVENESS OF MITIGATION SYSTEMS

This section of the questionnaire attempted to assess respondents' overall satisfaction with the various mitigation techniques employed. Respondents ranked the various techniques on a scale from 1 to 5 (1 = not satisfied at all, 3 = moderately satisfied, 5 = completely satisfied). Overall, respondents were at least moderately satisfied with the mitigation techniques they used. Active, externally applied CP with coatings had the highest average satisfaction ranking at 4.22. Hybrid organic/inorganic coatings—plasma electrolytic had the lowest average satisfaction ranking at 2.60.

The highest-ranked techniques, in terms of overall satisfaction, are shown in Table B.2, and. the lowest-ranked techniques, in terms of overall satisfaction, are shown in Table B.3.

Ninety-nine responses were received on the specific difficulties encountered with various techniques (questions 14 and 15 of the questionnaire give details). An informal review of respondents' answers showed that the considerations listed in Table B.4 seemed to be of general concern.

TABLE B.2 Highest-Ranked Techniques, in Terms of Overall Satisfaction

Technique	Average Ranking	Number of Responses
Externally applied CP with coatings	4.22	57
Material selection—other	4.07	15
Materials selection based on environmental application	4.00	40
Sacrificial anodes	3.98	50
Design of materials based on cost	3.97	38
Materials selection based on cost	3.90	49

TABLE B.3 Lowest-Ranked Techniques, in Terms of Overall Satisfaction

Technique	Average Ranking	Number of Responses
Hybrid organic/inorganic coatings—plasma electrolytic	2.60	5
Active sensors—automatic	2.91	11
Inorganic coatings—special layered organics	2.92	12

TABLE B.4 Considerations of Greatest Concern to Respondents

General Consideration	Specific Applications or Issues
Monitoring	For high-temperature applications
	For measuring (with sensors) localized corrosion
	Unreliability
	For underdeposit corrosion
	For stress corrosion cracking
	Remote sensing
Access to information	Materials database with updated costs
	Suitability of various materials in different environments
	Chemical inhibitors—their use and efficacy (debunking of the proprietary "cocktails")
Coatings	Surface preparation
	Protection under disbonded coatings
Cathodic protection	Insufficient training or knowledge of operators
Prediction	Prediction of lifetime
	Prediction of actual conditions
	Prediction of damage mechanisms

IDEALIZED OR STATE-OF-THE-ART MITIGATION SYSTEMS

This section of the questionnaire addressed current state-of-the-art technologies in corrosion mitigation.

Sixty-six respondents described the current state-of-the-art mitigation system for their application, with many citing a combination of methods. Active protection (cathodic or anodic), materials selection, and coatings/claddings were the most frequently cited techniques. Cathodic protection was often listed in combination with coatings. Chemistry/inhibitors/process control was next most frequently cited technique followed by sensors. Remote monitoring, modeling, pigging, and inspection were mentioned only one or two times each.

Sixty-four percent of those who responded said they used the state of the art, 24 percent said they used it in some instances, 3 percent did not use it, and the remainder, generally self-described as consultants, did not use the technologies at all. For those who used the state of the art, the most frequently given reason was that it worked and was either inexpensive or cost-effective.

ADVANCES IN MITIGATION

Having had an opportunity to consider the types of mitigation systems available, the efficacy of those currently used, and the state-of-the-art technologies available, respondents were asked suggest scientific advances that would contribute to the development of new and/or better mitigation technologies.

The majority (63 percent) of respondents thought that future research should include both fundamental and applied sciences, with some commenting that the balance should tilt toward applied research. Twenty-five percent felt that future research should be applied, and the rest were divided between fundamental and "don't know."

When asked where future research should focus specifically to enable advances that would help to develop new and/or better mitigation technologies, the top three areas were monitoring (50 percent), coatings (45 percent), and active systems (41 percent) (more than one option could be selected). Others suggested sensors (29 percent), passive systems (21 percent), and "other" (21 percent). Improvement in mitigation system lifetime and improvement in the costs of mitigation ranked the lowest (14 percent and 12 percent, respectively).

In the area of monitoring, the majority of the suggestions favored improved remote modeling or better sensors and a method of monitoring or measuring localized (pitting) corrosion. Improved inspection methods (nondestructive and/or not requiring shutting down facilities) and improved costs were also mentioned. With respect to coatings, the most frequently suggested improvements related to better high-temperature performance and less need for surface preparation (answers to question 20 of the questionnaire give details).

Respondents were also asked to craft questions they would like to see answered by future research in this field (questions 22 and 23 give details). Common themes included modeling (predicting lifetimes, modeling environments and new alloys, extrapolating the results of short-term testing to long-term performance), and monitoring or assessing localized corrosion, including pitting and microbially influenced corrosion.

C

Corrosion Modeling

The purpose of a corrosion model is to predict an outcome. As such, a model can test or express a theoretical hypothesis in order to increase understanding of a phenomenon. Models are useful only if they are validated and provide reasonable outcomes so that predictions can be tested. In this framework, models are particularly valuable tools to gain knowledge and insight relatively quickly for assessing difficult, complex corrosion problems. It is challenging to predict the result when, for example (1) structural materials are placed in a corrosive environment that can cause several degradation modes to interact with one another,(2) in-service stress conditions cause acceleration of the corrosion rate, or (3) the environment varies dynamically in its corrosion potential. Once validated, corrosion models can support a variety of analyses, such as estimating the required interval between maintenance and repair actions, gauging the effectiveness of various corrosion mitigation approaches, aiding in the selection of materials and coatings, and performing sensitivity analysis regarding the basic assumptions and the initial and boundary conditions used in a corrosion analysis.

The word “model” is itself ambiguous, and there is no uniform terminology to define models. Basically, a model is considered to be a representation of some object, behavior, or system that one wants to understand. Models are abstract vehicles for learning about the world. With a well-developed model, significant parts of scientific investigation could be carried out the results are verified by experiments.

The validity of a model rests not only on its fit to empirical observations but also on its ability to extrapolate to situations or data beyond those originally described in the model. The first step in the scientific method is to formulate a hypothesis or theory. A hypothesis is an educated guess or logical conclusion from known facts, which is then compared against all available data. If the hypothesis is found to be consistent with known facts, it is called a theory. Most theories explain observed phenomena, predict the results of future experiments, and can be presented in mathematical form. When a theory is found to be always correct over the course of many years, it is eventually referred to as a scientific law. But theories do not provide the algorithms for the construction of a model; models provide the algorithms needed to support a theory. A theory may be incompletely specified in the sense that it imposes certain general constraints.

There are many different types of models used across the scientific disciplines, although there is no uniform terminology to classify them. The most familiar are physical models, such as scale replicas. Algorithms constitute another, completely different type of model. A computer simulation is a computer program, or network of computers, that attempts to simulate an abstract model of a particular system. Frequently, computer simulations are needed to solve a difficult set of equations describing the governing laws of the system (in the case of deterministic models) or to handle a very large amount of data and/or heuristic knowledge (in the case of data-mining-based models).[1] In situations in which the underlying model is well confirmed and understood, computer experiments potentially could replace real experiments, which is especially useful when data collection is difficult and expensive. Computer simulations could also be heuristically important; for example, they may suggest new theories, models, and hypotheses based on a systematic exploration of a model's parameter space.[2,3]

Several different taxonomies can be used to describe problems in corrosion science: static and dynamic, well and poorly understood, and simple and difficult. For the problems that are well understood, simple, and static, models either exist or can be readily developed to describe the corrosion behavior and to make predictions. Dynamic systems are usually more difficult to model, especially if the evolution of the dynamic behavior is poorly understood. Models can be based in some understanding of the phenomenon or can be based entirely on mined data.

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[1] P. Humphreys, *Extending Ourselves: Computational Science, Empiricism, and Scientific Method*, Oxford University Press, Oxford, U.K., 2004.

[2] S. Hartmann, Models as a tool for theory construction: Some strategies of preliminary physics, pp. 49-67 in *Theories and Models in Scientific Processes* (W.E. Herfel, W. Krajewski, I. Niiniluoto, and R. Wójcicki, eds.), *Studies in the Philosophy of the Sciences and the Humanities,* Volume 44, Rodopi, The Netherlands, 1995.

[3] S. Hartmann, The world as a process. Simulations in the natural and social sciences, pp. 77-100 in *Modelling and Simulation in the Social Sciences from the Philosophy of Science Point of View* (R. Hegselmann, U. Mueller, and K.G. Troitzsch, eds.), *Series A: Philosophy and Methodology of the Social Sciences,* Kluwer Academic Publishers, The Netherlands, 1996.

The success of a model will depend strongly on the relevance and accuracy of the data collected, the level of understanding of the key parameters, and the observed knowledge.

One of the perennial debates in the philosophy of science has to do with realism: What aspects of science, if any, truly represent the real world? "Idealization" is a very important part of mathematical models. The degree to which a model has positive analogies is typically described by how "realistic" the model is; i.e., the idea is that more realistic models contain more truth than other models.

Model complexity involves a trade-off between the simplicity and the accuracy of the model. It is important to recognize that in addition to the measured observations, the data will contain biases and beliefs inherent in the method used for collecting the data, and uncertainties and inaccuracies due to measurement limitations.

For difficult corrosion problems, models built from the bottom up are realistic—models tied to experimental empirical data and observations of a particular system. Deterministic models are derived in a top-down manner from abstract laws and are typically less realistic but more general. Accordingly, there are two complementary approaches for developing corrosion models and predicting corrosion damage:

- Empirical models based on what has been measured or experienced, and
- Deterministic models based on known and established natural laws.

Within these two classes of models, there exist numerous subclasses. For example, within the empirical class, there are functional models, in which (discrete) data are represented by continuous mathematical functions or by approximations that sometimes follow a natural law. Within the broad class of deterministic models there can exist definite models that yield a single output for a given set of input values; and probabilistic models, in which the inputs are distributed, resulting in a distributed output from which the probability of an event occurring can be estimated.[4] Also, as mentioned above, there are other possible ways to classify models:

- *Linear versus nonlinear:* If all the operators in a mathematical model present linearity, the resulting mathematical model is defined as linear. Otherwise, a model is considered to be nonlinear.

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[4] G. Engelhardt and D.D. Macdonald, Unification of the deterministic and statistical approaches for predicting localized corrosion damage. I. Theoretical foundation, *Corrosion Science* 46(11):2755-2780, 2004.

- *Static versus dynamic:* A static model does not account for the element of time, whereas a dynamic model does.

Pure "determinism" is an ideal concept that is probably never achieved in reality and thus integrating deterministic and empirical models could provide the most effective method for predicting corrosion damage.

D

Acronyms

AASHTO	American Association of State Highway and Transportation Officials
ACE	*Assessment of Corrosion Education* (2009 NRC report)
AETOC	advanced electrochemical techniques for organic coatings
AFM	atomic force microscopy
API	American Petroleum Institute
ASM	American Society for Metals (now known as ASM International)
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
BRAC	base realignment and closure
CGC	corrosion grand challenge
CoSI	Coating Science International
CP	cathodic protection
DOD	Department of Defense
DOE	Department of Energy
DOT	Department of Transportation
ECS	Electrochemical Society
ESTCP	Environmental Security Technology Certification Program

FAA	Federal Aviation Administration
FDA	Food and Drug Administration
FGE	fuel-grade ethanol
FHWA	Federal Highway Administration
FIB	focused ion beam
FY	fiscal year
GDP	gross domestic product
HELP	hydrogen-induced local plasticity
HHS	Department of Health and Human Services
HIDE	hydrogen-induced decohesion
HPC	high-performance computing
HVAC	heating, ventilating, air conditioning
ICMSE	integrated computational materials science and engineering
IGC	intergranular corrosion
IGSCC	intergranular stress corrosion cracking
ISABE	International Association of Air Breathing Engines
ISO	International Organization for Standardization
KSC	Kennedy Space Center
LANL	Los Alamos National Laboratory
LMI	Logistics Management Institute
MEP	Manufacturing Extension Partnership
MMS	Minerals and Management Service
MRS	Materials Research Society
MSE	materials science and engineering
MTI	Materials Technology Institute
MURI	Multidisciplinary University Research Initiative
NACE	National Association of Corrosion Engineers
NADC	Naval Air Development Center (now Naval Air Warfare Center, NAWC)
NASA	National Aeronautics and Space Administration
NAVAIR	Naval Air Systems Command
NAVSEA	Naval Sea Systems Command
NCEL	Naval Civil Engineering Laboratory
NIST	National Institute of Standards and Technology

NRC	National Research Council
NRL	Naval Research Laboratory
NSF	National Science Foundation
OMB	Office of Management and Budget
OSTP	Office of Science and Technology Policy
PHMSA	Pipeline and Hazardous Materials Safety Administration
R&D	research and development
RE-C	rare-earth carbides
RE-S	rare-earth silicides
RITA	Research and Innovative Technology Administration
ROI	return on investment
SBIR	Small Business Innovation Research
SCC	stress corrosion cracking
$SCCO_2$	super-critical carbon dioxide
SECM	scanning electrochemical microscopy
SERDP	strategic environmental research and development program
SLSDC	Saint Lawrence Seaway Development Corporation
SPHERE	Simulated Photo Degradation by High Energy Radiant Exposure
START	Strategic Arms Reduction Treaty
STTR	Small Business Technology Transfer
UNENE	University Network of Excellence in Nuclear Engineering
UTC	university transportation center
UV	ultraviolet

E

Government Programs in Corrosion

Before describing individual government programs in corrosion it is worthwhile to reiterate that mitigation of materials degradation need not be done in isolation even though government departments have differing needs. One way the committee believe the current "go-it-alone" approach can begin to be alleviated is for the Office of Science and Technology Policy (OSTP) to launch a concerted, multiagency effort to support high-risk, high-reward research designed to develop technologies that mitigate the societal impact of corrosion. OSTP could, for example, as recommended by the committee in Chapter 5 of this report, constitute a multiagency committee on environmental degradation of materials with the responsibilities of documenting the current federal expenditures on corrosion research and mitigation and encouraging multiagency attention to issues of research, mitigation, and dissemination of information. Collaboration among departments and agencies could be augmented by collaboration with state government and private entities such as professional societies, industry consortia, and standards-making bodies.

THE DEPARTMENT OF HEALTH AND HUMAN SERVICES AND THE FOOD AND DRUG ADMINISTRATION

The Department of Health and Human Services (HHS) is the federal government's principal agency for protecting the health of all Americans and providing essential human services, especially for those who are least able to help themselves.[1] Within HHS, the Food and Drug Administration (FDA) is the agency that is most concerned about corrosion. The FDA is responsible for protecting public health by ensuring the safety, efficacy, and security of human and veterinary drugs, biological products (including blood, vaccines, and tissues for transplantation), medical devices, the nation's food supply, cosmetics, and products that emit radiation. The FDA regulates $1 trillion worth of products a year[2] and also enforces Section 361 of the Public Health Service Act and associated regulations, including sanitation requirements. Its interest in corrosion concerns issues such as maintaining antiseptic conditions for the manufacture and packaging drugs and for the handling and processing of food products; understanding corrosion products that can leach into the body from materials such as dental amalgams and implanted medical devices; and ensuring the safety of medical equipment such as tanks that hold and dispense medical gases. The FDA issues good guidance practices that set forth statutory and regulatory requirements, such as testing methods to be used to demonstrate capability, that relate to corrosion testing standards.

For example, the FDA addresses concerns about corrosion of implantable medical devices[3] through requirements for biocompatibility (i.e., a device's effect on the body) and biostability (i.e., the body's effect on a device). Implantable medical devices are becoming increasingly important, given that they can replace a failing heart valve, correct an irregular heart rhythm, replace a worn out hip or knee joint, save a patient from ischemia-induced fibrillation, or even stop the tremors associated with Parkinson's disease. Companies attempting to secure approval to sell implantable devices must demonstrate both biocompatibility and biostability. Biocompatibility is usually demonstrated by passing standardized tests that meet the guidelines set forth in ISO 10993-Part 1. Materials that corrode probably will not pass these tests because they will cause an inflammatory response or a sensitization reaction. Corrosion is also a major concern for ensuring biostability, which can be assessed in standard laboratory corrosion tests or in vivo from actual experience with implant. Typically, a manufacturer selects a specific type of test and information to submit to the FDA to demonstrate stability of a device in the body; the FDA reviews the data and may approve the submission or require additional data. It is because of these FDA requirements that implantable devices today are made from noncorrosive materials,[4] and corrosion is not currently a significant issue.

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[1] See http://www.hhs.gov/about/.

[2] See http://www.fda.gov/RegulatoryInformation/Legislation/default.htm.

[3] These devices are implanted in the body for long periods of time, sometimes a decade or more.

[4] Materials such as platinum, titanium, silicon rubber, some fluropolymers, and various polyurethanes are among the mainstays in this industry, along with a few exotic nickel-based superalloys. The most "common" material found in implantable medical devices is likely 316 stainless steel. Other than improved wear resistance, there is little driving force for advancing materials in this application.

DEPARTMENT OF COMMERCE AND NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY

The National Institute of Standards and Technology (NIST) has responsibility within the Department of Commerce for the technical areas related to corrosion. Corrosion research at NIST (formerly the National Bureau of Standards) laboratories dates back to 1911, and initially focused largely on aqueous corrosion of metals, and corrosion under coatings such as exterior paint. In the last of the studies on metals, conducted in the 1970s, fundamental work on stress-corrosion cracking helped to elucidate and quantify the combined effects of chemistry and mechanical stress on alloy degradation. Current corrosion research at NIST is centered in the Building and Fire Research Laboratory and includes a self-contained, accelerated testing facility (SPHERE) that enables realistic environments and simultaneous measurements of multiple variables.

DEPARTMENT OF DEFENSE

The Department of Defense (DOD), with supporting legislation, has introduced a comprehensive program aimed at preventing and mitigating corrosion of military equipment and facilities. The director of the DoD Corrosion Policy and Oversight Office leads the DOD development of an overarching long-term strategy across all the military services. The program emphasizes corrosion prevention and mitigation, incorporates uniform testing and certification of new technologies, facilitates the interchange of corrosion information, and establishes a coordinated R&D program with specific transition plans. The primary objective is reducing the effects of corrosion on the safety and readiness of the American warfighter, as well as lowering the cost of corrosion to the American taxpayer.[5] The R&D program priorities have been guided by field problems. It is estimated that corrosion accounts for 15 to 30 percent of the cost of maintaining military equipment, such as ships and ground vehicles. The top 10 corrosion drivers for each type of equipment are aggressively addressed through mitigation efforts. The effort has produced measurable results: over a 5-year period, 342 projects were submitted for funding, and 141 were selected based on calculated return on investment. The typical project

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[5] DOD Instruction 5000.67 provides direction to the military services. The policy establishes procedures and responsibilities concerning corrosion. It assigns specific responsibilities to the Army, Navy, Air Force, and Marine Corps in order to guarantee that they will manage corrosion programs on all military equipment and infrastructure across the life cycle. It also requires that each of the military services designate a corrosion executive who will be responsible for developing and recommending policy and guidance on preventing corrosion throughout their departments. It requires that the costs and labor required to maintain military equipment be considered in each department's acquisition process.

lasted 2 years, followed by implementation. The DOD estimates that the return on investment for the $138 million spent was greater than 50:1, since the life-cycle corrosion avoidance cost was calculated to be $5.75 billion.[6]

A set of Army, Navy, and Air Force laboratories in the federal laboratory system have historically addressed corrosion issues for DOD. For instance, U.S. Navy laboratories have supported corrosion research in seawater and/or marine atmospheres for many years. The lead laboratory with responsibility in corrosion science is the Naval Research Laboratory (NRL), which has conducted corrosion research for many years in the Corrosion Science and Engineering Branch. This branch is funded by the Office of Naval Research, sea systems commands, and specific project offices. Work in the 1950s and 1960s was some of the first to embrace fracture mechanics, developed by Irwin and others as a modern way to understand stress corrosion cracking and advance the concept of defect tolerance in the case of stress corrosion cracks and threshold stress intensity factors. Later, work on stress corrosion cracking of emerging titanium alloys was advanced at NRL on behalf of other agencies such as NASA. Work continues today at the NRL-Corrosion Division that includes topics ranging from environmental fracture to passivity. However, research is also conducted at various other Navy laboratories that are focused on subsets of naval equipment and infrastructure. These labs are now organized as a part of NAVSEA and/or NAVAIR warfare centers.[7] All of these labs have a specific mission, and corrosion topics as such are very applied and often funded from project offices and platform programs.[8] When a persistent fleet problem suggests that testing and evaluation be conducted, these NAVSEA/NAVAIR warfare labs could conduct the research. NRL could address generic science questions. The Army and Air Force fund basic research through the Army Research Office and the Air Force Office of Scientific Research, plus laboratories within the development and operational commands. But the corrosion R&D in these services is typically less comprehensive than that in the Navy, and corrosion research is a small portion of the portfolio for both internal and external work.

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[6] Return on investment calculated using procedures contained in OMB Circular A-94, dated October 29, 1992.

[7] These laboratories include the corrosion materials and coatings branch, formerly Naval Air Development Center, the Naval Civil Engineering Lab (Port Hueneme, CA), Naval Underway Engineering Lab (Newport), Carderock formerly David W. Taylor Naval Ship Research and Development Center (DTNSRDC) and Naval Surface Warfare Center–White Oak. Many of these labs were consolidated under BRAC. For instance, NADC is now consolidated at Patuxent River, and DTNSRC-Annapolis and NSWC-White Oak are consolidated at Carderock, Maryland, within one corrosion group.

[8] For instance, Carderock focuses on hull, machinery, propulsion, and structures, whereas NCEL (now NSWC–Port Hueneme) focuses on facilities and stationary undersea components.

DEPARTMENT OF ENERGY

The overarching mission of the U.S. Department of Energy (DOE) is to advance the national, economic, and energy security of the United States.[9] DOE funds R&D at its national laboratories, smaller federal institutes, universities, private research companies, and industry, in a wide range of technical areas. Most of this funding is awarded competitively and seeks to address key fundamental and technical issues impacting national and energy security. DOE's R&D portfolio encompasses pure discovery science, use-inspired basic studies, applied research, and technology maturation and deployment, with different offices devoted to different parts of this spectrum of activities. Fundamental research in corrosion science is funded primarily though the Office of Science. Most corrosion R&D under DOE's auspices has been in support of specific technologies, whether generically or to attack a specific targeted problem or goal, and is distributed throughout DOE's multiple technology offices. A few examples include the following:

- *Office of Fossil Energy:* Efforts to qualify and improve corrosion resistance of materials needed for advanced supercritical reactors or combined-cycle gasification.
- *Energy Efficiency–Distributed Energy, Fossil Energy:* Development of oxidation-resistant ceramic composites and bond coats for gas turbines.
- *Energy Efficiency–Industrial Technologies:* Development of corrosion-resistant alloys and refractories for materials and chemical processing.
- *Nuclear Energy:* Improved understanding of degradation modes and prediction of lifetimes for materials for long-term storage of spent nuclear fuels

Looking toward to the future in terms of technological driving forces and the scientific capabilities currently available or just emerging, DOE conducted two recent workshops that included consideration of basic research needs involving corrosion in relation to advanced nuclear energy and the behavior of materials in extreme environments.[10,11]

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[9] See http://www.energy.gov/about/index.htm.

[10] Department of Energy, *Basic Research Needs for Advanced Nuclear Energy Systems,* Report of the Basic Research Needs for Advanced Nuclear Energy Systems Workshop, July 31-August 3, 2006, available at http://www.sc.doe.gov/bes/reports/abstracts.html#ANES.

[11] Department of Energy, *Basic Research Needs for Materials under Extreme Environments,* Report of the Basic Energy Sciences Workshop on Materials Under Extreme Environments, June 11-13, 2007, available at http://www.sc.doe.gov/bes/reports/files/MUEE_rpt.pdf.

DEPARTMENT OF TRANSPORTATION

The Department of Transportation (DOT) was established by an act of Congress on October 15, 1966, with the mission to serve "the United States by ensuring a fast, safe, efficient, accessible, and convenient transportation system that meets our vital national interests and enhances the quality of life of the American people, today and into the future."[12] The DOT comprises 10 operating administrations:

- Federal Aviation Administration (FAA),
- Federal Highway Administration (FHWA),
- Federal Motor Carrier Safety Administration (FMCSA),
- Federal Railroad Administration (FRA),
- Federal Transit Administration (FTA),
- Maritime Administration (MA),
- National Highway Traffic Safety Administration (NHTSA),
- Saint Lawrence Seaway Development Corporation (SLSDC),
- Pipeline and Hazardous Materials Safety Administration (PHMSA), and
- Research and Innovative Technology Administration (RITA).

Each of the 10 operating administrations has some degree of involvement with corrosion—either through research (e.g., FAA, FHWA, PHMSA) or asset renewal (e.g., SLSDC). Most operating administrations provide guidance and in some cases requirements for mitigating and controlling corrosion. In addition, several operating administrations fund research in corrosion science and engineering. For example, the PHMSA sponsors research on regulatory and enforcement activities and on developing the technical and analytical foundation necessary for planning, evaluating, and implementing the pipeline safety program. The research and development projects focus mainly on providing near-term solutions to increase the safety, cleanliness, and reliability of the nation's pipeline system, including corrosion issues.[13] The RITA takes a different approach and funds university transportation centers (UTCs) that perform research on a broad range of research topics. Some topics researched under the UTCs include corrosion issues. In addition, the Office of Infrastructure Research and Development funds transportation infrastructure research, including research on corrosion in the infrastructure. Past corrosion research has included assessing the corrosion performance of different types of concrete reinforcement, assessment of corrosion protection systems, and assessment of materials and methods for corrosion control.[14]

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[12] See http://www.dot.gov/about_dot.html.

[13] See http://www.phmsa.dot.gov/doing-biz/r-and-d_opps.

[14] See http://www.tfhrc.gov/structur/pubs.htm.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

The National Aeronautics and Space Administration (NASA) began corrosion studies at the Kennedy Space Center (KSC) in 1966 during the Gemini/Apollo Programs with the evaluation of protective coatings. The Corrosion Technology Laboratory evolved from the need to better understand the corrosion processes affecting the KSC launch sites. Over the years, numerous material failures at KSC have been attributed to various forms of corrosion. To address these issues, basic and applied research is performed at the KSC Beachside Atmospheric Exposure Site to identify technologies that will prevent such failures. Research conducted for other NASA centers includes work at the Johnson Space Center in Houston, Texas; the Stennis Space Center in Hancock County, Mississippi; the Langley Research Center in Hampton, Virginia; and the Marshall Space Flight Center in Huntsville, Alabama. NASA also partners with universities to investigate corrosion. Two documents currently guiding NASA's corrosion efforts are NASA-STD-5008A, *Standard for Protective Coating of Carbon Steel, Stainless Steel, and Aluminum on Launch Structures, Facilities, and Ground Support Equipment,*[15] and TM-584C, *Corrosion Control and Treatment Manual.*[16]

NASA's hot corrosion research at the Glenn Research Center dates back to late 1970s. NASA has conducted extensive research on understanding the thermodynamics and kinetics of sodium sulfate deposition in gas turbine engines. The research resulted in identification of conditions leading to deposition of sodium sulfate in turbine engines and correlating salt deposition rates to turbine operating conditions. In the early 1980s NASA's hot-corrosion research focused on understanding hot corrosion of superalloys through laboratory and burner rig testing, as well as low-temperature hot-corrosion mechanisms of nickel-based alloys. NASA discontinued hot-corrosion research in 1985, but it is currently being revived to address issues related to corrosion of advanced turbine disk alloys.[17] Activities include understanding corrosion mechanisms and developing coatings to mitigate corrosion without adversely impacting mechanical properties. NASA Glenn has also made substantial contributions to the understanding of the high-temperature oxidation and degradation of superalloys, aluminides, silicon-based ceramics and

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[15] NASA, *Standard for Protective Coating of Carbon Steel, Stainless Steel, and Aluminum on Launch Structures, Facilities, and Ground Support Equipment,* NASA-STD-5008A, available at http://corrosion.ksc.nasa.gov/publications.htm.

[16] NASA, *Corrosion Control and Treatment Manual,* TM-584C, available at http://corrosion.ksc.nasa.gov/publications.htm.

[17] NASA GRC facilities to study hot corrosion include Mach 0.3 burner rigs and a high-pressure burner rig, a high-temperature mass spectrometer (one of the two in the country) to study chemistry of salt deposition, and a multitude of laboratory rigs, including microbalances, to study hot corrosion under controlled atmospheres.

ceramic composites, and other very-high-temperature materials. Researchers there were at the forefront of the development of environmental barrier coatings as well as specific experimental techniques for high-temperature studies, including extensive characterization and modeling of oxidation of alumina-forming alloys under thermally cycling conditions.

NATIONAL SCIENCE FOUNDATION

As described in its strategic plan,[18] the National Science Foundation (NSF) is the only federal agency with a mission that includes support for all fields of fundamental science and engineering,[19] except for the medical sciences. In addition to funding research in the traditional academic areas, the agency also supports high-risk, high-payoff ideas and novel collaborations. NSF ensures that research is fully integrated with education, so that today's revolutionary work will also be training tomorrow's leading scientists and engineers.

A brief survey of current research grants funded by NSF showed that more than 40 dealt with various aspects of corrosion research. Topical focus ranges from traditional aqueous corrosion of metals to atmospheric degradation of nanostructures, and from science-oriented topics to engineering issues related to civil infrastructure. Research projects were found in divisions with responsibilities including materials, chemistry, and civil engineering and others. But there do not appear to be clear themes for the corrosion research projects and no apparent program strategy regarding corrosion research.

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[18] National Science Foundation, *Investing in America's Future: Strategic Plan FY 2006-2011*, NSF 06-48, September 2006, available at http://nsf.gov/publications/pub_summ.jsp?ods_key=nsf0648.

[19] See http://nsf.gov/funding/aboutfunding.jsp.

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Committee Biographies

David J. Duquette (*co-chair)* is a professor of metallurgical engineering at Rensselaer Polytechnic Institute. He received his Ph.D. in materials science from the Massachusetts Institute of Technology (MIT) in 1968. Following his postgraduate work, he performed research on elevated temperature materials, joining the Rensselaer faculty in 1970. He is the author or co-author of more than 160 scientific publications, primarily in the areas of environmental degradation of materials and electrochemical processing of semiconductor interconnects. He is a recipient of the Whitney Award of the National Association of Corrosion Engineers for his contributions to corrosion science, and an Alexander von Humboldt Senior Scientist Award. He is a fellow of ASM International and of NACE International. Dr. Duquette's research interests include the physical, chemical, and mechanical properties of metals and alloys, with special reference to studies of environmental interactions. Current projects include studies of aqueous and elevated temperature corrosion phenomena, the effects of corrosive environments on fatigue behavior, the environmental cracking of alloys, and the role of corrosion science in understanding the planarization of metal interconnects on semiconductor devices, and electrodeposition of semiconductor interconnects. A fundamental understanding of material environment interactions is critical to engineering application of metallic materials. Dr. Duquette was a member of the now completed National Research Council (NRC) Panel on Electrochemical Corrosion.

Robert E. Schafrik (*co-chair*) is currently the general manager, Materials and Process Engineering Department at GE Aviation. He is responsible for developing advanced materials and processes used in GE's aeronautical turbine engines and their marine and industrial derivatives. He oversees materials application engineering activities supporting GE Aviation's global design engineering, manufacturing, and field support activities. He also operates a state-of-the-art in-house laboratory for advanced materials development, characterization, and failure analysis. Prior to joining GE in 1997, he served in 2 concurrent positions within the NRC, which he joined in 1991: staff director, National Materials Advisory Board, and staff director, Board on Manufacturing and Engineering Design. Under his direction, 33 final reports for studies were issued that addressed significant national issues in materials and manufacturing. Dr. Schafrik also served in the U.S. Air Force in a variety of R&D and system acquisition capacities; he retired as a lieutenant colonel. He has a Ph.D. in metallurgical engineering from Ohio State University, an M.S. in information systems from George Mason University, an M.S. in aerospace engineering from the Air Force Institute of Technology, and a B.S. in metallurgy from Case Western Reserve University.

Aziz I. Asphahani is presently serving as senior advisor to the "Corrosion Engineering" Curriculum Development at the University of Akron. He is also the CEO of Advanced Motion Technologies (a BioMechanics/Gait analysis start-up company). Dr. Asphahani served as the CEO of CARUS Chemical Company (1995-2005), following 20 years in the specialty metals industry with HAYNES International/CABVAL, where he served as CABVAL president, HAYNES vice president, director of R&D and corrosion engineer (1975-1995). Dr. Asphahani's degrees include "Diplome Ingenieur"-physics from Ecole Centrale de Paris (1970) and Ph.D. in materials science from MIT (1975). He holds 8 patents and authored 61 papers on corrosion of high-performance alloys. Two products of his patents won the 1991 R&D 100 Award and the 1984 Vaaler Award. Dr. Asphahani is a NACE fellow and ASM fellow. He served as ASM president (2001), on the boards of directors of NACE International, the NACE Education Foundation, the Chemical Education Foundation, and the American Chemistry Council Board. Dr. Asphahani is presently serving on the ASM Education Foundation board of directors, on the board of trustees of the Alpha-Sigma-Mu Honor Society, and the board of directors of the Goldin Institute.

Gordon P. Bierwagen is a professor in the Department of Coatings and Polymeric Materials at North Dakota State University (NDSU). He received his B.S. in chemistry and mathematics from Valparaiso University in 1964, his Ph.D. in physical chemistry from Iowa State University in 1968. In 1989, he joined the Polymers and Coatings Department at NDSU as professor. He has trained 14 Ph.D.'s and 8 M.S. students in his time at NDSU. He was chair of the Polymers and Coatings Department from 1999 to 2006. Dr. Bierwagen has recently been the leader in the invention of a new method of protecting aluminum alloys against corrosion without the use of chromate pigments or pretreatments by using magnesium pigments in coatings in a manner analogous to t Zn particles in Zinc rich paints. He and his co-workers have recently introduced the used of ionic liquids in studying the electrochemistry of coatings enabling the characterization of water transport out of coatings. He has authored or coauthored more than 120 refereed journal articles. His professional activities include being editor-in-chief (1995-present) and North American regional editor (1987-1995). He is currently on the Scientific Program Committee for CoSI, the annual Coating Science International Meeting held each June in Noordwijk, the Netherlands; the Scientific Program Committee for the AETOC (Advanced Electrochemical Techniques for Organic Coatings) 2009 Workshop to be held in Gardo, Italy, in April 2009; and is a member of the International Scientific Committee for 8th International Symposium on Electrochemical Impedance Spectroscopy—EIS 2010, which was held in Algarve, Portugal, in June 2010.

Darryl P. Butt is a professor and chair of materials science and engineering at Boise State University. He received his Ph.D. in ceramic science and his B.S. in ceramic science and engineering with a minor in technical writing from the Pennsylvania State University. Dr. Butt held several positions at Los Alamos National Laboratory (LANL) between 1991 and 1999. As a post-doctoral fellow he studied very-high-temperature hydrogen-solid reactions and thermodynamics of transition metal and actinide carbides. This work included developing planar laser induced fluorescence methods for characterizing and directly imaging plasmas produced during laser ablation processes, modeling gas-solid reactions, and modeling of binary, ternary, and quaternary phase diagrams. In 1994 he established the Materials Corrosion and Environmental Effects Laboratory within the Materials Science and Technology Division, where he lead efforts in a variety of areas, including aqueous and high-temperature oxidation of ceramics, alloys, and protective coatings, radiation effects on materials corrosion, gallium vaporization, sequestration of carbon dioxide, and development of high-temperature materials and seals, and carbon dioxide sequestration. In 1998, Dr. Butt became the lead project leader for weapons dismantlement and fissile materials transparency where he managed and oversaw technical efforts and policy development related to a possible START III treaty, and Russian-U.S. lab-to-lab technical interactions in nuclear non-proliferation. From 1998 to 2000, on leave from LANL, Dr. Butt lead an $85 million DOE-industry program at Ceramatec, Inc., in collaboration with Air Products and Chemicals Company, to develop microchannel gas separation membranes for the production syngas from natural gas. His research lead to a number of key patents in the field. From 2000 to 2005 Dr. Butt was an associate professor at University of Florida in the Department of Materials Science and Engineering, with close collaborations with the Department of Nuclear Engineering and Radiological Science. The author or co-author of approximately 160 publications and patents, Dr. Butt has received several awards, including a LANL 1994 Distinguished Performance Award and a 1999 Pollution Prevention Award for his research on Pu purification, and the American Ceramic Society's 1992-1993 Nuclear Division Best Paper Award, and 1997 Robert L. Coble Award for Young Scholars. He received the best teacher award, or Triple Point Award, from the University of Florida College of Engineering in 2005 and was named Professor of the Year by Boise State University's College of Engineering in 2008. Dr. Butt is a member of the American Ceramic Society and the Materials Research Society. He is currently an associate editor of the *Journal of the American Ceramic Society* and an affiliate of the Center for Advanced Energy Studies in Idaho Falls, Idaho.

Gerald S. Frankel is the DNV Chair and Professor of Materials Science and Engineering at the Ohio State University (OSU). He is also director of the Fontana Corrosion Center. He earned the Sc.B. degree in materials science engineering from Brown University in 1978 and the Sc.D. degree in materials science and engineering from MIT in 1985. Prior to joining OSU in 1995, he was a post-doctoral researcher at the Swiss Federal Technical Institute in Zurich, Switzerland, and then a research staff member at the IBM Watson Research Center in Yorktown Heights, N.Y. He has more than 200 publications, and his primary research interests are in the passivation and localized corrosion of metals and alloys, corrosion inhibition, and protective coatings. He is past chair of the Corrosion Division of the Electrochemical Society, past chair of the Research Committee of NACE, and a member of the editorial board of the journals *Corrosion*, *Materials and Corrosion*, and *Corrosion Reviews*. Dr. Frankel is a fellow of NACE International, the Electrochemical Society, and ASM International. He has received the Alexander von Humboldt Foundation Research Award for Senior U.S. Scientists, the H.H. Uhlig Educators Award from NACE, and the Harrison Faculty Award and Lumley Research Award from the OSU College of Engineering. He was on sabbatical at the Max Planck Institute for Iron Research in Dusseldorf, Germany, in 2005 and a visiting professor at the University of Paris in 2008.

Roger C. Newman is a professor in chemical engineering and applied chemistry at the University of Toronto. He has worked in corrosion research since he started his Ph.D. at the University of Cambridge in 1977. From 1980 to 1984 he was at Brookhaven National Laboratory, where he did basic research on corrosion and contributed to applied research programs associated with the Three Mile Island incident. Then he joined the University of Manchester Institute of Science and Technology (UMIST) as lecturer, progressing to professor by 1995. In 2004 he left to join the University of Toronto, where he holds an NSERC Senior Industrial Research Chair in association with the nuclear power industry. He has received most of the international awards for corrosion research, such as the Whitney Award of NACE International, the Evans Award of the Institute of Corrosion, the Uhlig Award of the Corrosion Division of the Electrochemical Society, and the Fischer Medal of DECHEMA. His research specialties are pitting corrosion, stress corrosion cracking, and alloying effects in corrosion. He has advised governments and industry in many countries, and serves, for example, as foreign member of the Scientific Advisory Board of the Max Planck Institute for Iron and Steel Research.

Shari N. Rosenbloom is a manager in Exponent's Mechanical Engineering and Materials/Metallurgy practice. Dr. Rosenbloom's expertise is in metallurgical engineering and electrochemical testing of medical devices. Dr. Rosenbloom conducts failure analysis investigations in order to determine the cause of failure in a variety of industrial settings, as well as for biomedical applications. She has developed expertise in analyzing a broad range of corrosion mechanisms (e.g., stress corrosion cracking, formicary corrosion, galvanic corrosion, underdeposit corrosion, pitting, erosion corrosion, cavitation, and general corrosion), as well mechanical failures (e.g., fatigue, overload, and failure due to manufacturing defects). Her work has focused on the failure modes of a number of metallic materials including steels, copper and copper-based alloys, aluminum alloys, and nickel-based alloys. She consults in a variety of industries including HVAC, petrochemical processing and refining, food handling, pharmaceutical, and chemical processing. Dr. Rosenbloom also consults on the topic of biocompatibility of medical implants with regard to their corrosion resistance in the body. She has extensive experience in assessing resistance to pitting corrosion per ASTM F 2129 and galvanic corrosion per ASTM G 71, as well as in designing customized testing protocols. She has developed expertise in the corrosion behavior of a broad range of implant materials such as stainless steel, nitinol, titanium alloys, and cobalt-chromium based alloys.

Lyle H. Schwartz (NAE) is a senior research scientist with the Department of Materials Science and Engineering at the University of Maryland. He was professor of materials science and engineering at Northwestern University for 20 years and director of Northwestern's Materials Research Center for five of those years. He then became director of the Materials Science and Engineering Laboratory at the National Institute of Standards and Technology where he served for more than 12 years. His experience there included metals, ceramics, polymers, magnetic materials, techniques for characterization, and standardization of these characterization techniques, and his responsibilities included management of the R&D agenda in the context of a government laboratory. Dr. Schwartz subsequently assumed responsibility for basic research on structural materials of interest to the U.S. Air Force, in addition to the areas of propulsion, aeromechanics, and aerodynamics. He then completed his government service as director of the Air Force Office of Scientific Research with responsibility for the entire basic research program of the

Air Force. His current interests include government policy for R&D, particularly for materials R&D, materials science education at K-12 levels, and enhanced public understanding of the roles and importance of technology in society. He is a member of the National Academy of Engineering. Dr. Schwartz received both his B.S. in engineering and Ph.D. in materials science from Northwestern University.

John R. Scully is professor of materials science and engineering and co-director of Center for Electrochemical Science and Engineering at the University of Virginia, which he joined in 1990. Previous to this, Dr. Scully served as a senior member of the technical staff in the metallurgy department of Sandia National Laboratories and ship materials engineer at the David W. Taylor Naval Ship Research and Development Center. Dr. Scully received his B.E.S., M.S., and Ph.D. degrees from Johns Hopkins University in materials science and engineering. His research interests focus on the relationship between material structure and composition and their environmental degradation or corrosion properties including hydrogen embrittlement, stress corrosion cracking, localized corrosion, and passivity. His corrosion research includes study of advanced aluminum, magnesium, titanium, ferrous and nickel-based alloys, stainless steels, as well as amorphous metals and intermetallic compounds. The development of methodologies for lifetime prediction engineering materials in corrosive environments is also of interest. Dr. Scully teaches materials science classes as well as classes on corrosion and electrochemical aspects of materials science at both the graduate and undergraduate levels. He is a fellow of the Electrochemical Society and the National Association of Corrosion Engineers. He received the A.B. Campbell and H.H. Uhlig Awards from NACE, the T.P. Hoar Award from the Institute of Corrosion (U.K.), and the Francis LaQue Award from ASTM for his research in corrosion. He is a past recipient of the National Science Foundation Presidential Young Investigator Award. He is chair of the NACE awards committee and past chair of the NACE research committee. He is past chair of ASTM subcommittee G1.11 on electrochemical techniques in corrosion. He has served on the editorial boards of *Corrosion Journal*, *Materials and Corrosion* (Germany), and *Metallurgical and Material Transactions*. He served as a technical consultant to the Space Shuttle Columbia Accident Investigation Board in 2003, was a member of the Office of the Secretary of Defense Science Board Task Force on Corrosion Control in 2004, and was the chair and organizer of the 2004 Gordon Conference on Aqueous Corrosion. He is a member of the NRC's Corrosion Education Workshop Organizing Panel and the subsequent study group.

Peter F. Tortorelli is the deputy director of the Materials Science and Technology Division at Oak Ridge National Laboratory (ORNL). He received his B.S. in physics from Manhattan College and his Ph.D. in metallurgy from the University of Illinois. He has extensive research experience in areas related to corrosion and degradation of properties of materials in high-temperature, aggressive environments, including gases, molten salts, and liquid metals, in the mechanical, physical, and chemical behaviors of protective oxide layers that may form under such conditions, and in materials development of high-temperature alloys, ceramics, and ceramic composites for applications in fossil energy systems, gas turbines, fusion reactors, and energy-intensive industries. He served as leader of the Corrosion Science and Technology Group at ORNL for 7 years and has been involved in program management for the Basic Energy Sciences–Materials Science and Engineering and Fossil Energy Materials programs at ORNL. He was vice chair of the 2009 Gordon Research Conference on High Temperature Corrosion and is chair of the 2011 conference. Dr. Tortorelli was a panel lead for the Workshop on Basic Research Needs for Materials Behavior under Extreme Environments for the Department of Energy's Office of Basic Energy Sciences in June 2007.

David Trejo is currently a professor in the School of Civil and Construction Engineering at Oregon State University. He received his bachelor's, master's, and Ph.D. degrees in civil engineering from the University of California, Berkeley, with minors in electrochemistry and materials science. He has significant background in investigating, testing, assessing, and evaluating mechanisms of deterioration of various material and structural systems, including pipes, walls, foundations, bridges, water tanks, and other structures. He has participated on federal and state research investigating the physical, chemical, and electrochemical deterioration and repair of infrastructure systems and has published significantly in these areas. He has more than 10 years of experience in the construction and engineering industry, where he worked on many infrastructure projects, including testing and evaluating materials and structures for deterioration.

Darrel F. Untereker is vice president of research and technology at Medtronic, Inc. He received his undergraduate degree from the University of Minnesota and a doctorate from the University of New York, Buffalo, both in chemistry. He followed that with post-doctoral work in surface science at the University of North Carolina. In 1991 he received his CER in business administration from Stanford University. He joined Medtronic, Inc., in Minneapolis, Minnesota, and has held several technical and managerial positions over the years involving power sources, materials science, and biomedical engineering of implantable medical devices. He has a broad range of interests in science, technology, and business and is currently applying his knowledge and interests to improve the design of future medical devices. Dr. Untereker has more than 60 publications in several fields, as well as 17 patents and has won many awards, including the Medtronic Star of Excellence, the Medtronic Outstanding Initiative Award, as well as being selected to the Bakken Society, which is the highest technical honor in Medtronic (named for Earl

Bakken, the founder of Medtronic). He currently serves on the Bioengineering Board of the University of California, Berkeley, and has served in the past on the CIE (now IPRIME) Advisory Board of the University of Minnesota and the Stout Technical Advisory Board of the University of Wisconsin. He is also on the Coulter Committee at Duke University. He has served on the boards of directors on commercial companies. Dr. Untereker's passion is for improving the quality of medical devices by applying scientific principles and understanding to their design and development. Outside Medtronic, he has served on many industrial advisory boards and was an associate editor of the *Journal of the Electrochemical Society* for 6 years as well as Battery Division editor for a number of years before that. In 2003 he was elected as a fellow in the Electrochemical Society. In 2006 he was selected as a fellow in the American Institute for Medical and Biological Engineering. He is a 2006 winner of the Charles W. Britzius Distinguished Engineer Award for lifetime achievement in and service to the profession of engineering. He also spends a lot of time mentoring younger scientists and engineers.

Mirna Urquidi-Macdonald is a professor of engineering science and mechanics at Pennsylvania State University. She received a B.S. in physics and mathematics from ITESM, Monterrey, Mexico, an M.A. and Ph.D. in plasma physics from the University of Paris, Sud. Prior to joining Penn State, she was a senior research scientist at the Sciences and Technology Business Group at SRI International (Stanford Research Institute) in Menlo Park, California. Dr. Urquidi-Macdonald's current research focuses on fuel cells, corrosion detection and assessment of underground pipelines, cathodic protection of underground structures, and corrosion and failure analysis. An expert in energy and related technologies, she has been a NASA/American Society for Engineering Education summer faculty fellow, an advisor to the U.S. Department of Transportation's Technical Pipeline Safety Standards Committee, and a consultant to the U.S. Department of State on water-cooled nuclear reactors at the International Atomic Energy Agency in Vienna, Austria. She is an elected fellow of ASM International and the National Association of Corrosion Engineers. Dr. Urquidi-Macdonald's work was cited among the "Great Advances in Science" by the Science Coalition in its report to the 105th Congress on the benefits of federally funded university-based research. Dr. Urquidi-Macdonald is the author or coauthor of more than 250 papers and publications and a recognized advocate for underrepresented groups at Penn State.