Metallized Coatings for Corrosion Control of Naval Ship Structures and Components

National Materials Advisory Board
Commission on Engineering and Technical Systems
National Research Council

NATIONAL RESEARCH COUNCIL
COMMISSION ON ENGINEERING AND TECHNICAL SYSTEMS

NATIONAL MATERIALS ADVISORY BOARD

The purpose of the National Materials Advisory Board is the advancement of materials science and engineering in the national interest.

CHAIRMAN

Dr. Donald J. McPherson
Vice President and Director of Technology (Retired)
Kaiser Aluminum & Chemical Corporation
300 Lakeside Drive
Oakland, CA 94643

PAST CHAIRMAN

Mr. William D. Manly
Senior Vice President
Cabot Corporation
125 High Street
Boston, MA 02110

Members

Dr. Arden L. Bement, Jr.
Vice President, Technology Resources
Science and Technical Department
TRW, Inc.
23555 Euclid Ave.
Cleveland, OH 44117

Dr. William J. Burlant
Director, Lexington Laboratory
The Kendall Co.
Lexington, MA 02173

Dr. James C. Burrows
Vice President
Charles River Associates
200 Clarendon Street
John Hancock Tower, 43rd Floor
Boston, MA 02116

Dr. Raymond F. Decker
Vice President, Research
Michigan Technological University
Houghton, MI 49931

Mr. Edward J. Dulis
President
Crucible Research Center
Colt Industries
P.O. Box 88
Pittsburgh, PA 15230

Dr. Brian R. T. Frost
Division Director, Materials Science
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Dr. Serge Gratch
Director of Chemical Science Lab
Engineering & Research Staff
Ford Motor Co.
P.O. Box 2053
Dearborn, MI 48121

Dr. Nick Holonyak, Jr.
Professor Electronic Engineering
University of Illinois-Urbana
Dept. of Electrical Engineering
Urbana, IL 61801

Dr. Paul J. Jorgenson
Stanford Research Institute
333 Ravenswood Avenue
Menlo Park, CA 94025

Dr. Alan Lawley
Professor Metallurgical Engineering
Drexel University
Department of Materials Engineering
Philadelphia, PA 19104

Dr. Raymond F. Mikesell
W. E. Miner Professor of Economics
University of Oregon
Department of Economics
Eugene, OR 97403

Dr. David L. Morrison
President
IIT Research Institute
10 West 35th Street
Chicago, IL 60616

Dr. David Okrent
Professor of Engineering & Applied Science
University of California, Los Angeles
5532 Boelter Hill
Los Angeles, CA 90024

Dr. R. Byron Pipes
Director, Center for
Composite Materials
Department of Mechanical &
Aerospace Engineering
University of Delaware
Newark, DE 19711

Professor James R. Rice
Gordon McKay Professor of
Engineering Sciences and Geophysics
Division of Applied Sciences
Harvard University
Peirce Hall
Cambridge, MA 02138

Dr. Brian M. Rushton
Vice President, Research & Development
Air Products & Chemicals, Inc.
P.O. Box 538
Allentown, PA 18105

Dr. William P. Slichter
Executive Director, Research
Materials Science and Engineering Division
Bell Laboratories
600 Mountain Avenue
Murray Hill, NJ 07974

Dr. William A. Vogely
Professor and Head
Department of Mineral Economics
Pennsylvania State University
University Park, PA 16802

Dr. Robert P. Wei
Department of Mechanical Engineering
and Mechanics
Lehigh University
Bethlehem, PA 18015

Dr. Albert R.C. Westwood
Director, Martin Marietta Labs
Martin Marietta Corporation
1450 South Rolling Road
Baltimore, MD 21227

NMAB STAFF

K.M. Zwilsky, Executive Director

1/83

50272-101

REPORT DOCUMENTATION PAGE	**1. REPORT NO.** NMAB-409	**2.** AD-A125660	**3. Recipient's Accession No.**

4. Title and Subtitle

Metallized Coatings for Corrosion Control
of Naval Ship Structures and Components

5. Report Date
February 1983

6.

7. Author(s)
Committee on Thermal Spray Coatings for Corrosion Control

8. Performing Organization Rept. No.
NMAB-409 ✓

9. Performing Organization Name and Address

National Materials Advisory Board
National Academy of Sciences
2101 Constitution Ave., N.W.
Washington, D.C. 20418

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C) MDA 903-82-C-0434
(G)

12. Sponsoring Organization Name and Address

Department of Defense/
National Aeronautics and Space Administration
Washington, D.C.

13. Type of Report & Period Covered
Final

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

In attempting to improve corrosion control, the U.S. Navy has undertaken a program of coating corrosion-susceptible shipboard components with thermally sprayed aluminum. In this report the program is reviewed in depth, including examination of processes, process controls, the nature and properties of the coatings, nondestructive examination, and possible hazards to personnel. The performance of alternative metallic coating materials is also discussed. It is concluded that thermally sprayed aluminum can provide effective long-term protection against corrosion, thereby obviating the need for chipping of rust and repainting by ship personnel. Such coatings are providing excellent protection to below-deck components such as steam valves, but improvements are needed to realize the full potential of coatings for above-deck service. Several recommendations are made regarding processes, materials, and research and development aimed at upgrading further the performance of these coatings.

17. Document Analysis a. Descriptors

Aluminum
Corrosion
Hazards
Metallizing
Paint
Safety
Ships
Steel
Testing
Thermal Spray
Zinc

b. Identifiers/Open-Ended Terms

[illegible] 1 1 1983

A

[illegible] approved [illegible] distribution is unlimited.

c. COSATI Field/Group

18. Availability Statement: For sale by the Defense Technical Information Center.	**19. Security Class (This Report)** Unclassified	**21. No. of Pages** 113
	20. Security Class (This Page) Unclassified	**22. Price**

(See ANSI–Z39.18) See Instructions on Reverse

OPTIONAL FORM 272 (4–77)
(Formerly NTIS–35)
Department of Commerce

METALLIZED COATINGS FOR CORROSION CONTROL OF NAVAL SHIP STRUCTURES AND COMPONENTS

Report of the

Committee on Thermal-Spray Coatings
for Corrosion Control

NATIONAL MATERIALS ADVISORY BOARD
Commission on Engineering and Technical Systems
National Research Council

NMAB-409
National Academy Press
Washington, D.C.
1983

A

NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

The National Research Council was established by the National Academy of Sciences in 1916 to associate the broad community of science and technology with the Academy's purposes of furthering knowledge and of advising the federal government. The Council operates in accordance with general policies determined by the Academy under the authority of its congressional charter of 1863, which established the Academy as a private, nonprofit, self-governing membership corporation. The Council has become the principal operating agency of both the National Academy of Sciences and the National Academy of Engineering in the conduct of their services to the government, the public, and the scientific and engineering communities. It is administered jointly by both Academies and the Institute of Medicine. The National Academy of Engineering and Institute of Medicine were established in 1964 and 1970, respectively, under the charter of the National Academy of Sciences.

The report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

This study by the National Materials Advisory Board was conducted under Contract No. MDA 903-82-C-0434 with the Department of Defense and the National Aeronautics and Space Administration.

This report is for sale by the Defense Technical Information Center, Alexandria, Virginia 22314.

Printed in the United States of America.

ABSTRACT

In attempting to improve corrosion control, the U.S. Navy has undertaken a program of coating corrosion-susceptible shipboard components with thermally sprayed aluminum. In this report the program is reviewed in depth, including examination of processes, process controls, the nature and properties of the coatings, nondestructive examination, and possible hazards to personnel. The performance of alternative metallic coating materials is also discussed. It is concluded that thermally sprayed aluminum can provide effective long-term protection against corrosion, thereby obviating the need for chipping of rust and repainting by ship personnel. Such coatings are providing excellent protection to below-deck components such as steam valves, but improvements are needed to realize the full potential of coatings for above-deck service. Several recommendations are made regarding processes, materials, and research and development aimed at upgrading further the performance of these coatings.

ACKNOWLEDGMENT

The cooperation of Navy representatives in providing access to ships and in making available test data is acknowledged with thanks.

National Materials Advisory Board

COMMITTEE ON THERMAL-SPRAY COATINGS FOR CORROSION CONTROL

Chairman

ROGER A. PERKINS, Member, Palo Alto Research Laboratory, Lockheed Missiles and Space Co., Palo Alto, California.

Members

NEIL N. AULT, Director of Research, Norton Company, Worcester, Massachusetts.

HERBERT HERMAN, Professor, Department of Materials Science and Engineering, SUNY-Stony Brook, New York.

FRANK J. HERMANEK, Manager, Technical Services, Alloy Metals, Inc., Troy, Michigan.

HENRY LEIDHEISER, Director, Lehigh University, Center for Surface and Coatings Research, Bethlehem, Pennsylvania.

FRANK W. LONGO, Manager, Materials Engineering, Metco, Westbury, New York.

WHITNEY G. SMITH, Manager, Materials Process Technology, The Boeing Aerospace Company, Seattle, Washington.

ROBERT SUMMITT, Professor, Department of Metallurgical Mechanics and Materials Science, College of Engineering, Michigan State University, East Lansing.

MERLE L. THORPE, President, TAFA Metallisation Inc., Bow, New Hampshire.

Liaison Representatives

ALEX KAZNOFF, Director of Materials Engineering, Naval Sea Systems Command, Washington, D. C.

DAVID LASHMORE, Corrosion Section, National Bureau of Standards, Washington, D. C.

CHARLES T. LYNCH, Office of Naval Research, Washington, D.C. (formerly with AFWAL/MLLN, Wright-Patterson Air Force Base, Ohio).

JEROME PERSH, Staff Specialist for Materials and Structures (Engineering Technology), Department of Defense, The Pentagon, Washington, D. C.

ROBERT A. SULIT, Director Facilities, Equipment, and Industrial Processes Division, Naval Sea Systems Command, Washington, D. C.

HANS VANDERVELDT, Program Manager, Materials Research and Development Program, Naval Sea Systems Command, Washington, D. C.

CONTENTS

Page

Chapter 1 INTRODUCTION 1
Scope and Objectives of this Report 4

Chapter 2 CONCLUSIONS AND RECOMMENDATIONS 7
Summary 7
Detailed Conclusions and Recommendations 7

Chapter 3 METALLIZED COATINGS FOR CORROSION CONTROL 17
Current Navy Practice 17
State-of-the-Art Summary 20
Committee Assessment 37

Chapter 4 METALLIZING PROCESSES 41
Current Navy Practice 41
State-of-the-Art Summary 44
Economics of Metallizing 49
Training and Certification 56
Committee Assessment 57

Chapter 5 COATING CHARACTERISTICS 63
Current Navy Practice 63
State-of-the-Art Summary 66
Committee Assessment 76

Chapter 6 TESTING AND EVALUATION OF COATINGS 81
Current Navy Practice 81
State-of-the-Art Summary 84
Corrosion Testing 86
Committee Assessment 89

Chapter 7 SAFETY CONSIDERATIONS 93
Current Navy Practice 93
State-of-the-Art Summary 93
Committee Assessment 96

REFERENCES 97

CURRICULA VITAE OF COMMITTEE MEMBERS 103

TABLES AND FIGURES

Page

Table 1 Melting and Boiling Point of Coating Alloys 27
Table 2 Result of 7-Year NBS Study of Coated Steel Piles 35
Table 3 Results of Port Hueneme Simulated Pile Tests Suspended From Test Dock 36
Table 4 BSI Code of Practice for Metallized Steel in Seawater Splash Zone or Salt Spray 37
Table 5 Hourly Energy Cost Comparison for Thermal-Spray Devices 50
Table 6 Comparison of Tensile Structure of Arc Wire Sprayed and Combustion Gas Wire Sprayed Processes 68
Table 7 Areas and Components Approved for Wire Sprayed Aluminum (WSA) Preservation Aboard Surface Ships 83

Figure 1 Corroded steam lines in machinery compartments of USS Saratoga 2
Figure 2 Corrosion of WSA-coated steel stanchion 18
Figure 3 Cross section of WSA-coated stanchion near site of local failure 22
Figure 4 Cross section of WSA-coated stanchion distant from local failure 23
Figure 5 Corrosion of WSA coating on steel J-bolt by exfoliation near a local failure site 24
Figure 6 The thermal-spray process 45
Figure 7 Schematic of coating cross section 46
Figure 8 Spray particle velocity 46
Figure 9 Effect of relative humidity on bond strength of WSA coatings 65
Figure 10 Effect of Ni-5Al bond coat on bond tensile strength of plasma spray Al coated steel 70
Figure 11 Representative microstructure of production quality 74
Figure 12 Microstructure of unsealed and sealed high-quality plasma-sprayed aluminum coatings 75
Figure 13 Densification of plasma sprayed aluminum coatings by glass bead shot peening 77

CHAPTER 1

INTRODUCTION

Historically, corrosion of below- and above-deck components of ships has been controlled by painting. A large fraction of a ship's crew is required to work on a steady basis cleaning and repainting metal surfaces to control corrosion. This chipping and repainting is considered nonproductive labor and in effect reduces a vessel's operational readiness by reducing the number of personnel available to operate it (Sulit et al. 1980).* Conversely, an inordinately large crew is needed to operate and maintain a ship. During the past 10 to 15 years, naval ships have not been manned adequately to accomplish all necessary corrosion control by painting. As a result, extensive refurbishing is required during periodic overhauls. Figure 1 shows the extent of corrosion in machinery compartments of the USS Saratoga at the time of major overhaul in 1981.

The National Bureau of Standards has estimated that nearly one-third of maintenance costs in the U.S. Navy can be attributed to corrosion (National Bureau of Standards 1978). The Navy is concerned with reducing both the nonproductive work load on ships and the total maintenance and repair costs. One approach selected has been to use thermal-spray aluminum (TSA) coatings on corrosion-susceptible steel structures and components wherever possible. Such coatings promise to reduce both the need for periodic repainting and the costs for repair and maintenance by extending greatly the useful life of coated components. Tests of TSA-coated steel structures in marine environments indicate that service life in excess of 10 years without the need for repainting may be possible (Navy, Department of 1966; National Bureau of Standards 1977; American Welding Society 1974).

The use of TSA coatings to control corrosion on Navy ships began in the early 1970s. Initial studies and shipboard tests were conducted with wire-sprayed aluminum (WSA) coatings using oxyacetylene torches to melt, atomize, and spray-deposit aluminum coatings on suitably prepared steel surfaces. This process, termed the "WSA preservation system" in Navy documents, is generally referred to as "flame-spraying" and is described in detail in Chapter 4 of this report.

---

*References cited throughout this report are listed in a seperate section following Chapter 7.

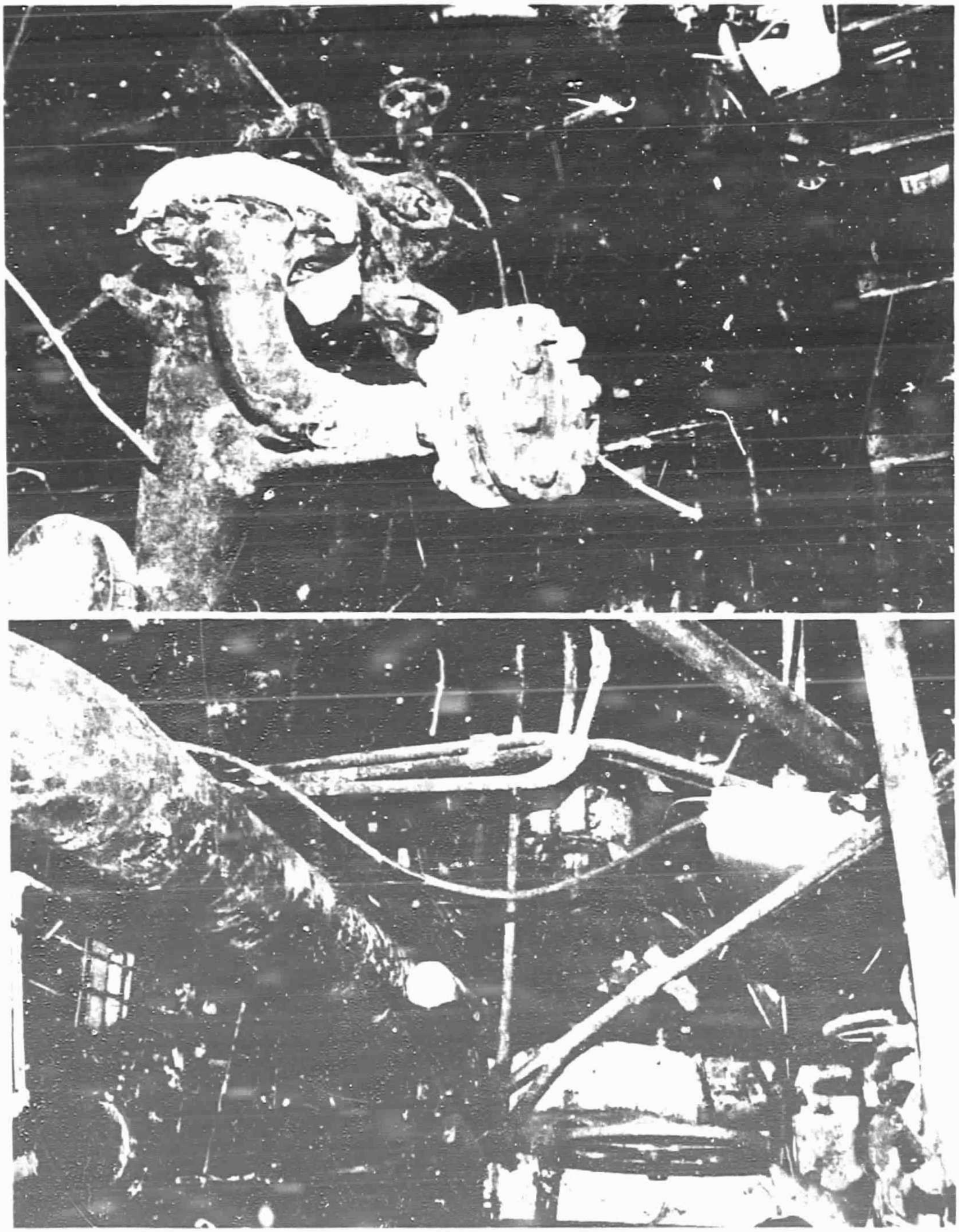


FIGURE 1 Corroded steam lines in machinery compartments of USS Saratoga at time of major overhaul, January 1981 (Courtesy COMNAVSURFPAC).

The WSA system has been used on aircraft carriers since 1974 to protect launch and recovery systems (Navy, Department of 1976). A nonskid deck coating applied by arc-wire-spray techniques also was developed and is now used routinely for jet-blast deflectors on carrier flight decks (Sulit et al. 1981). A test and evaluation program to implement WSA preservation in ships of the Naval Surface Force, U.S. Pacific Fleet (NAVSURFPAC), was initiated after 1974, but large-scale service tests did not begin until 1977 (Sulit et al. 1981). In that year one guided missile frigate, USS Schofield (FFG3); three guided-missile cruisers, USS William H. Standley (CG32), USS Fox (CG33), and USS Bainbridge (CGN25), and two Spruance-class destroyers, USS Hewitt (DD966) and USS David R. Ray (DD971), were fitted with selected components for shipboard evaluation of the WSA preservation system (Sulit et al. 1980). Coated items included steam valves, boiler skirts, ladders, instrument stands, lifeline stanchions, diesel exhaust stacks, missile exhaust deflectors, helicopter deck tiedowns, steam riser valves and piping, helicopter flight decks (nonskid coating), walkways, and missile launch work areas. This list has been extended since 1980 to include many more ships and varieties of components and structures.

Results of shipboard tests and evaluations to date have been mixed, with both good and poor performance, depending on the nature and area of application. In a majority of applications, results have been very encouraging, with a significant reduction in required maintenance and nonproductive labor. WSA-coated steam valves have been in service over 4 years without any significant degradation. The Navy is now implementing as a routine procedure the use of WSA preservation for components on which good performance has been demonstrated (Sulit et al. 1980). This procedure promises to reduce fleet maintenance hours and increase the useful life of a wide range of shipboard components.

Performance has been less than satisfactory in topside components, notably arc-wire-sprayed aluminum nonskid deck coatings (Navy, Department of 1982). Coating separation occurred in less than one year of service in several large installations on deck edge elevators and helicopter flight decks. Corrosion occurred within the coating, and the deck-coating interface was undermined. The cause of these failures is not clear at present, but the results indicate that current practices for WSA coatings may not always be appropriate. Process and product improvements may be needed to obtain maximum benefits from broad application of the WSA corrosion control system.

Performance to date has been judged on the basis of relatively short-term (< 5-year) exposures. While the short-term benefits of WSA preservation appear to be worthwhile, neither the long-term (>10-year) effects nor the performance limits of these coatings in shipboard applications are known. It is important that the potential limitations and problems that could affect the use of this technology be more clearly defined to provide guidance to the Navy in applying WSA preservation systems to a wider range of shipboard applications. New and emerging technology for thermal-spray coatings must be fully assessed in terms of Navy applications, and current practices must be modified as needed to provide the best possible preservation system.

SCOPE AND OBJECTIVES OF THIS REPORT

A committee organized at the request of the Navy reviewed thermal-spray coating technology and assessed its practical application for WSA preservation of shipboard components. Results of the committee's study and its recommendations for future actions are presented in this report.

The study consisted of a detailed review and analysis of WSA technology as used by the Navy and of the state of the art of metallization by thermal-spray processes for corrosion control. The committee took a broad view of the overall field of thermal-spray coatings with the intent to identify technologies not currently in use by the Navy that might aid in the development of improved shipboard preservation systems.

The primary objective of the study is to provide guidance for the expanded development and application of metallized coatings to control corrosion of shipboard components. Specific goals are to:

- Indicate the long-term (>5-year) potential for preservation of steel structures and components in Navy ships by metallized coatings.
- Identify problems that may arise in the application of metallized coatings for shipboard service and indicate the degree of risk involved in the use of this technology.
- Indicate what, if any, existing or emerging technology not currently in use by the Navy should be considered to improve the performance and expand the use of metallized coatings to solve a wider range of corrosion problems.
- Identify the optimum materials and procedures for metallized coatings in marine environments and indicate how this technology can best be used.
- Recommend areas for further research, development, or testing that may increase the performance of metallized coatings and expand applications to reduce maintenance in naval ships.

The Navy identified a number of problem areas that the committee was asked to examine:

1. Accelerated testing to estimate projected service life and time between repair and overhaul cycles.
2. Nondestructive testing and quality assurance techniques and procedures.
3. Updated standards for materials and processes.
4. Recognition and incorporation of WSA preservation in ship acquisition (new construction) versus repair and maintenance during overhaul periods.

5. Additional areas for retrofit on deployed ships.

6. Approaches to analysis correlation and dissemination of performance data as related to applications and processes.

7. Development of a technical information data bank for use by ship acquisition and logistic support managers and staff.

A further objective of the study is to resolve these problems where possible and to aid in the transition from paint to WSA preservation systems in the U.S. Navy.

Chapter 2 presents the committee's conclusions and recommendations. In the subsequent chapters, current Navy practice in a specific area, is first reviewed, followed by a discussion of the state of the art in that area. Committee findings with respect to existing or developing technology, which could be incorporated in the Navy program to improve performance or aid in developing improved shipboard preservation systems based on metallized coatings, are then presented.

CHAPTER 2

CONCLUSIONS AND RECOMMENDATIONS

SUMMARY

The committee strongly endorsed the concept of corrosion control through the use of thermal-spray coatings. Although information is not adequate to predict service life accurately, present evidence indicates that coatings are cost-effective (on a life-cycle basis, more economical than paint), require much less maintenance when ships are at sea, and, with an estimated service life of 10 to 20 years, may preclude the need for upkeep between major overhaul periods. Such coatings are providing excellent protection to below-deck components such as steam valves, but improvements are needed to realize the full potential of coatings for above-deck service. Corrosion-free life is controlled by coating defects. Therefore, major attention should be given to appropriate specifications, process controls, post-spray sealing, and training of operators and supervisors. Improvements in some procedures--principally maintaining a clean, dry surface before spraying and sealing of porosities--are needed. Three new or different approaches should be explored: utilization of the hot-dip process for removable items such as stanchions, the evaluation and development of bond coats, and, if it is determined that zinc or zinc-aluminum alloys do not constitute hazards, their use as alternates to aluminum. Finally, an amplified program of evaluating material and process variables, such as by shipboard or shore test panel installations, is needed to enable improvements to be identified and wrong choices to be avoided.

DETAILED CONCLUSIONS AND RECOMMENDATIONS

Conclusions

General Comments on Shipboard Utilization of Metallized Coatings

- Thermal-spray coatings of aluminum, zinc, and zinc-aluminum alloys are capable of providing effective long-term (>10 years) corrosion protection to steel in shipboard applications. Well-bonded, relatively dense, sealed coatings have the ability to protect both above- and below-deck components for many years with minimal periodic maintenance. These coatings have the potential, by preventing corrosion, to reduce significantly the nonproductive labor required to maintain Navy ships.

- WSA coatings are considered to be cost-effective for shipboard applications. In many applications metal spraying is competitive and sometimes lower in cost on an initial-cost basis when compared with high quality paints. When considered on a life-cycle basis, which includes maintenance and repair costs, thermal-spray coatings are more economical than paints.

- Widespread use of WSA-coated steels on naval ships does not present a personnel safety or fire hazard under either normal or wartime service conditions. Sparking, which could cause ignition of combustible vapors, is the only recognized potential hazard; this can occur when rusted steel strikes a clean aluminum surface. The risk of sparking appears to be negligible when the coating is sealed and/or painted. Zinc or zinc-aluminum coatings, on the other hand, appear to present a possible significant personnel safety hazard. Zinc oxide fumes can be produced in a shipboard fire or explosion, and the fumes are toxic. Widespread use of zinc could present a safety risk: however, a detailed analysis of the hazard potential has not been made.

Considerations Related to the Coating Material

- Aluminum, zinc, and zinc-aluminum coatings protect steel by acting both as barriers to corrosion and as sacrificial anodes at local defects where corrosion occurs. Zinc provides better galvanic protection, whereas aluminum is better as a less reactive barrier layer. Zinc-aluminum alloys appear to combine the better qualities of both materials, but thermal-spray coatings of these alloys have not been tested for long-term resistance to marine corrosion. Zinc coatings need to be painted for resistance to direct attack by corrosion. Aluminum coatings must be sealed for best performance. Suitably primed, sealed, and painted coatings of pure aluminum or zinc appear to offer equivalent long-term protection. No other metallized coatings are known to provide equal or better protection at comparable unit cost. The committee strongly supports and endorses the selection of unalloyed aluminum as the primary metallized coating for shipboard preservation systems. The effect of top coat paints on performance has not been defined adequately.

Process Considerations

- It is possible for thermal-spray coatings of acceptible structure and properties to be sprayed by either combustion-gas-wire, arc-wire, or plasma energy processes. No one process has been conclusively shown to be inherently better than any other process with respect to the structure and properties of sprayed-aluminum coatings that can be deposited on suitably prepared, clean steel substrates. The choice between processes can be based more on economic and producibility considerations than on coating structure and property considerations.

- The combustion-gas WSA coating process selected for the initial shipboard applications and used today for the majority of WSA preservation coatings permitted an early and effective demonstration of the broad capabilities of metallized coating systems. The process is considered to be suitable for continued and more widespread use. The arc-wire-spray process offers increased rates of production and lower cost operation. This process is well suited to high-rate production coating of large surfaces. Recent developments in small, precision guns promise to increase the versatility of the arc-wire process, particularly for coating small, complex parts.

- Process control is the only practical approach to product quality control and assurance for thermal-spray coatings. Strict adherence to process specifications at all times is required for uniformly high-quality coatings. Currently used practices and process specifications are based largely on experience in thermal-spray coatings for machinery repair and do not necessarily represent the best practices for a shipboard corrosion protection system. The major deficiency in current process specifications is in the control of moisture and surface contamination during grit-blasting for surface cleaning and preparation, during storage before coating, and during the coating process. High moisture and surface contamination contribute to low and variable bond strength, and current specifications do not provide for adequate control of moisture in cleaning, storage, and spray atmospheres. Specification of a time limit between surface cleaning and coating instead of a moisture limit in process and storage atmospheres, although helpful, is not considered to be an adequate method of control for WSA coatings.

- Thermal-spray coating is a technology in which product quality and performance are and will continue for some time to be governed by knowledge, understanding, and skill of designers, spray operators, and users. Close process control, education at all levels, and extensive operator training and certification are required to produce consistently high-quality coatings. This is not a technology in which low bids can be accepted on faith, and prime consideration must be given to technical excellence and skill rather than to cost in selecting coating sources. The current approach to training and certification of operators is limited in both scope and depth and needs to be expanded. Improved education and training also are needed for supervisors and engineers who make decisions concerning the manufacture, installation, and use of WSA coatings.

- Mechanization and automation of spray processes provides a means to reduce the variation in thickness, structure, and properties of WSA coatings. Feedback controls are needed for continual adjustment of process variables; the two most important are stand-off distance and gun orientation. Work in this direction has been started by the Navy for arc-wire-spray coating large deck areas and by the Air Force for plasma-coating turbine blades. Computer-controlled robot systems offer a major advance in improved quality and reduced cost for all thermal-spray coating processes. The risk encountered in using these systems can be decreased by reducing dependency on operator training and skill and increasing the degree of control over all aspects of the process.

- The integrity of the bond between the substrate and the coating is believed to be the single most important characteristic that controls performance. The bond is largely mechanical, and, hence, adhesive strength between coating and substrate is the primary measure of bond integrity. Low strengths indicate incomplete or poor bonding. A direct correlation between bond strength, bond integrity, and coating performance has not been made to date, and minimum values that will ensure good performance have not been determined.

- Coatings must be sealed or densified for maximum resistance to corrosion. Densification by mechanical deformation is effective but can result in bond separation and may, in effect, reduce useful life. Sealing, by infiltrating porosities with vinyl or aluminum/vinyl sealants, is considered to be the best overall approach. The useful life of existing coatings could be extended by more effective sealing of pores. Improved methods and approaches to sealing may be needed to improve compatibility with commonly used Navy top-coat paints.

- Fully dense coatings of aluminum, zinc, or zinc-aluminum alloys that are bonded metallurgically to the substrate can be produced by hot-dipping parts to be coated in molten metal or alloy. Hot-dip coating is a high-rate, low-cost production process that can produce a superior coating on small parts and components. Coatings of this type might be very useful for above-deck components exposed to the most severe environments. Long-term tests in marine environments have been made for zinc, but no data are available for aluminum-coated steel.

Testing and Evaluation Considerations

- Currently used NDE and mechanical tests for WSA coatings represent the best state of the art available for product and process quality control. Bond strength is measured by tensile and bend tests but neither method is adequate for production quality control. The bend test is considered to have the best potential for day-to-day control of production but is not standardized and results have not been correlated with either bond strength or performance. Improved methods for assessing bond strength are needed.

- Available NDE tests for bond integrity and porosity are not adequate and cannot be used effectively for process or product control. Newly developing techniques, however, do show promise for detecting bond separation and excessive porosity. These are a modified ultrasonic technique and optical holography used singly or in combination. They appear to have good potential for more effective product control and quality assurance in the future.

- The Navy corrosion test program has moved rapidly from minimal laboratory and field tests of corrosion resistance to a full-scale service evaluation of shipboard components. However, a comprehensive program has not been devised to document, track, and characterize most shipboard components. In addition, there is no plan to conduct either laboratory or field tests in which variations in coating performance can be related to variations in process variables or in coating composition, structure, and properties. This is considered to be a major deficiency in the corrosion control program. A technically sound supportive corrosion test and evaluation program will reduce the risk in the overall program. While the committee agrees that the WSA preservation system has the ability to provide over 10 years of maintenance-free service, it doubts that all coatings as currently produced have this capability. Extensive corrosion testing and evaluation are needed to develop the optimum material, production practices, and process controls.

- Service-environment field tests of limited scope are essential for planning wide-scale implementation of corrosion protection systems, as well as to monitor their performance after adoption. The Navy has made good use of such testing, but, because of limited resources, less than adequate effort has been spent in the statistical planning of experiments, system performance evaluation, and failure analysis. Additional field test sites are needed where test panels and/or components can be evaluated by controlled corrosion tests in more realistic shipboard environments.

Recommendations

Recommendations Regarding the General Program

- The committee strongly supports and endorses the shipboard preservation system of metallized coatings as introduced by the Navy and recommends more widespread use in both new ship construction and in repair and overhaul of deployed ships. Corrosion-prone shipboard components and structures currently protected by paint should be replaced with WSA coatings wherever possible. WSA preservative systems should be incorporated in all new ship construction, particularly in below-deck and machinery compartments. A more careful review and analysis should be given to above-deck applications in terms of acceptable properties and quality levels.

- The committee recommends that the Navy sponsor and conduct a comprehensive coating research and development program to provide the technical basis needed for an effective, long-life WSA preservation system. The program should comprise a statistically sound evaluation of the most important product and process variables for WSA coatings as deposited by both combustion-gas and arc-wire thermal spraying. It should establish by controlled experiments the minimum levels of bond strength and porosity for acceptable performance and should define limiting process parameters to achieve these levels. Capabilities and limitations of each process should be more clearly defined. The program should be conducted as two separate but interrelated studies:

1. A study that correlates coating performance and useful life with variations in bond strength, porosity, defects, and thickness for both sealed and unsealed WSA coatings. This study will define the limiting conditions in terms of structure and properties for acceptable performance and will provide a technical basis for predicting useful life.

2. A study that correlates bond strength, porosity, defects, and thickness with major process variables, including surface preparation and surface cleanliness. This study will define reasonable and realistic process controls and will provide the technical basis for improved process specifications.

Performance of coatings should be evaluated on a statistically sound basis. Use of the Weibull distribution function is recommended.

o Education and training courses should be developed for designers, supervisors, and users of WSA coatings as well as for spraygun operators. More effort should be given to developing a technical understanding and appreciation of how these systems work and how they must be prepared and used in order to be effective. Civilian contractors should receive equal education and training. University short courses may provide a basis for training non-Navy personnel. It is recommended that only fully educated, trained, and certified personnel be used to produce and to specify the use of WSA coatings for shipboard applications.

Recommendations Relating to Coating Materials

o All WSA coatings should first be treated with a strontium chromate wash primer followed by application of vinyl or aluminum-pigmented vinyl sealers before being placed in service. This is the best known available sealing practice and is recommended for use on all shipboard components and structures, particularly for above-deck, sea-exposed areas. Manufacturers' recommendations for application of sealers should be strictly adhered to for effective sealing of pores.

o A research and development program should be initiated to improve compatibility between thermal-spray coatings, sealants, and top-coat paints. The behavior of pure aluminum, pure zinc, and zinc-aluminum alloys with a variety of top-coat paints, primers, and sealers should be studied in both laboratory and shipboard corrosion tests. Consideration should be given to the use of duplex coatings such as zinc or zinc-aluminum sprayed over wire-sprayed aluminum on steel to provide a more suitable surface for paints. New organic or inorganic sealers more compatible with Navy paints or new paints more compatible with vinyl sealers should be developed. The WSA coatings should be treated as a composite organic/inorganic coating and should be optimized for maximum stability and resistance to corrosion.

- It is recommended that the Navy initiate a test program to evaluate the effectiveness of bond coats such as nickel-aluminum and iron-aluminum. Effect on bond strength and corrosion behavior of WSA coated steel should be defined and the optimum materials and processes identified.

- Limited shipboard testing of zinc and zinc-aluminum alloy thermal-spray coatings on steel is recommended. These materials should be considered as alternate or possible replacement systems for WSA coatings in above-deck applications. A detailed hazard analysis with respect to possible toxic effects of zinc oxide vapor should be conducted before any large-scale use of zinc-based coatings is contemplated.

- A study should be undertaken to define the defect tolerance of WSA coatings and to relate performance to flaws likely to be formed in manufacture and use. Suitable repair procedures should be developed and tested. It is important to know what types of anodic coatings, post-spray sealings, and combinations of these methods would be most effective in minimizing the damage from scratches or gouges.

Recommendations Relating to Processes

- Process specifications should be amended to include a destructive test for coating quality control in day-to-day production. Use of the bend test is recommended for this purpose. A random sample of production should be taken at periodic intervals to assess bond strength and coating quality.

- The requirements for atmosphere control in process specifications should be changed to reduce surface contamination that contributes to low bond strength. Specifically, the moisture content (humidity) of air used for surface-cleaning, grit-blasting, and thermal-spraying should be specified and controlled at a reasonable and acceptable low level. It is recommended that refrigerator dryers be used to reduce the dew point of air to 35°F in all permanent installations operating on a continuous basis. In portable or temporary setups, dessicant driers with a capacity of 35 cfm/spray torch should be used. A compressor after-cooler may be needed to keep air temperature below 100°F for effective drying with dessicants. In addition, air cleaners should include a 5 μm filter with automatic water dump and a coalescing filter to remove oil.

- Atmospheres in which parts are stored between grit-blasting and coating should be controlled with respect to temperature, humidity, and cleanliness. Recommended conditions are a temperature of < 80°F and a dew point < 35°F. WSA coating facilities in both Navy and civilian plants as well as in shipboard (field) sites should be upgraded to controlled-environment conditions. Air-conditioned facilities are recommended wherever possible. Portable equipment and tents can be used for on-site atmosphere control. Cleaned and blasted parts should be stored in covered bins or sealed bags to prevent surface contamination.

- It is recommended that the Navy initiate a manufacturing development program on hot-dip coating of steel with aluminum. The program should demonstrate the practicability of batch-coating small parts in high-rate production. Optimum process variables should be established, and coated components should be evaluated in shipboard corrosion tests. In addition, consideration should be given to the support of work leading to the development of aluminum-clad steel plate for use in new ship construction. Continuous or batch hot-dipping and roll or explosive bonding of steel plate should be developed as low-cost production practices.

- It is recommended that mechanical densification such as shot-blasting not be used to seal porosity due to a high potential for weakening or loss of bond. Shot or grit blasting also should not be used to remove paint from WSA coatings for the same reason. Surface cleaning by wire brushing is recommended.

- The Navy should initiate and support a manufacturing development program on automated AWS processes for shipboard components. The program should be conducted with combustion-gas, and arc-wire spray equipment with the goal of reducing dependency on operator skill. It should include the use of microcomputers and feedback controls to improve coating uniformity and quality for a wide range of applications.

Recommendations Relating to Testing

- A standardized bend test should be developed to assess bond strength and coating quality in an expeditious and effective manner. Bend behavior should be correlated with test parameters, specimen geometry, coating thickness, tensile bond strength, and coating performance in order to establish a technical basis for the design of a more effective production quality control test.

- The committee recommends that shipboard sites be made available for more extensive testing and evaluation of coated test panels and small components under realistic field conditions. Corrosion test racks should be installed on selected ships for "at sea" corrosion tests in both above- and below-deck locations. In addition, specific ships should be designated as corrosion test facilities for limited testing and evaluation of actual components in a manner similar to that used in the USS Standley for the coated steam valve program.

- A research and development program should be inititated to define the defect tolerance of WSA coatings and to establish the useful life of coatings with the presence of representative flaws or defects produced in manufacture and use. Types of defects that require early repair or maintenance should be identified, and suitable repair practices should be developed. Both short-term repairs by painting and long-term repairs by respraying should be considered.

- A statistically sound approach to the testing of coatings should be used. The use of extreme-value distributions such as the Weibull function is recommended for analysis of data. More extensive use should be made of metallographic and various electron beam materials analysis techniques (AES, EMP, SEM, TEM, and XRD) in the evaluation of coating behavior. Failure analysis studies of in-service components should be conducted on a periodic basis to provide a better technical basis for development and use of WSA coatings.

CHAPTER 3

METALLIZED COATINGS FOR CORROSION CONTROL

CURRENT NAVY PRACTICE

The only material currently in use as a metallized coating for shipboard corrosion control in the U.S. Navy is aluminum to MIL Std. 6712 (Navy, Department of 1980a; Sulit et al. 1980). The design goal in 1977 was to deposit coatings 0.004 to 0.006 in. (4 to 6 mil) thick. Parts operating above 125°F (i.e., steam valves) were sealed with silicone-aluminum paint. Navy paint primers and color topping without sealers were used on many above-deck surfaces and components operating at ambient temperatures. All components were treated with a strontium-chromate wash primer prior to sealing or painting. Some components were sealed with an epoxy sealer (epoxy polyamide). The 4 to 6-mil thickness was selected on the basis of the American Welding Society's 19-year corrosion study (American Welding Society 1974) which indicated that 3 to 5-mil wire-sprayed aluminum would give complete base-metal protection.

Most components from these early tests demonstrated protection for 1-1/2 years without further preservation work required. However, some items did show local areas of degradation and base-metal corrosion. A local corrosion failure of a WSA-coated deck stanchion after 7 months of service in the Pacific is shown in Figure 2. Failures of this type were attributed to thin areas of coating (Sulit et al. 1980). It was concluded from these tests that coating thickness should exceed 5 mil to minimize or eliminate local thin spots. WSA coating thicknesses in the range of 7 to 10 mil currently are recommended for ambient-temperature components (Navy, Department of 1980a). Thicker coatings (10 to 15 mil) are applied to components that operate above 125°F (e.g., steam valves).

Perhaps the best performance to date has been exhibited by WSA coatings on hot steam valves in below-deck machinery compartments. No further work or preservation has been needed, and no signs of local deterioration are evident as of the fourth inspection in September 1980 (Navy, Department of 1981a). Coated valves were installed in May through August 1978. Similar valves painted with heat-resistant aluminum paint operating in the same environment have been repainted between 5 and 7 times during the same time period. This test program involves some 350 steam valves and associated flanged piping on the USS W.H. Standley (CG 32). This ship was visited by members of the committee in May 1981, and a cursory inspection indicated no

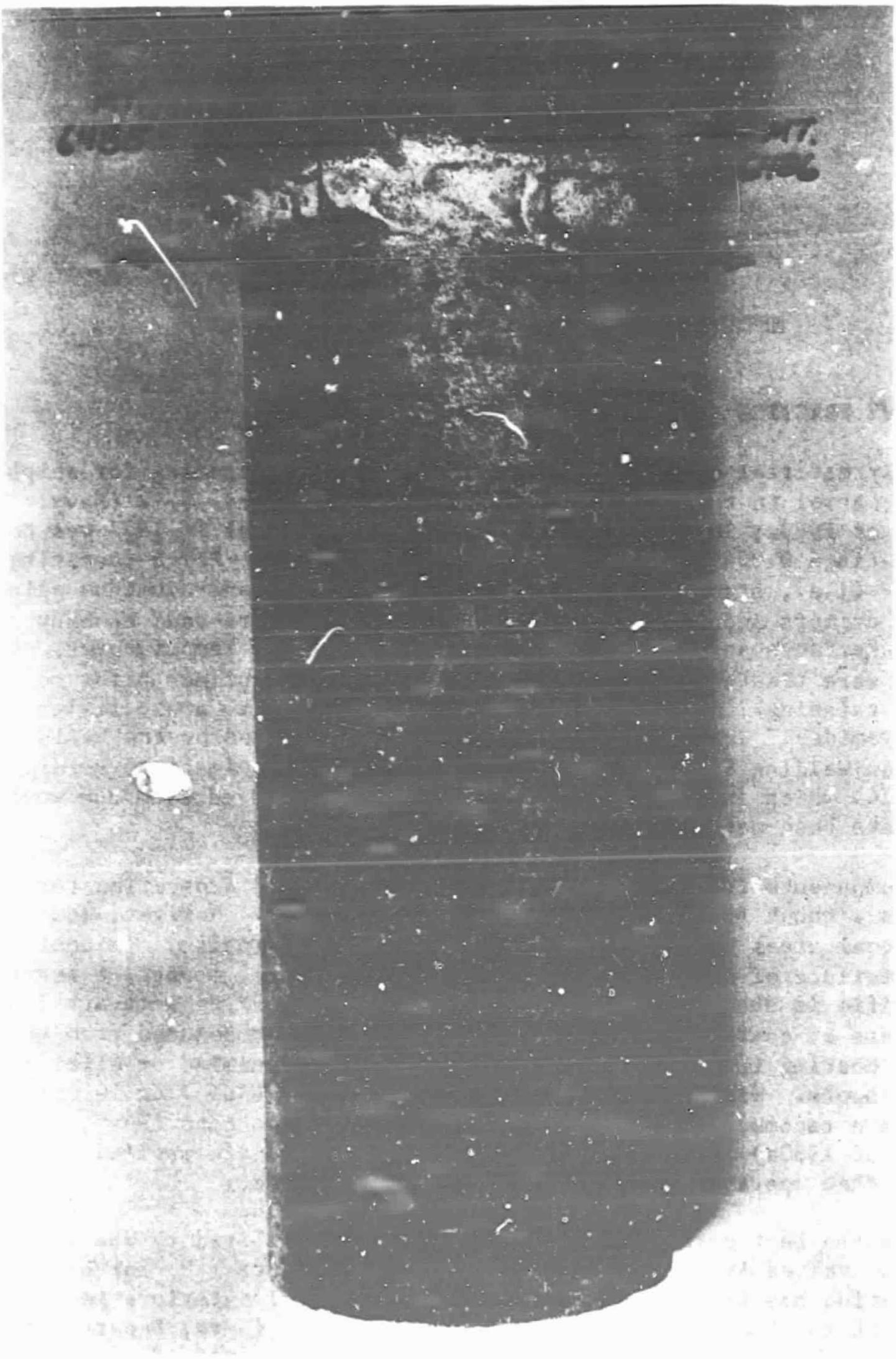


FIGURE 2 Corrosion of WSA-coated steel stanchion after 7 months of service on the USS Standley (CG 32) (Courtesy Lockheed Missiles and Space Co.).

change in the condition of WSA-coated steam valves. The Naval Sea Systems Command adopted the use of WSA preservation for steam valves in May 1979 to replace heat-resistant aluminum paint.

The only problems encountered with WSA coatings have been with above-deck components that are exposed directly to seawater by alternate immersion, washing, or spray. Some problems can be attributed to locally thin areas. Major problems have been encountered with thick nonskid metallized deck coatings; these have been due to corrosion within the coating, accelerated galvanic corrosion from coupling with dissimilar metals (notably stainless steel), or formation of a poor interface bond. The committee inspected a helicopter flight-deck coating on the USS Fox (CG 33) where bond separation and coating delamination occurred in large areas. These were areas in which gas-WSA was applied by hand-held torch. The main part of the coating, in which arc-WSA was machine-applied was intact and offered good protection except in local areas where stainless-steel lamp covers and straps were in contact with the coating.

Three different coating systems are currently being evaluated for nonskid deck applications:

1. Spray- or roller-coated conventional (organic) nonskid over an arc-WSA undercoat 5 to 8 mil thick.

2. Arc-WSA nonskid overcoat 10 to 25 mil thick over an arc-WSA undercoat 5 to 8 mil thick.

3. One-coat arc-WSA nonskid and barrier (corrosion protection) layer 15 to 45 mil thick.

System 1 (conventional nonskid over a 5 to 8-mil-thick arc-WSA cover or corrosion-control coat) is being service-tested on the USS Donald B. Beary (FF 1085) by the Naval Surface Force of the U.S. Atlantic Fleet, the Naval Sea Systems Command, and the Naval Air Engineering Center. This system is expected to last 3 to 5 years with only minor repairs to replace worn or damaged conventional nonskid areas. The WSA corrosion-control coat is expected to last from one overhaul to the next.

System 2 (double-coat arc-WSA) has been applied to the helicopter flight decks of the USS Hewitt (DD 966) and the USS Fox (CG 33). The USS Fox deck coating was applied in June 1979 and is in use and under observation. The USS Hewitt's flight-deck coating was applied in September 1978. It had a 1.1 to 0.9 coefficient of dry static friction. However, it was covered over with a spray-on conventional nonskid coating making it equivalent to System 1. Because of lack of sufficient technical and safety service testing, no data are available on wear qualities compared to conventional nonskid decks versus time and use conditions and friction degradation with cosmetic painting and fuel/oil spills. There is no sign of degradation to date. When mechanically damaged or chipped, the conventional nonskid coating is more easily repaired because the WSA precludes corrosion of the substrate.

System 3 (one-coat arc-WSA 15 to 45 mil thick) was applied to the walkways and ASROC-launcher work area on the forecastle deck of the

USS Bainbridge (CGN 25) in May 1979. This nonskid coating has survived ASROC and Terrier missile launchings that destroyed adjacent conventional paint-preserved areas. System 3 also was used in nonskid coating of aluminum alloy X deck-edge elevators, which failed by internal corrosion and coating separation in less than 1 year. Multiple guns (quadrahead) were used in this application, which increases the rate of deposition and hence reduces cost (Navy, Department of 1982), but which also increases heat input that can cause debonding due to high thermal stress induced at the coating-substrate interface. The cause of this premature failure was still under investigation at the time of writing, and no conclusions can be drawn at present.

The use of WSA preservation coating for the control of shipboard corrosion has proved highly effective in most applications. A number of COMNAVSURFPAC ships have had a wide range of items or spaces preserved with WSA, such as propulsion-plant steam valves and piping, boiler skirts, deck hardware and machinery, topside deck surfaces, helicopter deck tiedowns, and nonskid flight-deck and weather-deck walkways. These applications have demonstrated a reduction in repetitive, nonproductive ship's force preservation work. The potential exists for additional significant reduction in such preservation work by the widespread use of WSA coatings on topside, well decks, machinery space, and other corrosion-prone areas. The Naval Sea Systems Command is implementing a program for WSA preservation in the acquistion, repair, and overhaul of U.S. Navy ships (Sulit et al. 1980).

STATE-OF-THE-ART SUMMARY

Basis for Corrosion Protection

The primary agency by which a metallized coating protects a steel surface from corrosion is physical in nature. The coating, like paint, is a barrier that separates the steel substrate from the corrosive environment. However, with aluminum and zinc coatings in marine environments, cathodic protection provides a second and perhaps equally important basis. When a simple inert coating such as paint is damaged, substrate corrosion occurs rapidly at the defect site. Corrosion often spreads along the interface, further destroying the coating. However, with an active metal coating that is more electronegative than steel, corrosion of the substrate will not occur at local defect sites.

Pure zinc, zinc-based aluminum alloys, and pure aluminum act galvanically to protect the more noble steel substrate in electrolytic solutions (such as saline environments). The metallized coating is essentially a sacrificial anode and will be consumed with time. These metals, being particularly active electrochemically relative to iron, afford a high degree of cathodic protection to steel. Even if the coating is penetrated or damaged mechanically, the coating will continue to provide effective cathodic protection to the adjacent exposed substrate. In conditions where substrate geometry is such that complete metal coverage is not possible, aluminum and zinc are known to afford cathodic protection through their high electrochemical activity.

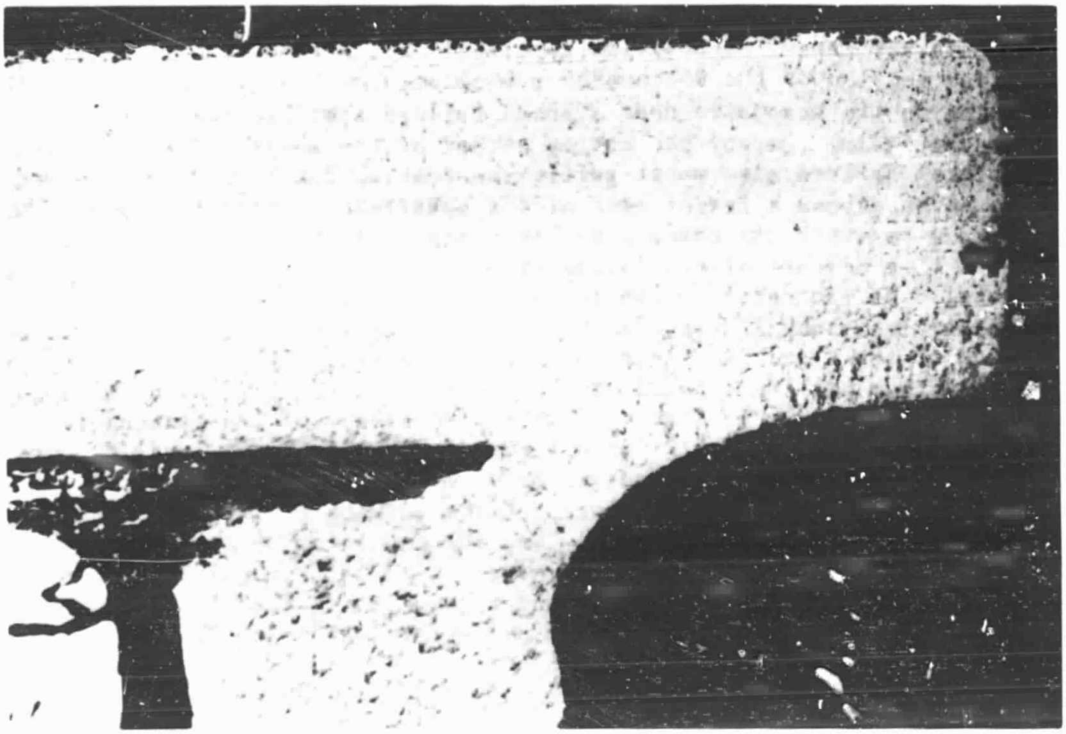
This key aspect of behavior is clearly illustrated by Figure 3, which is a cross section of the WSA-coated stanchion shown in Figure 2. The aluminum coating on the stanchion near a local failure spot has been attacked preferentially, thereby preventing attack of the steel. This occurs around the local failure site until sufficient coating has been dissolved and removed to expose a larger area of the substrate to direct attack. The distance to which the coating can be stripped back before substrate attack occurs is a measure of the degree of cathodic protection offered by the coating. As indicated by the local failure shown in Figure 2, this is probably less than 1/2 in. for WSA-coated steel. That is to say, direct attack of the steel is likely to occur where selective attack and removal of the aluminum coating exposes an area of steel about 1/2 in. or more in diameter. As shown in Figure 3, selective attack of the coating is occurring within about 1/2- to 3/4-in. distance from the local failure site. Coating has been dissolved from the lower side and edge of the stanchion cap just above the failure site but not from the coating on top or on the opposite side of the cap. Coating condition on the opposite side of the cap is shown in Figure 4. The coating is continuous and uniform over the top and edge of the cap, with an average thickness of about 6 mil. This indicates that failure most likely did not result from a localized thin spot but was the result of anodic dissolution of the coating in an area adjoining a very small local defect. It is believed that a mechanical or physical defect in the coating set up a local electrolyte cell by exposing a small area of substrate to direct seawater exposure.

Anodic dissolution of the coating results in a form of exfoliation attack, as shown in Figure 5. The reaction products from corrosion of the aluminum are voluminous and tend to rupture the coating in layers, causing a mechanical as well as a chemical breakdown. Zinc or zinc-aluminum coatings on the whole do not behave in this manner, since their corrosion products are not as voluminous. These coatings are degraded primarily by straight chemical attack.

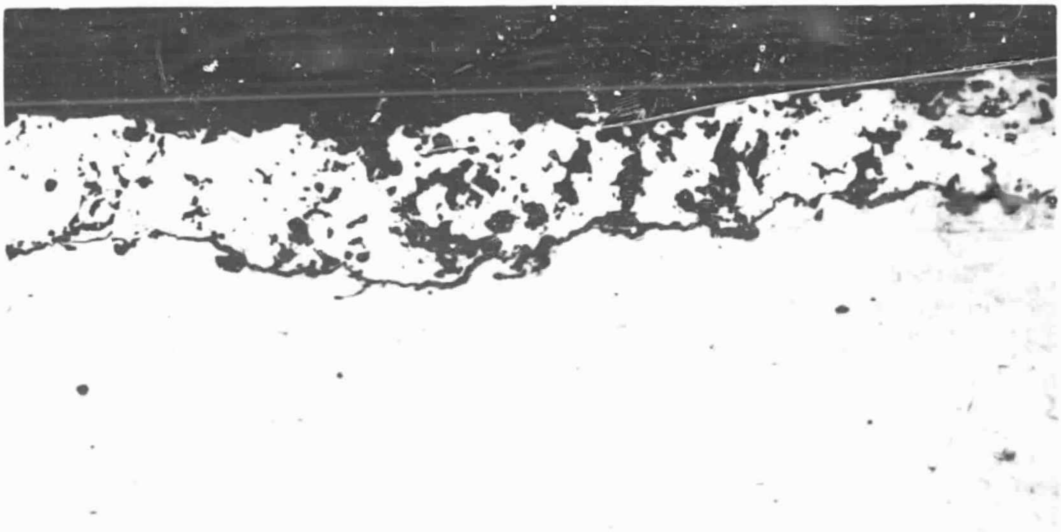
Coating Materials

Cathodic protection of steel in marine and industrial environments is obtained by the application of a continuous active metal coating. Thermal-spray metallization with aluminum, zinc, and zinc-base aluminum alloys is a highly effective means of forming such a coating. There are significant differences in both the chemical and electrochemical behavior of these materials that will have a major infuence on the useful life of a coating with respect to time to first maintenance and eventual wearing out of the coating.

The resistance of aluminized steel to corrosion is reported to be better than that of galvanized (zinc-coated) steels in many environments (Van Horn 1967). This is largely due to the protective nature of oxide films formed on aluminum. The rate of attack of aluminum in plain corrosion will be very low compared with that of zinc but its ability to protect at local defects in the coating will be significantly lower. Pure aluminum is more electronegative than zinc under reducing conditions, but in the presence of oxygen the electrode potential is increased by the formation of thin alumina films that are electrically insulating. These films limit corrosion currents and provide a very high over-potential for anodic dissolution

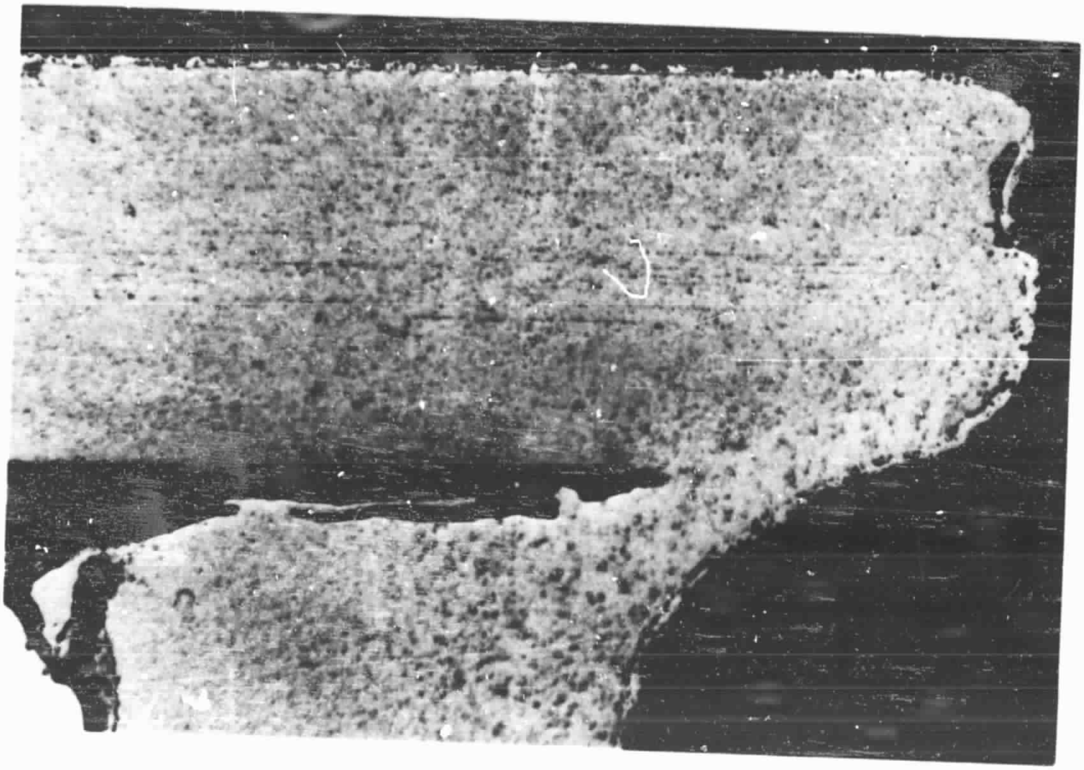


a. Loss of coating from edge and corner above failure site. 100mm



b. Continuous remaining coating on top above failure site. 125μm

FIGURE 3 Cross section of WSA-coated stanchion near site of local failure shown in Figure 2 (Courtesy Lockheed Missiles and Space Co.).



a. Continuous coating over top and side.

b. Remaining coating on top surface.

FIGURE 4 Cross section of WSA-coated stanchion distant from local failure shown in Figure 2 (Courtesy Lockheed Missiles and Space Co.).

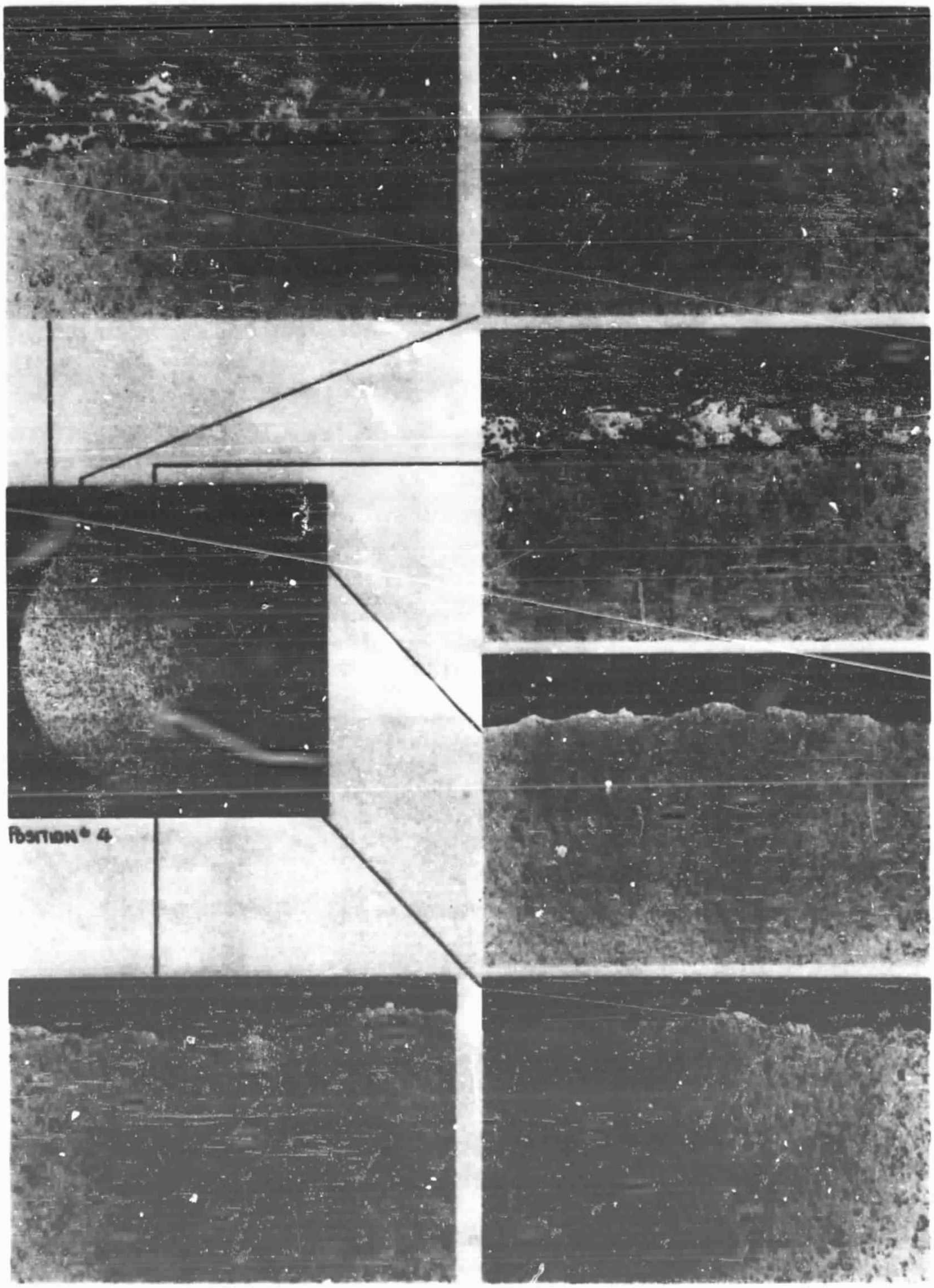


FIGURE 5 Corrosion of WSA coating on steel J-bolt by exfoliation near a local failure site, aboard USS Schofield (FFG 3) after 7 months service (Courtesy Lockheed Missiles and Space Co.).

(Sempels and Leclercq n.d.). This accounts for the large differences between calculated thermodynamic and measured corrosion potentials for aluminum and actually limits the ability of aluminum coatings to protect steel cathodically. Once a coating fails, the zinc-based material will provide better overall cathodic protection but for a much shorter period of time because of the rapid anodic attack of the zinc. A failed aluminum coating will provide less overall cathodic protection but will provide that level of protection for a much longer period of time at local failure sites. Results of the AWS 19-year study (American Welding Society 1974) confirmed that the life of low defect aluminum coatings on steel exceeds that for zinc coatings at equal coating thickness (3 mil) for each material. In general, zinc coatings are qpplied more thickly than aluminum coatings to offset the more rapid rate of several corrosion.

Both zinc and aluminum are more electro-negative against stainless steel than against low-carbon steel. Coupling of metallized coatings with stainless steel will accelerate greatly the anodic dissolution of either coating and should be avoided. Accelerated corrosion of these active coating metals as a result of dissimilar metal contact becomes a very important consideration in the design and application of metallized components. Coupling with copper and copper-based alloys also should be avoided.

Underrusting is a serious problem with aluminum coatings, and corrosion at local defects spreads rapidly along the interface between steel and coating. Zinc coatings, on the other hand, are not susceptible to this type of attack. Zinc provides much more effective cathodic protection and will delay the onset of substrate corrosion and preclude spread of substrate attack along the interface (underrusting). In addition, zinc is more resistant to pitting corrosion than aluminum (Sempels and Leclercq n.d.).

It would be desirable to have the better properties of both materials embodied in one metallized coating. The desired material would combine the excellent resistance of aluminum to direct corrosive attack with the strong cathodic protection provided by zinc. This can be accomplished by coating steels with binary zinc-aluminum alloys (Horton 1978). These elements are completely miscible in the liquid state but immiscible in the solid state. Small crystals of pure zinc and aluminum crystallize from the molten alloys on cooling. Thus, the coatings formed from such alloys will have a range of properties dependent on the size, distribution, and volume fraction of the zinc and aluminum phases produced in the coating. It should be noted that aluminum is a lightweight element and that small increases in the weight percentage of aluminum in the alloy will produce large increases in the volume fraction of the aluminum phase. At 28 weight percent aluminum, the alloy is 50 volume-percent aluminum and 50 volume-percent zinc.

At this equivolume fraction composition (72 weight-percent zinc, 28 weight-percent aluminum) the zinc phase is just sufficient to prevent underrusting of the coating but is not sufficient to provide effective cathodic protection. Such a coating behaves no better than pure aluminum (Sempels and Leclercq n.d.). At high zinc contents (>95 weight-percent zinc), the zinc phase predominates and the coatings behave more like pure zinc. Coatings with 5 to 22 weight-percent aluminum (78 to 95 weight-percent zinc) exhibit a behavior that combines the better properties of both materials. Large amounts of the zinc phase can be dissolved anodically to provide needed cathodic protection. After the zinc is totally dissolved, the remaining porous residual coating of aluminum can be electrochemically activated to provide a reasonable potential of -0.6 volt, providing additional cathodic protection.

French investigators report that the optimum performance of zinc-aluminum coatings occurs at the 85 weight-percent zinc, 15 weight-percent aluminum composition (Sempels and Leclercq n.d.). Metallized coatings of this alloy have a continuous network of elongated aluminum particles (30 volume percent) separated by pores filled with a finely divided zinc-rich phase. The improved resistance to corrosion relative to either pure zinc or aluminum coatings is the result of more efficient self-healing by corrosion production coupled with effective cathodic protection by the zinc-rich phase (Sempels and Leclercq n.d.). The alloy is being used commercially as wire-sprayed coatings to protect steel from corrosion (TAFA Metallisation, Inc. 1981).

U.S. researchers, on the other hand, have concluded that a 55 percent aluminum, 45 percent zinc alloy is the optimum composition for use as a coating on steel (Horton 1978). This alloy is mostly alpha aluminum, with an interdendritic zinc-rich phase. It is applied as a hot-dip coating and is reported to combine the best properties of pure zinc and pure aluminum coatings. Hot-dipped sheet with this coating is produced commercially by Bethlehem Steel Co. under the trade name Galvalume sheet (Horton 1978).

While a reasonably extensive technical literature is available for on-site tests of thermal-sprayed corrosion protection coatings, little has been done to understand the actual protection mechanisms and the problems associated with such coatings. Few electrochemical studies have been carried out, and the metallurgically relevant features of these coatings are not fully appreciated. In one study, however, it has been shown that the electrode potential of WSA coatings is much more electronegative than the solid aluminum wire used to form the coating (Magome et al. 1980). The potential was decreased from a normal level of -0.92 volts for solid wire to a level of -1.13 volts for the sprayed coating in saline solutions. These data indicate that sprayed aluminum coatings would tend to be more active electrochemically compared with bulk aluminum metal. The ability of aluminum to cathodically protect steel may be enhanced as a result of thermal spraying.

Alloy melting and boiling points are important factors that also must be considered in the selection and application of shipboard corrosion control coatings. These are of primary concern with respect to safety and fire hazard, as discussed in Chapter 7. A summary of melting and boiling point data for the four most widely used corrosion control coatings is presented in Table 1 below:

TABLE 1 Melting and Boiling Points of Coating Alloys

Alloy		Melting Point		
Al (wt.-%)	Zn (wt.-%)	Solidus °C	Liquidus °C	Boiling Point °C
100	--	-----660-----		1810
55	45	495	600	--
15	85	380	450	--
--	100	-----420-----		907

Zinc and the high-zinc alloy melt at 380 to 420°C (716 to 788°F) and would be marginal to unsuitable for use on superheated steam lines or valves or in jet exhaust or missile blast deflectors. The low boiling point of zinc also may be marginal or unsuitable from a damage control point of view if a ship is under attack. Aluminum or the high-aluminum-zinc alloy appear to be more suitable for general shipboard use based on this criterion.

Life Prediction

The foregoing discussion indicates that a rational basis for estimating or predicting useful coating life in marine environments probably does not exist. Based on simple and direct dissolution of the coating by corrosion, life could be calculated from valid surface-recession rate measurements. Unfortunately, data of this type are very limited for both aluminum and zinc in marine environments. Aluminum should be a superior material to zinc, since it corrodes at a slower rate in seawater. The corrosion rate of zinc in natural seawater ranges from 0.5 to 7.8 mil per year (Zinc Substitute, Inc. 1971). Typical rates in tropical Pacific Ocean waters are 0.57 to 0.9 mil per year. At this rate, an 8-mil thick zinc coating would be dissolved by corrosion in 9 to 14 years. With aluminum-coated steels, over 90 percent of the original coating thickness remained after 67 months (5.6 years) of exposure to severe Pacific Coast atmospheres (Van Horn 1967). Galvanized steel lost 90 percent of the coating under the same conditions. Expressed as surface recession, the loss was 0.85 mil for aluminum and 3.8 mil for zinc in 5.6 years of exposure. One might reasonably expect a typical zinc coating to have a useful life of at least 10 years but no more than 15, whereas a typical aluminum coating should survive for 50 years or more. These values might be taken as the maximum life expectancy of a "perfect" metallized coating in which the coating acts only as a physical barrier to separate steel from a corroding atmosphere.

The life of coated steels, however, does not depend only on the resistance of the coating material to direct corrosive attack. In a large degree it depends instead on what happens when defects are formed in the coating during manufacture or service. Defects are defined as local regions in which the base iron substrate is exposed to contact by the corroding media. They may be formed in many ways--cuts through the coating; coating removal in thin areas by corrosion; excessive porosity in the coating;

coating removal by abrasion, impact, or spalling; bond line separation; and/or pitting corrosion. No coating is perfect, and defects of one type or another are unavoidable. The defects may be formed during manufacture or may be developed during installation or service.

Coating failure will be accelerated by defects as a result of anodic dissolution of the coating at defect sites to protect the steel cathodically. With aluminum coatings, underrusting will occur to accelerate failure. With zinc, rapid dissolution of the coating will result. The rate of attack in either case will depend on the nature, size, shape, and distribution of defects. Predicting what the useful life will be under these conditions is not possible for three reasons:

1. It is not possible with available NDE techniques to detect all defects that will degrade performance in as-coated components and large, complex structures.

2. It is not possible to predict when and what kind of defect will be formed in service.

3. There are no data on the effect of various defects on residual coating life in marine environments.

Research and development is needed in each of these areas to provide at least some technical basis for estimating performance and to aid in the more effective selection and use of coatings.

Sealants and Top Coats

Thermal-sprayed metallized coatings of either zinc or aluminum tend to be porous, which may allow electrochemical corrosion at the coating substrate interface. Steel corrosion products often are observed on the surface of thin (< 5 mil), porous WSA coatings (Sempels and Leclercq n.d.). Through-porosity can generally be eliminated by depositing thick (>9 mil) coatings, but these may have poor adhesion due to a thermal-expansion mismatch, which causes bond-line separation to occur. As a rule, aluminum coatings are deposited between 5 to 8 mil thick to minimize through-porosity and maximize bond-line adhesion. It is generally recommended that such coatings be sealed or painted to close residual pores and prevent underrusting of the steel (Sempels and Leclercq n.d.). Zinc coatings also should be sealed and painted to retard general coating corrosion and extend useful life. Use of appropriate sealers and paints appears to be essential for long life (10 to 20 years) of both zinc- and aluminum-metallized steel in marine environments. These materials not only inhibit or retard initial breakdown of the coating but also provide an effective repair to seal off coating defects. Sealed coatings continue to protect the substrate electrochemically but with greatly improved effectiveness.

A wide variety of sealants and paints have been developed for these materials to provide maximum performance in a wide range of environments. Polymeric, low-viscosity sealers, such as vinyl chloride acetate copolymers or unmodified phenolic resins, enhance both the corrosion protection of thermal-sprayed active metal coatings (through increased passivation) and the mechanical strength of the coatings. Sealers are particularly important when metal coatings thinner than 5 mil are employed, and, in fact, sealers will permit the application of substantially reduced metal coating thicknesses, thus saving material and labor time. Furthermore, pigment-bearing sealers can be used to enhance appearance. When such considerations are important, it should be noted that unsealed thermal-spray coatings pick up dirt and tend to appear unattractive with the passage of time. It is possible to further enhance the role of the sealer by adding metal powder to it. When zinc coatings are sealed with such formulations, they become particularly effective in marine environments.

Following thermal-spray metallization, the surface should be primed with a zinc chromate wash primer. The sealer is then applied (generally by spraying), penetrating the pores of the coating and filling them. The porous quality of the as-sprayed coating acts as an excellent base for the application of vinyl, with good adhesion being achieved. Aluminum-pigmented vinyl is considered to be the best overall sealant for thermal-spray coatings (private communication, F. Longo, Metco, Inc., 1981). Bare metal will be covered and the top of the coating will be smooth. Capillary action will draw the sealer into coating pores, and surfaces should be kept wet for 4 to 6 hours with repeated sealant applications for effective sealing. The lifetime of this coating system is estimated to be in excess of 20 years, and it is easy to clean and maintain. In fact, a simple brushing and local resealing will normally be all that is required after a number of years. Overall, sealers greatly simplify maintenance. Sealing is especially indicated in acidic and alkali environments (for sprayed-zinc coatings at pH levels below 5 and above 12 and for sprayed aluminum at pH levels below 4 and above 9). In any case sealing is strongly indicated for protection against specific chemicals.

Technical guidance for the selection and use of sealers and top coats in marine applications is limited at best. Few definitive performance tests have been conducted, and virtually no work leading to an improved mechanistic understanding of behavior has been undertaken. Each major coating vendor has his own proprietary brand or type of recommended sealer.

Effective sealants for marine use are aluminum-pigmented vinyl, low-viscosity epoxy, anaerobic polyester resins, low-viscosity polyester resins, air-drying phenolic resins, and clear polyvinyl chloride solutions (Brown 1979). There are new sealers that may find useful application over sprayed coating to enhance resistance to marine corrosion. These are not recommended at this time but are suggested for potential evaluation, since there is limited experience in marine exposure. One of these is silicone aluminum--a silicone resin-aluminum flake, air-drying type of coating material for application over sprayed metal to provide corrosion resistance at temperatures up to 900°F. Another new sealant that may be useful for zinc coatings is ethyl silicate. Commercial preparations exist containing zinc dust and a special ethyl silicate making them usable to seal pores in zinc. Since the zinc is still exposed to the seawater, an overcoat with a suitable resin may be required for further protection (such as epoxy [polyimide cure], vinyl, or acrylic). An aluminum-vinyl sealer would be satisfactory.

Thermal-sprayed active metal coatings (e.g., zinc and aluminum) can be mechanically treated to close surface-connected pores and to improve surface smoothness. Rolling and shot-peening have been used for this purpose, with major improvements being achieved. Although sealing of pores mechanically can have a beneficial effect on corrosion resistance, it could lead to coating degradation as well. The coating/substrate bond with aluminum is largely mechanical, and deformation of the coating by peening or rolling could induce bond separation. It is recommended that these processes be considered for use on sprayed aluminum only under conditions where high strength bonds resistant to separation have been produced.

Properly sealed coatings will accept virtually any top-coat paint. The coating provides an excellent paint base, and painted surfaces will offer years of maintenance-free service as a result of cathodic protection of the steel provided by the coating. The need for frequent repainting of uncoated steel surfaces is the result of iron corrosion beneath the paint. With aluminum- or zinc-coated parts, corrosion of the steel is prevented, and top-coat paints have very long lives. The two most commonly used top coats are polyurethane or epoxy polyamide-type paints. The polyurethanes have been particularly effective on both aluminum and zinc coatings in marine environments (Sempels and Leclercq n.d.).

Established Performance

Metal spraying is used extensively for the corrosion protection of steel and iron in a wide range of environments and has been shown to afford very long-term protection (over 20 years) in both marine and industrial locations. The British Standards Institution (BSI) Code of Practice specifies that only metallization will give protection of greater than 20 years to first maintenance for every type of environment considered and that only sealed sprayed zinc or aluminum will give such protection in areas of immersed seawater or in seawater splash-zones (British Standards Institution 1977). The corrosion tests of flame-sprayed coated steel carried out by the American Welding Society, as given in its 19-year report, confirm the remarkable effectiveness of sprayed zinc and aluminum coatings over long periods of time in a wide range of hostile environments (American Welding Society 1974).

Industrial Applications

The application of both flame- and arc-sprayed zinc and aluminum coatings is increasingly displacing both painting and hot-dip galvanizing for reasons of both effectiveness and economics. Over the years thermal spraying has been used in a broad variety of corrosion-protection schemes. In Europe, where metal spraying has been far more widely used than in the United States for corrosion protection, there are numerous case histories of structures successfully sprayed, some as long as 40 years ago, that have been maintained in good condition with minimal maintenance.

An important use of thermal spraying for corrosion protection has been for bridges. In the United Kingdom the suspension chains and other components of the Menai Straits Bridge were zinc-sprayed just before World War II. During the war the bridge received no maintenance, and when it was inspected after the end of the war the sprayed areas of the bridge were found to be in excellent condition. The steel deck structure, on the other hand, which had been painted but not sprayed, was rusting. Some 20 years after the original metal spraying, the protective coating of the sprayed areas was still intact, and only simple renewal of the paint top coats was necessary. The obvious reduction in required maintenance of the bridge prompted the British to apply sprayed-metal coatings to numerous other road and railway bridges over the past 30 years (Bailey 1976).

Some, like the Forth Road Bridge in 1961, were sprayed prior to construction. The Forth Road Bridge, which remains the largest such structure to be metal-sprayed, was zinc-coated and then painted. When the bridge was inspected after 12 years, there was some breakdown in the paint treatment, but the zinc coating was found to be almost completely intact. This experience was in remarkable contrast to the neighboring Forth Railway Bridge, which was not metal-sprayed and which required a continuous program of maintenance painting (Bailey 1976). The British have used zinc spraying to renovate older bridges as well--among others, parts of the Tower Bridge in London.

Bridges have been sprayed in many parts of Europe, especially in France and the Scandinavian countries, as well as in the United States, Canada, South Africa, Australia, and the Persian Gulf countries. In Norway, where the weather conditions are severe and the need to reduce routine maintenance is imperative, the experience with metal-spraying all sorts of road, ferry, railway, and crane bridges has been so favorable that metal-spraying has been routinely applied to all new steel bridges with only a few minor exceptions.

Another interesting example of corrosion protection of bridges by thermal spraying is the kilometer-long Pierre-Laporte Bridge in Quebec, Canada, which is zinc sprayed and is the largest structure to be metal sprayed following erection (Bensimon 1976). The three-span bridge was completed in about 1970 and was originally protected against corrosion with a system of lead silico-chromate, oil, and alkyd paint. However, maintenance and paint retouching procedures became prohibitively expensive, and the Canadian government carried out a cost evaluation of metallizing. The report stated: " ...a comparative cost analysis was made covering a 130-μm thick conventional paint system, with an approximate 8-year life span, requiring frequent touch-ups and the erection of mobile scaffoldings, and the alternative, expenditures for a 175 μm zinc coating with a probable life of 20 to 25 years, requiring no major touch-ups." Upon consideration of the sums involved, together with probable inflation and annual increases in labor costs, metallizing was chosen for the job (Jodoin and Nadeau 1980). The bridge was cleaned by grit blasting and thermal-spray coated with zinc.

There is also a long history of corrosion protection by metal-spraying of structural steelwork for buildings and other outdoor structures such as steel towers, radio and TV antenna masts, steel gantry structures, high-power search radar aerials, steel outdoor overhead walkways, railroad overhead line support columns, electrification masts, tower cranes, bollards on traffic islands, railings along streets and bridges, etc. The British, in particular, have long used zinc spraying to protect such structures, especially in remote areas where maintenance is difficult or in highly polluted areas where other methods such as painting or galvanizing have failed to provide sufficient protection. An outstanding example of sprayed zinc being used for corrosion protection of the steelwork of an entire building is the Centre Pompidou in Paris. On the other end of the scale, zinc spraying has been used successfully to protect wrought-iron outdoor furniture in highly corrosive conditions that had defeated all previous attempts at protection.

There have been many uses of metal-spraying in the chemical and petrochemical industies. Since the 1950s wellhead assemblies for offshore use have been zinc-coated to protect them from the highly corrosive salt atmosphere along the Gulf Coast. Metal-spraying has been used for flare stacks, refinery columns, and external protection of oil and propane gas storage tanks. In the United Kingdom, liquid-propane gas cylinders are required by code to be zinc-sprayed, since galvanizing would degrade the structural integrity of the vessels. Aluminum is normally used for protection of steel in gas and chemical plant uses under conditions of high temperatures and corrosive atmospheres, but there is evidence that sprayed-aluminum coatings should be avoided whenever there is a fire or explosion hazard, as in mines, oil rigs, etc., because of the conceivable possibility of impact sparking (Bailey 1978). Sprayed zinc is always used in coal mines for this reason (Bensimon 1976).

Other industrial uses for metal spraying against corrosion include the protection of railway tank cars and similar vehicles, which have been sprayed since 1940 against both corrosion and contamination. The interiors of fluid cargo tanks have been zinc-sprayed to control the fluid purity, especially to guard against iron pickup, and also to avoid discoloration of the cargo. Tanks designed to carry glycerine, ethyl alcohol, styrene, xylene, benzene, and various ketones are treated in this manner. Steel railroad cars have also been externally zinc-sprayed against corrosive attack, and it is expected that these coatings should last the lifetime of the cars, precluding the necessity to remove the cars from service for painting approximately every 5 years.

Spraying has also been used to protect pipelines against many environments. Lengths up to 40 feet have been successfully coated internally. Pipe couplings, manhole covers, and other small industrial items are often metal-sprayed. Zinc-spraying can restore corrosion protection to areas of products where galvanizing is removed during fabrication, as in the case of the threaded ends of electrical conduit or along the welded seam areas inside galvanized barrels and drums. In many cases arc-spraying is particularly advantageous for restoring the zinc coating to ends of pipes or conduits because it ensures uniformity and reproducibility of the thickness of the coating, even for pipes with different diameters. Also, the superior integrity of the bond obtainable with arc-spraying makes this method especially suitable for spraying small areas where high bond strengths are essential—e.g., the ends of armored electrical cable.

Marine Applications

The corrosion protection of steel in salt-water and marine environments by sprayed coatings of aluminum or zinc has been accepted and proven practice for many years. Ship superstructures, hulls, and fittings that have been flame-sprayed with aluminum to a thickness of 0.15 mm or with zinc 0.15 to 0.30 mm thick, and sealed with a solvent based resin or suitable paint have long and exceptional corrosion-free performance (Conde et al. 1981). Hulls, deck sections, and parts of the superstructure of barges, scows, tugs, and fishing vessels have been sprayed with excellent long-term results in Norway, Britain, Iceland, and Canada. Lifeboats and floating caissons have also been metal-sprayed, as well as smaller items such as ship rudders and the axles of boat trailers. In Scandinavia, ferry berths are metal-sprayed. In many parts of the world, it is common to metal-spray marine piers and pilings. Sluice gates and canal lock gates that have been zinc-coated have remained in perfect condition with virtually no maintenance for decades. The St. Denis Canal Lock Gates in France, coated in the early 1930s, are an outstanding example. The locks of the Panama Canal have also been zinc-sprayed (private communication, F. Longo, Metco Inc., Westbury, New York 1981).

Controlled Comparative Evaluation

A number of carefully planned and controlled tests have been conducted to compare the long-term performance capabilities of thermal-spray aluminum and zinc coatings in marine environments. The 19-year AWS study (American Welding Society 1974) is the one most commonly quoted; its results indicated that 3 to 6 mil of flame-sprayed aluminum on steel would provide long-term (>19 year) protection. Complete protection was provided in all test sites by both sealed and unsealed sprayed-aluminum coatings. Sealed or unsealed zinc coatings required a minimum of 12-mil thickness for complete protection in seawater. Sealed zinc coatings behave similarly to sealed or unsealed aluminum coatings in marine atmospheres (no seawater immersion), although the rate of attack for zinc was greater than that for aluminum at equivalent thicknesses.

Vinyl sealers were found to provide good protection for aluminum but were ineffective on zinc in seawater immersion tests. Vinyl sealers deteriorated rapidly on zinc during seawater immersion but not in coastal atmosphere tests. High chloride concentrations appear to degrade vinyl sealants on zinc (American Welding Society 1974). The AWS report clarifies the performance and the effect of sealers on aluminum coatings. Both sealed and unsealed WSA panels were rated as protected after 19 years of exposure in seawater immersion and in coastal atmospheres. This was based on the criteria that no measurable surface recession of the steel substrate occurred. However, there were numerous areas where the coating blistered and the substrate rusted. In one marine atmosphere test, unsealed panels had over 20 blisters per square inch, each up to 1/8-in. in diameter. Vinyl-sealed panels had 6 to 20 blisters per square inch, each less than 1/8-in. in diameter. The vinyl sealant reduced both the size and number of blistered spots. In immersion tests, blisters up to 5/16-in. in diameter formed on unsealed panels and many blisters broke open, revealing underrusting but no significant surface recession. Although the panels are rated as protected, the coatings have failed and substrate corrosion has started. Nineteen years would appear to be close to a maximum useful life under these conditions.

It should be noted that these test panels are not truly representative of production WSA-coated hardware and structures. They are, in effect, close to perfect coatings that by and large are free of both common manufacturing and service defects. The panels were machine-sprayed, 36 at a time, under rigidly controlled conditions to produce uniformly thick, dense, and bonded high-quality coatings. Also, immersion tests were conducted in still seawater at full and half tide and in slowly flowing (3 knots) seawater. Splash, spray, or impingement tests were not conducted. The results of these tests probably represent the best performance that can be expected and should not be considered typical behavior. Commercially coated structures in service with numerous defects present would be expected to have significantly shorter lives.

In some tests of WSA, a 1-mil bond coat of iron was applied first to improve bonding of the coating to the steel. Analysis of the results indicated no effect on performance; samples with and without the bond coat behaved the same (American Welding Society 1974). On other tests, different surface preparations were employed before spraying. These included blasting with fine or coarse silica sand or with chilled iron grit. No noticeable difference was found in the behavior of the different surface preparations during seawater immersion tests.

A 7-year exposure test of coated steel piles imbedded in a surf area at Virginia Beach, Virginia, yielded results similar to those of the 19-year AWS test (National Bureau of Standards 1977). Production-coated structural elements more representative of actual coated hardware were used in these tests. Steel H-piles 8 by 8-in. square and 35 ft long were driven into the sand and extended up into the air in a beach surf zone. The piles were exposed to sand abrasion, seawater immersion, seawater splash, and marine atmosphere conditions. Coating systems tested and the results are summarized in Table 2. The best material was wire-sprayed aluminum sealed with clear vinyl. Attack on this system was negligible except in the sand erosion zone. The unsealed WSA coating had significantly more corrosion in all zones. Hot-dipped zinc and sealed wire-sprayed zinc were comparable to unsealed WSA. Vinyl-coated wire-sprayed zinc was attacked severely. The top coat failed on this material in the first year.

TABLE 2 Result of 7-Year NBS Study of Coated Steel Piles

Coating		Penetration (mil/year)				
No.	Type	Avg.	Imbedded Zone	Erosion Zone	Immersion Zone	Air Zone
10	Hot Dip Zn	0.14	0	0.67	0.32	0.06
13	WS Al + clear vinyl	0.03	0.01	0.17	0.07	0
14	WS Al, unsealed	0.16	0.19	0.39	0.19	0.03
15	WS Zn + polyvinylidene chloride	0.10	0	0.14	0.12	0.29
16	WS Zn + vinyl red lead primer	1.40	0.08	3.20	1.80	2.30

A more extensive series of tests conducted over a 21-year period by the Navy produced results similar to those reported for the AWS and NBS tests (Navy, Department of 1966; Alumbough and Curry 1978). Coated flat panels 1/4 in. by 4 in. by 10 ft long were field-tested in the harbor area at Port Hueneme, California. Panels were suspended vertically from a dock in the harbor mouth so that the top portion was exposed to atmosphere (zone A), the midportion to tidal splash (zone B), and the lower area to total immersion (zone C). Coating systems tested and the results are summarized in Table 3. These tests were conducted as top coat (paint) evaluation tests, and the thermal-sprayed metal coatings were treated as primer coats for the organic top coat. As shown in Table 3, the sprayed-metal coatings were thin (2.5 to 5.15 mil) and the paint top coats were thick (3 to 7.5 mil).

The standard reference coating, Saran paint, began to deteriorate at 9 to 10 year of exposure, with significant pitting and corrosion observed at 14 years. Corrosion was heavy at 20 years. The following metallized coatings greatly surpassed this performance with no significant corrosion observed in 20 years of exposure: 1. flame-sprayed aluminum (powder) unpainted, 2. wire-sprayed aluminum unpainted; and 3. wire-sprayed zinc with (a) Saran paint, (b) vinyl lead paint, and (c) epoxy paint.

Unpainted sprayed-zinc coatings had poor performance, with general failure in 2 to 4 years. Surprisingly, the sprayed-aluminum coatings were degraded by the application of paints. Saran, vinyl red lead, clear vinyl phenolic, epoxy, and grey Saran paints all degraded sprayed-aluminum coatings, with failure in 4 to 8 years. In general, the paints were not compatible with the aluminum and blistered within the first several years. Severe corrosion of the aluminum then occurred. Vinyl-base primers were the worst, losing adhesion and blistering within 2 to 3 years. All the paints were compatible with zinc, with the best performance by vinyl red lead, although the paint had moderate to dense blisters at 20 years. Clear vinyl on zinc failed at 15 years, with loss of the zinc coating and rusting of the steel.

TABLE 3 Results of Port Hueneme Simulated Pile Tests Suspended From Test Dock

No.	Coating Type	Thickness (mil)	Top Coat Type	Thickness (mil)	Results
12	FS Zn powder	3	None		Poor, failed 2 yr
13*	FS Al powder	4.5	None		Excellent to 21 yr
14	FS Zn wire	5.5	None		Poor, failed 4 yr
15	FS Al wire	5.0	None		Good, failed 10.5 yr
83	FS Zn wire	4.0	None		Poor, failed 4 yr
84*	FS Al wire	4.0	None		Excellent to 18.5 yr
18*	FS Zn wire	2.5	Saran	7.5	Good, failed 18 yr
19	FS Al wire	3.5	Saran	5.5	Fair, failed 6.5 yr
22*	FS Zn wire	2.5	Vinyl red lead	4.5	Excellent to 20 yr
23	FS Al wire	4.5	Vinyl red lead	4.0	Poor, failed 4 yr
26	FS Zn wire	3.0	Vinyl acrylic	5.0	Poor, failed 5.5 yr
27	FS Al wire	2.5	Vinyl acrylic	5.0	Poor, failed 4 yr
34	FS Zn wire	2.5	Vinyl finish	5.0	Good, failed 15 yr
35	FS Al wire	3.0	Vinyl finish	4.5	Fair, failed 7.5 yr
39	FS Al wire	3.0	Phenolic primer	5.0	Poor, failed 5.5 yr
			Phenolic finish	5.0	Poor, failed 5.5 yr
42*	FS Zn wire	3.0	Epoxy finish	5.5	Good, failed 18 yr
43	FS Al wire	2.5	Epoxy finish	6.5	Poor, failed 5.5 yr
64	FS Al wire	3.5	Al vinyl	3.0	----
50*	FS Zn wire	3.0	Grey furan	4.0	Good, failed 15 yr
51	FS Al wire	3.0	Grey furan	4.0	Poor, failed 5.5 yr
16**	---		Saran	6.5	Good, failed 14 yr

* Designates system with 15 to 20 years' life.
** Standard reference paint coating.

Organic paints on flame-sprayed zinc were better than the same paints on steel and far superior to the same paints on flame-sprayed aluminum. When the paints blistered and began to fail, the zinc provided protection from rusting and did not deteriorate the paint. Sprayed aluminum, on the other hand, rapidly degraded the paint and in turn was degraded when the paint began to fail. Results of these tests indicate that direct application of paint to sprayed-aluminum coatings would not be advisable for marine service. It should be noted that the sprayed-aluminum coatings were not primed and sealed before painting. The use of a zinc chromate wash coat followed by a clear vinyl sealer might alter this behavior. More definitive and mechanistic studies are needed of the interaction between sprayed-aluminum coatings and organic top-coat paint in marine environments.

Thermal-sprayed zinc-aluminum alloys have not been tested in long-term marine exposures, and data do not exist to compare their performance with that of either sprayed-aluminum or -zinc coatings. There has been, however, a long-term comparative evaluation of hot-dip aluminum, zinc, and zinc-aluminum alloy coatings on steel in tests at Kure Beach (Navy, Department of 1982). These coatings were 0.8 to 1.0 mil thick on 18-mil-thick sheet-steel samples. All samples had sheared, uncoated edges. Pure zinc coatings began to rust through in 4 years, whereas the 55 Al-45 Zn alloy and pure aluminum were in good condition after 14 years. The corrosion rate of zinc-based coatings decreased with increasing aluminum up to 7 percent, but then increased with further addition of aluminum to 21 percent. The corrosion rate decreased steadily beyond this point with increasing aluminum content. All coatings galvanically protected the sheared edges, but after 14 years the corrosion of cut edges was creeping inward on the coated faces of even the best materials. The average coating loss by corrosion in 12 years at Kure Beach was about 0.2 mil for aluminum, 0.4 mil for 55 Al-45 Zn, and >1 mil for zinc hot-dip coatings on steel.

Experience in the United Kingdom with respect to long term performance capabilities of thermal-spray coatings is summarized in Table 4. These data are from the British Standards Institution (1977) and constitute a code of practice for use of coated steels. They are not actual test results or test data.

TABLE 4 BSI Code of Practice for Metallized Steel in Seawater Splash Zone or Salt Spray

Required Life (yr)	Minimum Coating Thickness (mil)					
	Hot-Dip Zinc	Sprayed Zinc			Sprayed Aluminum	
		Unsealed	Sealed	Painted*	Sealed	Painted*
< 5	3.3	3.9	--	3.9	--	--
5-10	5.5	5.9	5.9	--	3.9	--
10-20	8.3	9.8	6.9	3.9	--	3.9
>20	—	—	9.8	--	5.9	--

* 2.4 to 3.9-mil-thick top coat organic paint.

Minimum coating thicknesses of 6 mil for sealed aluminum and 10 mil for sealed zinc are specified for >20 years service. Unsealed sprayed zinc is slightly less protective than hot-dipped (galvanized) zinc and significantly less protective than sealed zinc or aluminum. The BSI code does not specify unsealed sprayed aluminum for use in marine environments.

COMMITTEE ASSESSMENT

Thermal-sprayed (metallized) coatings of either aluminum or zinc are capable of providing effective long-term corrosion protection for steel in a wide range of marine environments. Such coatings when properly sealed or painted can reduce significantly the maintenance requirements for a wide range of shipboard applications. Corrosion protection for up to 20 years without the need for periodic maintenance is possible with low-defect coatings.

It is recommended that more extensive use of these materials be made in both shipboard and shore-based applications. Corrosion-prone shipboard components and structures currently protected by organic paints should be replaced with thermal-spray metallized corrosion protection systems wherever possible. The committee strongly supports and endorses the shipboard preservation system of metallized coatings introduced by the Navy in 1974 and recommends more widespread use in both new ship construction and repair and overhaul maintenance of existing ships.

An analysis of 10- to 20-year field test data and preliminary performance data for shipboard installations indicates that thermal-sprayed and sealed aluminum coatings have the best demonstrated long-term resistance to corrosion. The Navy's choice of wire-sprayed aluminum (WSA) for the shipboard preservation program is considered to be correct, although the best practice with respect to use of sealers has not been followed consistently. Available performance data indicate that the optimum performance system consists of a strontium chromate wash primer followed by application of an aluminum-pigmented vinyl sealer. The latter is specified for many applications in parts exceeding 175°F (i.e., steam valves) but has not been required for lower temperature applications. An unpigmented vinyl sealer could be used for low-temperature applications where top-coat paints will be applied. Proper application of the sealer is important, and care must be taken to ensure that the sealer adequately infiltrates coating parts by capillary action.

Thermal-sprayed zinc coatings do not appear to offer any significant advantage over aluminum with respect to performance as a metal preservation system. They are equal in many respects, however, if suitably primed and painted and are capable of providing up to 20 years of maintenance-free service. Zinc coatings may provide a better base for application of top-coat paints and should be considered as an alternate or possible replacement system for aluminum coatings in above-deck applications. Selective shipboard testing and evaluation of zinc coatings is recommended. However, it should be recognized that use of zinc coatings may be limited by the low melting and boiling point of zinc.

Zinc-aluminum thermal-spray coatings have the potential to offer improved performance over either pure aluminum or zinc. These alloys combine the better properties of both aluminum and zinc but have not been tested in long-term exposure to marine environments as thermal-spray coatings. Shipboard testing and evaluation of sealed and unsealed 85-15 and 45-55 zinc-aluminum alloy sprayed coatings are recommended, but with the reservation that low melting and boiling points may limit use.

Field-test data indicate a potential problem in top-coat painting of wire-sprayed aluminum coating. A mutual degradation between many different paints in use by the Navy and WSA coatings appears to exist. A research and development study to more clearly define the nature and mechanism of such reactions should be initiated. Paint formulations and conditions leading to unacceptable mutual degradation should be identified. Acceptable top-coat painting systems for WSA coatings should be more clearly defined. Field data also indicate that such reactions do not exist with zinc coatings.

Consideration should be given to the use of duplex coatings, such as wire-sprayed zinc or zinc-aluminum alloy over wire-sprayed aluminum to produce metal preservation systems more compatible with top-coat paints. The bulk of field test data on both sprayed aluminum and zinc coated steel is on unpainted structures. Lack of knowledge in this area introduces a risk factor in the more widespread application of WSA coatings for above-deck applications. Useful coating life may be reduced from anticipated values of more than 20 years to actual values of less than 5 years by unexpected interaction between WSA and top-coat paints.

The majority of field-test data from which useful life is predicted is based on tests of near-perfect coatings. Few, if any, defects have been introduced in manufacture and service. Since these coatings preserve by cathodic protection at local defect sites, their useful life will be shortened significantly by local defects arising in manufacture and use. This introduces an additional risk factor in the use of such coatings, since defects are bound to exist. A research and development study is recommended to characterize the defect tolerance and life degradation by representative flaws or defects for typical coating systems. Systems most tolerant of defects must be identified. In addition, types of defects that require early repair or maintenance should be identified and suitable repair practices for shipboard use developed.

Finally, more effective sealants for both zinc and aluminum sprayed coatings would appear to be desirable, particularly for extending life beyond 20 years. State-of-the-art technology for sealants is quite old, and little definitive research has been conducted in recent times. A research and development study is recommended to establish more clearly how a sealer functions and to identify how its performance could be improved. Life-limiting factors and modes of degradation must be identified. Consideration should be given to the use of inorganic sealers or low-temperature curing sealers of the phosphate-bonding type that may seal coating pores more effectively.

CHAPTER 4

METALLIZING PROCESSES

CURRENT NAVY PRACTICE

Two processes are being used to apply WSA to shipboard components--gas wire-spray and arc wire-spray. In the first process, aluminum wire is melted in an oxyacetylene flame, atomized, and sprayed with the combustion gas onto the work. In the second, two aluminum wires are melted by arcing and the molten droplets are atomized and propelled to the work by a blast of air (Rogus and Vapniarek 1980). The majority of work is done with flame wire-spray equipment, using hand-held guns and relying strictly on operator skill and control to produce a uniform, high quality coating. In some applications, notably for anti-skid deck coatings, mechanized arc wire-spray guns have been used (Navy, Department of 1978). In these cases, the gun-to-work distance and rate of travel are set and controlled mechanically, which improves significantly the quality and uniformity of the coating.

Wire-sprayed coatings are deposited at naval shipyards, aboard naval ships, at shipbuilding yards, and at industrial coating shops by both Navy and civilian operators. Initial work on WSA coatings for shipboard corrosion control was performed at the Naval Air Engineering Center, Lakehurst, New Jersey. Subsequent pioneering work to develop ship applications was accomplished by the Shore Intermediate Maintenance Activity (SIMA), San Diego, and an industrial contractor, Flame Spray, Inc. of San Diego (Vanderveldt et al. 1981). At present, all naval shipyards and most intermediate maintenance facilities have wire-spray capabilities and are providing WSA preservation services. Both SIMA and Puget Sound Naval Shipyard also provide arc-WSA services for deck coverings, with Puget Sound being the lead yard for improving the process and developing equipment for cost-effective production. In addition, combustion-WSA facilities have been installed on a number of repair and fighting ships, including the USS Samuel Gompers (AD 37), USS Hector (AR 6), USS Dixon (AS 37), and USS Coral Sea (CV 43) (Vanderveldt et al. 1981). The principal industrial contractor has been Flame Spray Inc., of San Diego. The Ingalls Shipbuilding Division, Pascagoula, Mississippi, is providing the first application of WSA coatings in the area of new ship construction (Vanderveldt et al. 1981). This is the first commercial shipyard to develop a production WSA preservation capability.

The choice of oxyacetylene combustion (flame) wire-spray equipment has been based on both technical and economic considerations. From a technical point, coatings with levels of bond strength and porosity that are acceptable for most applications can, under carefully controlled conditions and with skilled operator control, be produced using combustion gas wire-spray equipment. Test samples for the 19-year AWS, NBS, and Port Hueneme field tests (American Welding Society 1974; National Bureau of Standards 1977; Navy, Department of 1966) of aluminum-metallized steels were prepared by gas combustion powder and/or wire-spray procedures. Results indicated a 15 to 20-year preservation capability in marine service. Wire spray was selected over powder-spray largely on the basis of improved bond strength and general quality for WSA coatings. In addition, both naval shipyards and civilian contractors had been using combustion flame (powder and wire) equipment for machinery repair. Facilities, process specifications, and skilled personnel were available to produce WSA preservation systems. From an economic point of view, combustion gas spray equipment was readily available at low capital cost, and operating costs were low. Equipment was portable and could be used easily for shipboard on-site coating or coating repair.

The cost-effectiveness of this approach is clearly indicated by the very successful steam-valve coating program. In two shipyards, over 5,000 valves have been coated with the WSA preservation system at a cost of 1 to 1-1/2 man-hours per valve (labor plus materials) (Sulit et al. 1980). The SIMA facility at San Diego has coated thousands of valves at a rate of about 1 man-hour per valve since 1977. Another shipyard has coated 500 valves at an estimated cost of 3/4 man-hour per valve. Many of these valves have been in service for over 4 years without the need for repainting, repair, or maintenance. On a life-cycle basis, the WSA preservation system on steam valves is more cost-effective than paint preservation systems by at least a factor of 2 (Vanderveldt et al. 1981).

Process Control and Quality Assurance

The thermal-spray military standard, DoD-STD-2138(SH), is the basic document establishing the thermal-spray facility and process requirements for WSA preservation systems on naval ships (Department of Defense 1981). It specifies in detail the equipment, materials, and procedures that must be followed in preparing WSA preservation systems by arc and gas wire-spray processes. In addition, it sets forth requirements for training and certification for both Navy personnel and civilian service contractors.

This is a new specification, issued for the first time in November 1981. Up until that time, WSA coating was done in accordance with the military specification for machinery and ordnance coating applications, MIL-STD-1687(SH) (Navy, Department of 1980b). Since this standard did not address all of the requirements and controls for WSA preservation systems, a series of process instructions and orders were issued by the Navy to add needed controls. Surface preparation was governed by the Steel Structures and Paint Council (SSPC) specification 5-63. Coating application was governed by NAVSEA 56435-AE-MNA-010/W sprayed CTT as developed for WSA coating of steam valves (Navy, Department of 1981b). A detailed process instruction for WSA coating of deck areas was prepared by the Puget Sound Naval Shipyard (Navy, Department of 1980c).

Significant factors to note with respect to the current specification (Department of Defense 1981) are as follows:

1. Bond strength of coatings is assessed by tensile and bend tests only in certification of operators. There is no requirement for sampling and destructive testing of day-to-day production as a means of quality control.

2. There is no standardized bend test for quality control although this test is used for daily checks of product quality.

3. Purity and dryness levels for compressed air used both for grit blasting and thermal spraying are not specified in terms of measureable parameters suitable for process control.

4. Surface contamination is controlled by specification of a maximum holding time between grit blasting and spraying. Purity, temperature, and control of storage atmospheres is not specified.

5. Coating thickness is specified by area of application with 10 to 15 mil required for machinery space components (i.e., steam valves) and 7 to 10 mil for other topside or wet interior space equipment.

6. Coating porosity levels are not specified in terms of any measureable or controllable variable.

The basic approach to quality control and assurance is through the use of process controls. There are few satisfactory NDE procedures for product control, and those that are available in general cannot be relied on to ensure good product quality for large or complex coated parts and structures. NDE can be used to evaluate effectively small test strips or panels, which in turn are used to certify the quality of products produced using the same operator, equipment, materials, and procedures to coat parts that were used to coat the test strips. That is, for each batch or lot of parts produced, product quality test strips also are produced. Results of various tests on the strips are used as an indirect form of quality assurance. No changes in process, materials, or operators are allowed.

Several direct product quality assurance tests also are made directly on production parts. These include tests on cleaned and grit-blasted surfaces for anchor tooth profile, thickness tests on coated surfaces using magnetic-type gauges, and visual inspection for a wide range of coating defects.

Training and Certification

An indispensable aspect of implementing thermal-spray technology is the training, certification, and recertification of thermal-spray operators and instructors in conjunction with the equiping and certification of thermal-spray facilities or shops in the Navy and thermal-spray service contractors in industry (Vanderveldt et al. 1981). The Navy's approach is to use the American Welding Society standards, guidance, and recommendations wherever possible for process, facility, operator, and instructor certification and control. The Navy can and does control use in the public sector, as evidenced by the development and use of technical manuals for WSA corrosion control (Bless and Moskowitz 1979; Navy, Department of 1980d). The U.S. Naval Reserve is also developing an extensive training program consisting of some 350 slides-with-sound for indoctrinating and qualifying the naval reservist to apply the WSA preservation system (Navy, Department of in press).

For COMNAVSURFPAC, WSA operators are now being trained and certified by the West Coast naval shipyards. A San Diego-based thermal-spray service contractor, Flame Spray, Inc. has delivered training programs and certified operators for several ships--e.g., USS Samuel Gompers (AD 37); USS Hector (AR 6); USS Coral Sea (CV 43); and USS Dixon (AS 37)--and has trained and "started up" Ingalls Shipbuilding Division in its metallizing corrosion control work for the U.S. Navy. Formalized training, work experience, and certification and recertification requirements and procedures for thermal-spray instructions have yet to be developed.

The thermal-spray military standard (Navy, Department of 1980b) is the basic document establishing the thermal-spray facility and operator requirements and certification for both Navy and civilian service contractors in the area of thermal-spray applications for wear coatings and restoration of dimensions. The Navy is incorporating this information into its rate training manuals for machinery repairmen and will teach it in its technical or "C" schools (Navy, Department of 1981c).

STATE-OF-THE-ART SUMMARY

Thermal-Spray Processes

Thermal spraying is the process of depositing molten metal, alloy, and ceramic coatings on properly prepared substrate materials so that they solidify and mechanically bond to the substrate materials. Thermal-spray coatings are applied to improve surface-wear characteristics, to provide resistance to heat, oxidation, and chemical environments; to restore dimensions or to build up the surface of a worn part so that it can be remachined or ground to its original specifications; to reduce erosion wear; and to improve corrosion control. The thermal-spray coating does not usually add to the structural strength of the component. When used to restore dimensions, the worn or damaged component must be structurally sound for the intended service prior to applying the thermal-spray repair.

Thermal spraying can be defined as the buildup of a coating by melting and projecting onto a substrate any heat-fusible material. The various thermal spraying processes used to apply such coatings include a number of different techniques, equipment, and heat sources. The spray materials can be metallic or nonmetallic, and in the form of wire, rod, cord, or powder. As the materials pass through the spray unit they are heated to a molten or semi-molten state and then atomized and/or accelerated and carried to the substrate in this form (Figure 6).

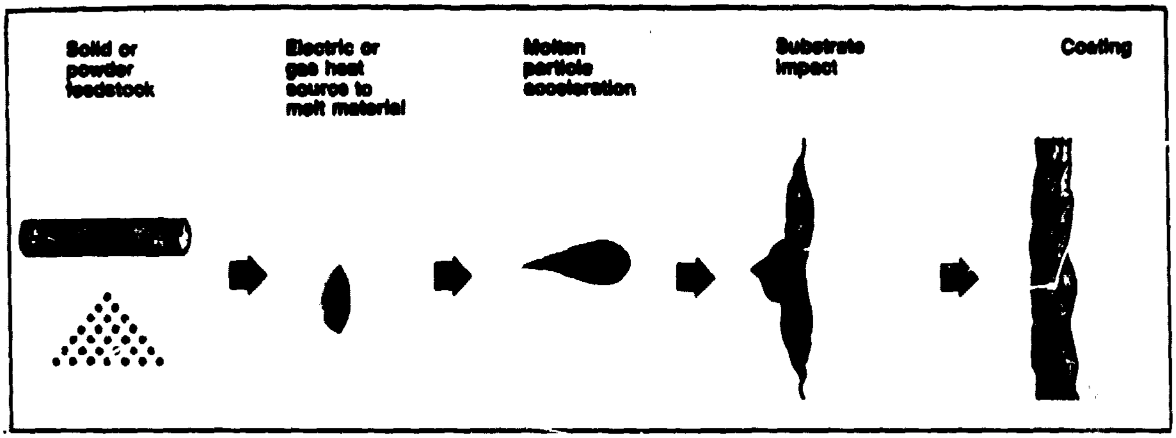


FIGURE 6 The thermal spray process.

The heating is accomplished by gas flame, electric arc, plasma, or detonation of a combustible mixture. The hot particles are conveyed from the spray equipment to the substrate by the gas jet, which also accomplishes the atomization and particle acceleration. As the sprayed particles impinge on the substrate they cool and build up, particle by particle, into a cast-like structure. The particles, as they strike the surface, flatten and form thin platelets which conform to the irregularities of the previously prepared surface, as well as to each other.

Most metals, oxides, cermets, and hard metallic compounds, as well as some organic plastics and certain glasses, can be deposited by one or more of the process variations. The substrates onto which the thermal-spray coatings can be applied include metals, oxides, ceramics, glass, most plastics, wood, and some disposable substrates. Not all sprayable materials can be applied to all substrates, and some require special techniques.

The bond between the sprayed coating and the substrate may be mechanical, metallurgical, chemical, or a combination of these. In general, proper surface preparation of the substrate prior to spraying is the most critical influence on the bond strength of the coating. The bonding mechanism is affected by the coating material and substrate, the process temperature before, during, and after spraying, and other processing parameters. The bond strengths of sprayed coatings are significantly less than in welding.

The deposited structure of thermally sprayed coatings is different from that of the same material in the wrought form due to the incremental nature of the coating buildup and the fact that the composition is often affected by reaction with the process gases and the surrounding atmosphere while the material is in the molten state. For example, where air or oxygen is used as the process gas, oxides of the material applied may be formed and become a part of the coating. In the case of metals the deposited coating tends to be harder, more brittle, and more porous than the original material. The as-applied structure of all thermally sprayed coatings will be similar in lamellar nature but will exhibit varying characteristics depending on the particular thermal spraying process used, parameters and techniques employed, and the material applied. A schematic coating cross section microstructure is shown in Figure 7.

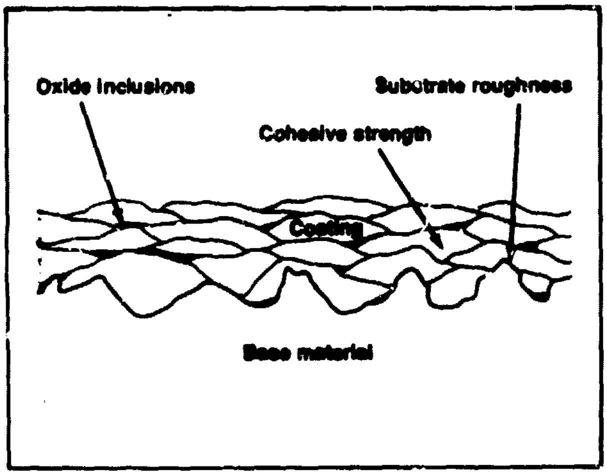


FIGURE 7 Schematic of coating cross section.

The density of coatings will vary, usually depending on the working temperature of the particular process involved and the particle impingement velocity. Figure 8 shows the range of particle impact velocities developed by each of the commonly used spray techniques. For example, the oxy-fuel powder spray gun has an impact velocity of about 80 to 100 ft/second, producing the lowest density, hardness and bond strength of the thermal-spray processes.

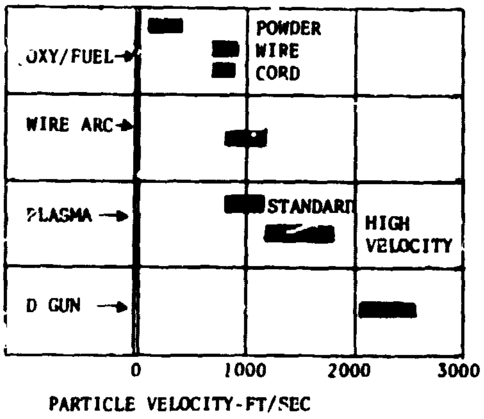


FIGURE 8 Spray particle velocity.

Preparation of the Substrate

Preparation of the substrate prior to spraying is necessary and common to all thermal-spraying processes and is virtually the same regardless of which process is used. Items to consider are surface cleaning, roughness, and preheating. Surface roughening serves the dual purpose of cleaning the surface to eliminate any contamination that might inhibit the bonding of the coating to the substrate, as well as creating a profile of minute surface irregularities that will enhance the adhesion of the coating and give greater effective surface area (see Figure 7). Chemical cleaning is used on parts that are contaminated or impregnated with material that cannot be removed by other preparation techniques.

Preheating is sometimes used on certain metal substrate applications immediately before depositing the coating to drive off any moisture that might have developed (especially with flame guns) as well as to expand the workpiece to minimize stresses formed in the coating as it cools. The amount of preheating required will vary with the substrate material, the process used, and the material applied, but as a general rule the temperature will be in the neighborhood of 121°C (250°F). To be effective it is important that the preheat soak entirely through the workpiece and not be restricted to the surface.

Consistent success in the use of thermally sprayed coatings relies heavily on the establishment of parameters for surface preparation, preheating, and deposition of the coating, followed by exacting attention in observing them in practice. One overriding truth in thermal spraying is that variations from the standards set for a particular process and inattention to detail can be expected to produce unreliable results. A detailed description of each process and its capabilities and limitations is presented in a manual on thermal spraying to be published by the American Welding Society in 1983 (American Welding Society, in press).

Hot Dip Metallizing

Hot-dip metallizing is highly effective for forming an active metal coating for cathodic protection of steel in a wide range of environments. Furthermore, it is economical and long-lasting. From a processing point of view, a wide range of shapes may be employed, from small parts to sheet stock, where continuous hot-dip galvanizing systems have been developed (Schaper 1979). It is possible to modify the coating alloy to the extent that a large spectrum of zinc-aluminum alloys have been employed. For example, a 55-45 zinc-aluminum alloy trade-named "Galvalume" has recently been receiving considerable attention. There are also available zinc-rich (85-15 zinc-aluminum) alloys that show excellent behavior. The process produces a coating that is fully dense and metallurgically bonded to the substrate. The negative aspects of hot-dip galvanizing include size limitations; the need to grit-blast to white metal (limiting its application to relatively new parts); the potential for degrading the strength of heat-treated steel parts in the hot molten bath; the possibility of forming embrittling intermetallics at the part surface due to metallurgical reactions; and problems associated with proper paint adhesion to hot-dip galvanized coatings, although advances have been made in this regard and it is now possible to achieve reasonable paint adhesion to hot-dip galvanized parts, for example, in decorative finishing.

The major problems, however, are size limitation and the need to remove the part to a molten metal bath facility. Hot-dip galvanizing will thus be indicated principally when the parts in question are new, small, and the galvanized coating will not be disturbed or removed during subsequent fabrication or installation steps. A case where hot-dip galvanizing is used together with thermal-spray metallization is in the production of steel conduit for the electrical industry. In this instance, it is common practice to hot-dip galvanize the pipe prior to end-threading and then to apply zinc to the threaded ends by arc-spraying techniques. Such an approach is eminently suitable for any number of production problems.

Hot-dip metallizing is not confined to zinc coating (galvanizing), as might be implied from the foregoing discussion. A large number of steel parts also are coated with aluminum for corrosion protection by hot-dipping (Schaper 1979). Aluminum hot-dipped parts are about 20 percent higher in cost than zinc-coated parts because of the higher bath temperatures and the need for more meticulous surface cleaning. The only limitation on size of parts that can be coated by hot-dipping is the limit on size of the molten aluminum bath in which parts are dipped. The largest parts commercially hot-dip coated by a single immersion are 40 in. diameter by 8 ft long. The length could be doubled by dipping first one end and then the other. Small parts are well-suited to coating by this process and can be batch hot-dipped at high rates of production. Typical coating thicknesses are in the range of 2 to 4 mil. Coatings are fully dense and metallurgically bonded to the substrate. Parts are coated by dipping in molten aluminum at 1,100 to 1,290°F for 1 to 2-1/2 minutes. The bath is covered with a molten flux to prevent oxidation of the surface before and after dipping. Up to 40 lb of small parts are commonly coated at one time in a steel basket. Excess aluminum is removed by shaking, air blasting, or centifuging.

Other Processes

There are many other processes for aluminum coating of steel, including vapor deposition, pack cementation, explosive bonding, surface fusion, electroplating, and roll-bonding. However, none of these are really suited to low-cost high-volume production coating of shipboard components. They are not considered to be viable processes for shipboard corrosion control coatings, with one possible exception: roll-bonded or clad steel (Schaper 1979). It is conceivable that large plates of roll-bonded steel could be produced for use in new ship construction. This material might provide a low-cost, highly protective structural material for bulkheads, decks, hulls, or other structure. All cut edges and welded joints would have to be coated by WSA preservation techniques to produce a fully corrosion-resistant structure.

Advanced Thermal Spray Processes

Automated, computer-controlled, robotic handling systems have been developed to improve the uniformity, quality, and reproducibility of thermal-spray coatings (Alloy Metals, Inc. 1981). A number of these units have been operating for coating industrial parts since 1978 with considerable success. Most of these are dedicated to a single, simple task, such as repetitive coating of cylindrical shapes or flat surfaces. However, with recent advances in robotics and microcomputers, complex shapes can now be sprayed effectively. Process controlling variables such as gun stand-off and travel, gas flows, and wire or powder feeds are accurately measured and set without operator intervention. Spray parameters for each part are established in advance and then stored in a computer memory or on a disk for repetitive coatings of similar parts. Equipment at present is relatively expensive. However, as the trend to computer-controlled robotics for all types of industrial processes continues, costs can be expected to decrease. High initial capital costs at present can also be largely offset by savings in labor and by reduction in scrapped parts due to improved process controls.

The density and bond strength of thermal-spray coatings are governed by the temperature, velocity, and cleanliness of sprayed-metal particles that impact on the substrate surface. All of these factors are improved by spraying in air at low pressure (partial vacuum) instead of air at ambient pressure. Coatings produced under such conditions are very dense (>98 percent) and have very high bond strengths (Gupta and Pennici 1981). Chambers up to 6 ft in diameter by 6 ft long are commercially available for low-pressure spraying. These are coupled with computer-controlled robotics to produce a fully automated system for production of the highest quality thermal-spray coatings available (Gupta and Pennici, 1981). Current systems are used to plasma-spray intermetallic (carbide, boride, aluminide, etc.) coatings. Although they have not been used to spray pure aluminum, the equipment should be easily adaptable for this purpose.

ECONOMICS OF METALLIZING

In this section the different thermal-spray processes are compared in terms of relative costs. Although any analysis of economics becomes quickly dated if specific numbers are used, it is difficult to develop a working knowledge of a process without using specific examples and related costs. Readers, therefore, are cautioned that the numbers in this section should be considered just numbers; all data should be regenerated based on a specific situation under consideration. The comparisons presented, however, can be considered valid and can be used as a basis for generating cost figures. A detailed discussion of economics of metallizing is presented in the thermal-spray manual (American Welding Society, in press).

Costs for Thermal-Spraying Equipment

The basic equipment costs for different types of thermal-spraying systems vary considerably. They are estimated to be as follows: for powder combustion, $3,000 to $4,000; for wire combustion, $5,000 to $6,000; for electric arc, $8,000 to $10,000; and for plasma arc, $15,000 to $60,000. Support equipment such as exhaust systems, scrubbers, and soundproofing rooms can add from $5,000 to $50,000 or more to initial installation cost.

A significant item in many thermal-spray systems is the cost of gas and electricity, which would depend on the amount used, the geographic location, and associated transportation and demurrage costs. Table 5 gives typical operating costs of various thermal-spray devices when certain gas and electric rates are assumed. The numbers will give the reader a feel for the relative operating costs of the various devices. Material costs vary widely from apparatus to apparatus, and gas consumption costs are sometimes overshadowed by higher costs of consumables. Furthermore, some spray devices cannot be easily turned on and off, so the actual energy consumption, whether gas or electricity, can be much higher than shown by a simple analysis of spray rates and gas consumptions during a given spraying time. In such cases a factor should be allowed for the on time of the heat source which could be longer than the spray time. In the case of spraying, the importance of these factors varies with the type of material being sprayed. For example, if one is spraying material such as zinc costing $1 per pound, energy costs are more significant than they would be when spraying a material costing $30 per pound.

TABLE 5 Hourly Energy Cost Comparison for Thermal-Spray Devices*

Type	Cost per Hour ($)		
	Air and Gas	Electricity	Total
Nontransferred plasma	8.57	3.72	12.29
Wire arc	0.32	0.18	0.55
Combustion wire	4.75	0	4.80
Powder combustion	13.44	0	13.44

*The various units were compared spraying the same material (stainless) at 10 lb./hour (except rod gun).

On an overall cost basis, with the expense of future maintenance included in the calculations, metal-spraying has long been competitive with paint as a corrosion-protection system. A 1971 study of structural steel protection costs in Great Britain found, for example, that metal-spraying zinc or aluminum was approximately 10 to 20 percent more expensive than comparable paint schemes on an initial cost basis. However, these paint schemes, in the same environmental conditions, provide a minimum of 5 to 15 years shorter maintenance-free protection lifetime than metal spraying. Thus, with the expense of maintenance, the apparent relative advantage of paint schemes on an initial-cost basis is quickly eliminated. In long-term use, metal-spraying provides better protection at an equal or lower cost.

This experience is being confirmed in the United States as well. For example, in a service evaluation program started in 1978, a fleet of railroad tank cars has been metal-sprayed to test the performance and economy of various thicknesses of zinc-coatings both with and without sealers. The cost of zinc coating an average tank car in this program was $1,365 or approximately 2-1/2 times the cost of an average paint job. However, the spraying cost could have been substantially reduced had the cars been treated during manufacture, where the benefits of automation would have been possible. Futhermore, it is expected that the zinc coatings will last the life of the cars, with only cosmetic touch-ups required. A tank car that was painted, on the other hand, would have to be taken out of service and undergo repainting approximately every 5 years over a 20-year lifetime. Thus, even without the lowered cost made possible by automation, thermal-spraying will yield a substantial savings over the lifetime of the car. For example, in the program cited above, it has been projected that thermal spraying of the railroad tank car fleet will lead to an annual savings of $80,000.

It is important to note that more recent studies indicate that there is a trend towards metal-spraying becoming cheaper than comparable paint schemes, even on a first-cost basis alone. A survey was made in the United Kingdom in November 1977 of the comparative costs per square meter of surface for protecting different types of fabricated steelwork using different protection systems. The survey, which was based on actual cost estimates from painting and metal-spraying companies, found that unsealed zinc was approximately 20 percent cheaper on a first-cost basis than the comparable paint schemes. Sealed sprayed zinc was about the same or slightly cheaper than comparable paint schemes on a first-cost basis.

Thus it is now often true that zinc or aluminum sprayed coatings are completely competitive, even on an initial cost basis, with high-quality paint schemes. When the increased maintenance costs and lower protection times that paint systems normally entail are included in the economic calculations, the cost advantages of corrosion protection by metal spraying are obvious. Furthermore, it is important to recognize that inadequate corrosion protection may lead not only to the need for extensive and expensive maintenance operations but also to the premature failure of the structure as a whole, thus necessitating its replacement long before its planned lifetime. In an age when conservation of the world's natural resources is a financial as well as an environmental priority, corrosion protection methods must both last the life of the structure and lengthen the life of the structure. Metal-spraying not only extends the life of iron and steel structures but also avoids the waste of resources required for their replacement and maintenance. The more reasons society has to perpetuate the life of existing or new steel structures, the more metal-spraying is seen as economically desirable.

Costs for Hot-Dip Metallizing

Equipment for the hot-dip process, compared with gas or arc wire thermal-spray processes, is more expensive. Costs include furnaces, power supplies, flux handling, fume collection, and surface-cleaning equipment. Such installations would be suitable only for large shore-based coating facilities. Once installed, actual production coating costs would be comparatively low. Valves or stanchions, for example, could be hot-dip galvanized or aluminized in batches at a fraction of the current WSA coating costs. Costs for hot-dip aluminizing will be about 20 percent more than for galvanizing.

The major economic advantage of hot-dip aluminizing would come from high production rates, particularly for small and sometimes complex parts such as valves, stanchions, brackets, clamps, and fittings. Using batch hot-dip processes, 50 to 100 or more parts could be aluminum-coated in a few minutes. In comparison, the current practice for WSA spraying of steam valves requires 3/4 to 1 hour per valve. Hot-dip galvanizing (zinc or Galvalume coating) could be done in many existing industrial facilities and would be very practical for use in new ship construction. Hot-dip aluminizing is not in use today, but technology exists to set up and operate aluminum hot-dip facilities. All current work on hot-dip coating with aluminum is in continuous rather than batch processing. Dipping facilities at Navy yards probably would be needed for repair and overhaul coating of parts currently in naval service. Another economic advantage of this process accrues from the fact that sealing of hot-dipped coatings would not be required. The coatings are fully dense and would only need to be primed to accept top-coat paints where needed. It is also possible that unique duplex coatings of improved performance could be produced at very low cost by a double hot-dip process involving first the hot-dip coating of aluminum followed by hot-dip coating with zinc or a zinc-aluminum alloy to improve galvanic protection and provide a better base for painting.

Process Control and Quality Assurance

Experience with thermal-spray coatings has shown that meticulous process control and care are required to achieve the high standard of quality necessary for shipboard applications (Conde et al. 1981). The risk encountered in using WSA preservation systems decreases as the degree of control over all aspects of the coating process increases (Putzier et al. 1980). Many users consider WSA preservation as a means to reduce cost and maintenance requirements and are not willing to invest in the higher costs of materials, equipment, and process controls needed to produce high-performance coatings. Some coating shops are just not aware of the influence of process variables on coating quality and performance. Users of sprayed coatings should be fully aware of the risk if components are not properly sprayed and should be prepared either to make the required financial investment in their own spray equipment and control instruments or to pay a coating contractor an adequate price for the high technology required.

W. E. Ballard, who is considered the dean of metal-spraying and is the author of an often-cited text (Ballard 1963) stated:

> In most cases, when applying coatings for purposes of protection, the pistol is used as a hand tool, and the ultimate behaviour of the deposit will therefore depend to some extent on the operator. One of the standard criticisms of the metal-spraying process is its dependability on the human element, and it is therefore necessary to consider how best to avoid unsatisfactory work.

Ballard first wrote this in 1926. Times have not changed; additional meters and controllers have been added to the equipment, but it is still the human operator who is relied on to produce a quality product. This is true not only of the deposition process but also of the raw material and ultimate end product. Controls must be applied and enforced to all phases of the operation to assure a consistantly reliable end product. A constantly high-quality sprayed coating can be achieved only if all the variables which influence quality are closely monitored and controlled. These are:

1. Grit blast media (for surface cleaning)
2. Ambient atmosphere (for both cleaning and spraying)
3. Spray materials--wire, powders
4. Gases--compressed air, oxygen, acetylene
5. Equipment (gauges, controls, etc.)
6. Surface preparation and storage procedures
7. Spray procedures--spray control settings, workpiece heating, spray-to-work distance and angle, and work and/or gun movement

A detailed discussion of the significance and recommended control of each of these variables is given in the thermal-spray coatings manual (American Welding Society in press). The following is a summary of the more important variables that often are a source of coating defects and variability as a result of misuse or neglect on the part of coating producers.

Ambient Atmosphere

One of the most important variables that influences coating quality, and in particular coating bond strength, is the ambient atmosphere in which parts are surface-cleaned, stored, and sprayed. All too often this factor is totally ignored, or at best is recognized by specifying that parts should be coated within 2 to 4 hours after surface-cleaning by grit-blasting. Unfortunately, this approach will not necessarily result in high-quality coatings and more likely will introduce an uncontrolled variation into product quality.

Moisture is the most critical component of the atmosphere that needs to be controlled. Tests have shown that aluminum coatings sprayed onto moist surfaces have less than half the bond strength than those sprayed onto dry surfaces. Relative humidity in the atmosphere where parts are both surface-cleaned and sprayed needs to be controlled for good-quality reproducible coatings. Shop facilities are best located in a temperature and humidity-controlled area where the relative humidity is low and the temperature is kept between 68 and 75°F. Reaction rates of clean steel surfaces with moisture in the air will increase as an exponential function of temperature, and this variable must be controlled along with relative humidity. Few coating facilities, Navy or industrial, use such controls today. Most equipment is in large sheds or open bays exposed to the local environment. Best atmospheres are those located in a desert region.

Dry atomizing air for the thermal-spray gun is essential. If coating is applied using air which contains water droplets, the coating bond strengths can be impaired. The thermal-spray compressed air system must provide clean, dry air and should include an air compressor, an air or water cooled after-cooler, filters and an air dryer. Even new compressors without proper water removal systems can produce water droplets on humid days. The recommended solution is the use of a water removal unit in the air line. For continuous operation, a refrigerated dryer is recommended to reduce the dew point of the air to 35°F. On temporary installations, a desiccant dryer with a capacity of 35 cfm per spray torch can be used. Such dryers must be operated below 100°F to operate efficiently, thus a compressor after-cooler is recommended. A typical filter system with refrigerated dryer unit includes a 5 micron particle filter with automatic water dump and a coalescing filter to remove oil droplets. They are best selected by consultation with a good filter/regulator manufacturer.

Relative humidity and temperature are not the only variables that must be controlled. Handling and storage also should be considered. Grit-blasted clean surfaces should never be handled with bare hands or common (soiled) work gloves; use of clean cotton gloves is recommended at all times. Parts should not be stored in shop or yard areas where dust or dirt can settle on cleaned surfaces prior to spraying. Also, they should not be stored in or near a spray booth where airborne sprayed-metal particles can settle on the surface; only one part should be in a spray area at a time. Stored parts awaiting spraying should be in covered containers or in sealed plastic bags.

It is recommended with respect to atmosphere control that controlled conditions be established in surface cleaning, storage, and spray areas. An air-conditioned room would be ideal. However, while this can be done on shore-based facilities, it is not possible to establish such conditions for on-site (shipboard) coating. This should not preclude, however, attempts to keep a clean area and to control relative humidity. Cleaning of spray areas to remove dust and debris is essential. In addition, cleaned surfaces can be protected with plastic covers or tents in conjunction with dry-air purge atmospheres until spraying is possible. The great importance of this variable must be recognized and all possible precaution taken. Where at all possible, parts should be sprayed in shore-based, clean facilities rather than on-site.

Procedures

Surface Preparation

Cleaning--To ensure a strong bond between the coating and substrate, the substrate interface must first be cleaned to a "white metal" condition; i.e., all dirt, oxidation products (rust), grease, paint, and bituminous products must be removed. Then it must be roughened by pressure blasting or a self-bonding bond coat.

Blasting may be used for cleaning provided it is done as a separate operation before the final roughening blast. Where greasy, dirty parts are cleaned by blasting, a disposable abrasive, such as fine sand or dry-ice pellets, should be used. Since the abrasive will pick up the contamination, it should not be reused. Cleaning and surface roughening should not be combined in one operation. Where dirty work is cleaned by blasting, the job should be done thoroughly, since the first pass over the surface simply drives some of the contaminant into the metal.

It is generally recognized that clean surfaces are essential to the satisfactory bonding of sprayed metal. No compromise should be made on this point. If oil spots appear in the coating during the spraying operation, there is no solution but to stop spraying, remove the coating, reclean the part, and start over. This is expensive, even if required only occasionally. It is far less expensive to do the cleaning properly in the first place.

Grit Blasting--It has been shown that if a surface is blasted at an angle from one direction and sprayed at an angle from the opposite direction, a weak bond will result (Brown 1979). This clearly demonstrates that the sprayed metal particles must penetrate the pits in order to mechanically key the coating to the surface. It is generaly considered essential that the angle of impingement of both the blast and the spray be maintained as close to 90° as possible for maximum bonding.

It is not sufficient to simply blast until the surface is reasonably well pitted. If keys or anchors are to be formed, it is necessary to continue blasting beyond the point where the surface appears completely pitted. This will ensure that a large number of pits have been deformed sufficiently to provide "reverse draft" and positive keying.

Spraying

The optimum spray conditions must be determined for each particular spray facility operator and the part being sprayed. It is not possible to set conditions of universal applicability. Instead, carefully controlled experimentation must be used to establish the optimum conditions for each particular job. The following is a summary of the factors that must be considered.

Spray Control Settings--Each spray gun, whether combustion gas or arc, is different, and individual control settings unique to that particular gun are required (Jones 1960). Each gun must be set and adjusted by an operator to achieve proper spray conditions. Gun operation is not simple and cannot be directed by manufacturers' or specification recommendations for control settings. These are merely guidelines, and actual settings are established by experiment. The skill and attention of the operator in setting and regulating his particular spray gun is the key to good process and product control.

A similar requirement exists in the use of arc wire-spray equipment. Arc wire-spray equipment is very prone to misuse, particularly by running at excessive power levels with resultant overheating of the work. Excessive thermal stress may be induced, resulting in bond separation. As a general rule, these guns should be run far below the recommended current settings to produce good-quality sprayed aluminum coatings (Jones 1960). Basically, two different settings are needed to use this equipment properly: one is a bond setting, which is required to establish a proper bond coat, and the other is a spray setting, which is required to deposit the bulk of the coating.

Workpiece Heating--Aluminum metal has a higher coefficient of thermal expansion than steel (24 x 10^{-6} versus 12 x 10^{-6}/°C). This results in a tensile stress in the coating and at the bond line upon cooling from above room temperature and can result in loss of adherence (spall). Stresses that can cause spall increase as coating temperature and thickness are increased. Coatings must be applied under conditions that will minimize stress. Ideally, the substrate should be preheated to 150± 20°C prior to spraying and the coating should be sprayed onto a substrate that is cooling and contracting (Jones 1960). The temperature used during coating should not exceed 100°C. Careful temperature measurement and monitoring before and during coating will greatly improve coating adhesion.

Spray Distance--The optimum spray distances for good-quality coatings are specified in terms of nozzle- or gun-to-work separation in inches. For example, for gas wire-spray with a 1/8-in. wire, the specified gun-to-work distance is 6 to 8 in. and nozzle-to-work distance is 4 to 6 in. However, the optimum gun distance probably will lie between 4 and 10 in. and must be determined experimentally for each particular gun and job (Jones 1960). Once the proper distance is established, it should be held within a limit of ±0.2 in. to maintain good quality (Brown 1979). This important aspect of control normally is not included in process specifications, and it generally is assumed that maintaining a distance of 6 to 8 in. will produce good results. Much closer control of gun spacing is required than is currently in use at most shops today. Spray distance controls particle velocity and temperature at impact as well as temperature of both coating and substrate. This governs both bond strength and density. The needed level of control (±0.2 in.) probably is not attainable with a human operator unless some type of feedback control and mechanical support is used.

TRAINING AND CERTIFICATION

Experience has shown that training of personnel at all levels concerned with the specification, manufacture, and ultimate use of WSA preservation coatings is essential for long life (Conde et al. 1981). All too often, the only training considered is that of the operator who physically deposits the coating. However, equal training in terms of WSA preservation technology should be given the following personnel:

- Engineers or officers who specify use of coatings and select components for coating.
- Engineers or officers who direct the coating operation or select and supervise industrial contractors.
- Coating equipment operators and their direct supervisors.
- Inspectors.
- Personnel concerned with shipboard installation.
- Ships engineering staff responsible for equipment or areas in which WSA preservation systems are used.
- Ship- and shore-based repair and maintenance officers or supervisory staff.

A general training program has been created by the United Kingdom Admiralty Marine Technology Establishment for managers, designers, inspectors, supervisors, and operators aimed at achieving both proper use and a high standard of application of WSA preservation coatings (Conde et al. 1981). A thermal-spray manual has been prepared as a simple practical guide for the various levels of staff involved. Training ranges from a short 3-day acquaintance course for managers to 5 days for designers, inspectors, and supervisors to a 10-day course for operators. The initial training is aimed at a practical introduction to the use and application of coatings. This is followed by post-course advice and assistance as each shore facility and ship begins to work with WSA systems.

COMMITTEE ASSESSMENT

The selection of the combustion wire-spray aluminum (WSA) coating process to initiate and develop the Navy's shipboard metal preservation program was based largely on expediency. It is considered to be a wise selection, in that an early and effective entry of the WSA preservation system was possible. During the past 5 years, the Navy has been able to demonstrate clearly the value of this system through extensive shipboard tests and evaluation. In addition it has demonstrated the ability to effectively protect a wide range of shipboard structures and components with WSA. It is unlikely that the great progress made during this period would have been possible had any other metallizing process been selected at the time.

An assessment of shipboard applications of WSA coatings during the past 7 years indicates that performance and useful life are more than adequate on some components and structures but are marginal to inadequate on others. The deciding factor appears to be the degree of direct exposure to the marine environment and possibly the degree of mechanical abuse. The coating as applied to below-deck components such as steam valves is excellent, and there is no indicated need for change in processes or process controls at this time. Above-deck, sea-exposed components, on the other hand, appear to be deteriorating more rapidly than would be predicted from the results of long-term field tests and evaluations. The coatings as currently produced are not exhibiting consistently the performance that is considered possible from this type of preservation system in a severe marine environment.

A change in processes and/or process controls appears to be needed for applications in which direct exposure to the marine environment is likely to occur. Other metallizing processes such as arc-wire-spray, plasma spray, and hot-dip coating offer the potential for improved product quality with respect to characteristics such as bond strength and porosity. It is likely that these characteristics also could be improved significantly for the currently used combustion wire-spray process through better controls on materials, process variables, ambient atmospheres, and by improved personnel training and certifications. The procedures and processes currently used basically follow manufacturers' recommendations and specifications for thermal-spray coatings as developed by the manufacturers and by the American Welding Society. These, however, are largely directed toward the application of coatings for machinery repair and do not necessarily represent the best practices for a corrosion-preservation system. The British Admiralty, for example, has recommended much tighter specifications and controls for WSA preservation than those currently used by the U.S. Navy (Conde et al. 1981).

It is believed that the major factors contributing to accelerated attack on direct exposure to the marine environment are inadequate bonding to the steel substrate, excessive coating porosity, and insufficient coating thickness. This is not to say that the specified values of these parameters are not adequate. It is more likely that uncontrolled variations in one or more of the parameters is the major source of difficulty. This conclusion is based on the fact that long-term field tests in severe marine environments of WSA test panels prepared to similar specifications but under carefully controlled laboratory conditions to produce uniform quality exhibited a life expectancy of at least 20 years. Shipboard failures to date are believed to be random occurrences resulting from variable quality with respect to bonding, porosity, and/or thickness. In some cases this appears to be the direct result of using procedures that deviate significantly from the recommended optimum procedures.

There are three possible solutions to this problem: (a) follow rigorously the recommended optimum procedures for gas and arc wire-spray deviation, (b) improve overall product quality through improved process control and product inspection and (c) increase bond strength and density through process modification or use of other metallizing processes. Whereas a higher bond strength per se may not be needed for a uniform, high-quality coating, it does provide in the case of a nonuniform coating a higher baseline value so that random variations below that value are less likely to result in accelerated corrosion. Thus, if it is not possible to reduce variability in bond strength, porosity, and thickness, the level of these parameters should be adjusted to accommodate the variations that reasonably can be expected to occur in production coatings. The conservative approach to the use of these coatings would dictate that the highest level of bond strength and density attainable with practical processes and controls be sought, even though there is no direct evidence to indicate that a specific value of bond strength or density is required for good performance

It is recognized that the recommended use of different processes and tighter controls may increase the cost of WSA preservation systems. It is possible, however, that increased equipment, facilities, materials, and quality control costs will be offset by significantly reduced production costs for alternate or new processes. In addition, coating costs should be looked at from a life-cycle rather than from an installed-cost basis. Properly controlled and applied WSA coatings should have a long (15 to 20 year) low-maintenance life. Inferior quality coatings, on the other hand, may need replacement or repair in 2 to 5 years. The risk encountered in the use of these coatings will decrease as the degree of control over all aspects of the coating process is increased. The Navy should be willing to invest in higher cost equipment, materials, and process controls if significant gains in performance are possible.

It should be recognized that this is a technology in which product quality and performance are and will continue for some time to be governed by knowledge and understanding of the product by designers, producers, and users; technical skill of spray operators; and rigid adherence to tight materials and process specifications. It is not a technology in which low bids can be accepted on blind faith, and prime consideration in selection of coating sources must be given to demonstrated technical excellence and skill rather than cost. Experience to date with thermal-spray preservation coating systems indicates that meticulous process control, education at all levels, and extensive operator training and certification are required for production of consistently high-quality coatings. It is important to understand that thermal-spraying is not a forgiving process in which shortcuts can be used to increase production rates or reduce cost. Strict adherence to recommended procedures and practices is essential.

The following paragraphs summarize specific areas in which the technology in use today is considered to be less than what the current state of the art has to offer in terms of coating productivity, cost, product quality, and performance. Recommended courses of action are included.

Processes

The combustion wire-spray process is considered to be adequate for coating parts that are not exposed directly to severe marine environments. With the use of better process controls, it would most likely be adequate for coating most topside components and structures. This process is labor-intensive and is highly dependent on the training and individual skill of operators. Labor is the pacing item in both quality and cost. It is unlikely that production rates can be increased and costs decreased much beyond current level without sacrificing quality and performance.

An effort should be made to phase-in alternate processes during the next 5 years to reduce overall coating costs and to improve the quality and performance of corrosion-prone topside structures and components. Two processes deemed most likely to achieve these aims are hot-dip coating and arc-wire-spraying.

Hot-dip coating will be particularly useful for high-rate, low-cost production coating of comparatively small parts. In addition, it will produce a fully dense coating metallurgically bonded to the substrate. It has the potential to produce a wide variety of coating including aluminum, zinc, zinc-aluminum, and duplex coatings of zinc over aluminum. For larger fabricated structures such as decks and bulkheads, consideration should be given to the use of aluminum-clad steels produced by continuous hot-dipping or roll-bonding. It is recommended that the Navy initiate a manufacturing development program in the area of hot-dip aluminizing and galvanizing for shipboard preservation. This should include an evaluation of process variables and shipboard testing of coated components using a variety of coating compositions.

The arc-wire-spray process is particularly well-suited to coverage of large surface areas at high production rates. It promises to reduce overall coating cost. In addition, the process can be readily mechanized and automated, providing the basis for a significant improvement in coating quality and uniformity. An effort should be made to mechanize and automate wherever possible to reduce dependency on operator skill.

The arc-wire-spray process also has the potential to produce a higher bond strength for equal surface preparation compared with the combustion-wire-spray process. In general, it can be more forgiving of inadequate surface preparation. This process is being used to a limited extent for the application of nonskid deck coatings. It is recommended that development of this process for Navy use be continued and that applications be expanded to include all applicable WSA preservation systems.

Process Specifications

Currently used process specifications and instructions do not provide for adequate control of those variables considered important to a high-quality marine corrosion protection system. Specific areas in which improved or tighter controls are deemed desirable include ambient atmospheres, instrumentation, spray parameters, and surface preparation. As a start, specifications and instructions should be modified to follow more closely those that have been adopted by the British Admiralty (British Standards Institution 1977, Brown 1979).

A review of the various practices and specified procedures indicates a large degree of uncertainty and contradictory directions in terms of spray parameters and controls. It is believed that much of this understanding of behavior as related to parameters results from uncontrolled tests and observations, incomplete and at times incorrect analysis of results, and results taken out of context or adopted from other areas of spray technology on the questionable assumption of a direct transfer capability. In many cases, parameters are based on what is readily attainable rather than on what actually is needed.

It is recommended that the Navy initiate an in-depth controlled study of process variables for both combustion- and arc-wire-spray preservation systems to define the precise range of parameters and process controls required to produce acceptable coatings. This should comprise at first a laboratory study in which coating structure and properties are correlated with process variables. The study should be sound from a statistical point of view and should include analyses of variance to establish both the individual and interactive effect of process variables. The second phase of the study should consist of accelerated laboratory, extended field, and shipboard corrosion tests of both coupons and hardware produced with the best practices. These also should be conducted on a statistically sound basis. Results of these studies should then be used to provide the basis for more reasonable and realistic process specifications for WSA coating systems.

Education, Training, and Certification

The current approach to training and certification is considered to be adequate but somewhat limited in both scope and depth. An expanded education and training program more along the lines of that used by the British Admiralty (Brown 1979) appears desirable. The Navy should consider setting up training schools under the Naval Training Command at several different locations. Education and training courses should be developed for designers, supervisors, and users of WSA preservation systems as well as for spray-gun operators. More effort should be given to developing a technical understanding and appreciation of how these systems work and how they must be prepared and used to be effective.

Consideration also should be given to the education and training of civilian contractors as well. If it is not feasible for this to be done at Navy facilities, it may be possible to use university or technical school short courses with Navy or other qualified instructors. It is recommended that only fully educated, trained, and certified Navy and civilian (industry) personnel be used in specifying, producing, and installing metal-sprayed coatings.

WSA Preparation Facilities

Surface preparation is considered to be a key factor in the production of uniform high-quality coatings with maximum bond strength. Practices currently in use for both surface cleaning and roughening are good and within the current state of the art. However, the retention of a surface suitable for spraying is not controlled consistently, and considerable variation in surface condition is likely to exist in both Navy and vendor coating facilities. This is considered to be the result of inadequate control of the ambient environment in which surfaces are prepared, parts are stored, and coatings are applied. Shop environments in the majority of spray facilities are dirty and in addition do not control humidity or temperature. Variable degrees of surface contamination can occur between the time of surface cleaning and coating application. The specification of a time limit (e.g., 2 hours) between cleaning and coating is not considered adequate to resolve this problem.

The committee recommends that WSA preservation coating facilities in both Navy and civilian plants be upgraded to provide conditions at controlled humidity and temperature. Dust and dirt should be minimized or eliminated, and humidity should be maintained at low levels. Surface preparation and spraying should be conducted in closed, separately air-conditioned areas if at all possible. Cleaned parts should be handled only with clean gloves and should be stored under low-humidity, dust-free conditions.

CHAPTER 5

COATING CHARACTERISTICS

CURRENT NAVY PRACTICE

The most important characteristics of a WSA preservation coating are the uniformity and integrity (strength) of the bond to the substrate and the overall thickness, thickness uniformity, and structure of the coating. These characteristics are governed by the spray process variables and reflect the skill and control of the operator who applies the coating. The following is a summary of these important characteristics for coatings as currently produced by Navy shipyards and industrial contractors for shipboard preservation systems.

Interface Bonding

The bond of WSA coatings to steel as produced by combustion-metal-spray processes is largely mechanical in nature. Highest bond strength is achieved when the coating is sprayed on suitable roughened (anchor tooth) surfaces that are clean and dry. Current specifications require an anchor tooth 1 to 4 mil deep and limit the time between surface cleaning and spraying to 2 hours. There is no requirement for control of ambient temperature or humidity during surface cleaning, storage, or spraying. The specification requires a demonstration by tensile test that the average bond strength (of 5 tests) is 2,000 psi or more and that no single value (of 5 tests) is less than 1,500 psi (Department of Defense 1981). All current production meets these acceptance criteria.

In a development program for production of anti-skid deck coatings by aluminum metallizing, the Puget Sound Naval Shipyard (Navy, Department of 1978) found that the average tensile bond strength of arc-wire-sprayed aluminum bond coats on steel was 5,525 psi. This is almost 3 times the specification minimum. Similar tests were conducted with modified Metco arc-spray equipment with a single air orifice in the spray head and two remote power supplies. The average bond strength in these tests was 2,665 psi, above specification minimum but only half the strength obtained when the unmodified Metco arc-spray equipment was used. These results indicate that significant increases in bond strength are possible when equipment and controls are adjusted to vary spray conditions.

Few systematic studies of process variables and their relation to bond strength have been made, and to date no concerted effort has been made to increase bond strength much beyond the specified minimum values. One important study recently conducted by Flame Spray, Inc. for Southwest Marine, Inc., indicates that control of relative humidity and temperature during storage between cleaning and coating has a major effect on bond strength (private communication between Flame Spray, Inc. and Southwest Marine, Inc., San Diego, California, July 1981). Seventy-two samples were cleaned and anchor tooth blasted by similar procedures. Three samples were WSA-coated within 1 hour of blasting as a control group. The remaining samples were then placed in a temperature- and humidity-controlled area for up to 64 hours. Temperature was held at 85 to 95°F and relative humidity at 14 to 20 percent. Three specimens were removed at 4-hour intervals and coated. Tests of bond strength indicated that samples could be held in the controlled environment for up to 48 hours with no degradation in bond strength when compared with the control samples (no hold). However, samples held for 2 hours at a relative humidity of less than 10 percent but at a temperature of 115 to 120°F had a significant strength reduction, with many values below 2,000 psi and several below 1,500 psi.

These data have been analyzed statistically by R. A. Perkins at Lockheed's Palo Alto Research Laboratory using a Weibull distribution function. The Weibull is an extreme-value type of distribution that has proved to be particularly useful in the control and interpretation of strength data for metals (King 1971). It is used widely in the automotive industry for product and process control. The Weibull distribution as calculated for the bond test data in private communication between Flame Spray, Inc., San Diego, California and Southwest Marine, Inc., San Diego, California, July 1981 is plotted on Weibull probability paper in Figure 9. This is a plot of percent failure, which is properly interpreted as "cumulative percent equal to or less than" versus the stress (bond strength) in logarithmic units. The data from the humidity-temperature holding experiment fit the Weibull distribution nicely, with a very high value (6.7) for β. This indicates good process control with predictable properties and a "wear-out" mode of failure. The value for 63.2 percent failed occurs at a stress level of 4,800 psi (θ) for this distribution. This is close to the average stress of 4,027 psi for the three control samples with less than 1 hour hold between cleaning and coating. This is an exceptionally high stress level for a flame-sprayed coating and indicates a significant product improvement. An extension of the Weibull line to the horizontal axis shows that only 1 percent of the tests will have a strength equal to or less than 2,400 psi.

A similar plot of tensile data for a 2-hour hold at higher temperatures also is shown in Figure 9. A curved plot is obtained, indicating a non-Weibull or perhaps a mixed distribution. The data are significantly different and indicate a major change in distribution of strength values.

Interface bond strength is not routinely measured in the production of coated parts. Instead, this test is used to qualify operators and facilities and to check periodically on continuing coating quality. It has not been common practice to prepare bond test samples with each coating job. Once satisfactory bond strength has been demonstrated, many parts may be coated before this parameter is rechecked.

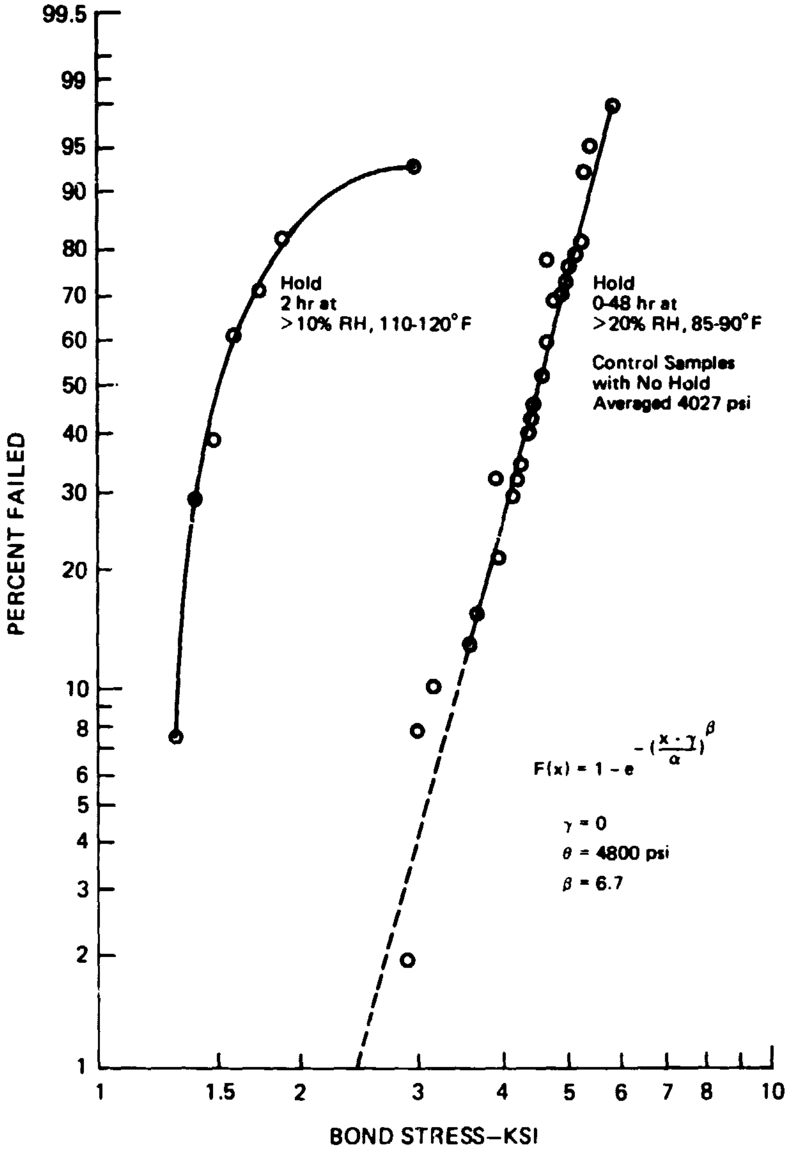


FIGURE 9 Effect of relative humidity on bond strength of WSA coatings (private communication between Flame Spray, Inc. and Southwest Marine, Inc., San Diego, California, July 1981).

The Navy does, however, routinely assess product quality on a day-to-day basis by means of a bend test. At Puget Sound Naval Shipyard, for example, test coupons are sprayed several times each day and whenever new grit is used for anchor tooth blasting. This test is used primarily to assess the adequacy of surface preparation to accept the coating. Coatings applied to poorly prepared surfaces will laminate and spall on bending. The tensile test is considered to be too expensive and is not timely for use in this important aspect of process control.

Thickness and Structure Control

Coating thickness is measured routinely on each part using magnetic-permeability-type gauges. Parts with areas that exceed the maximum specified thickness are rejected. Those that are under specified thickness are given additional spray coats as needed to meet specifications. Coating thickness normally is measured intermittently while the coating is being applied.

It has not been determined how much of these data have been recorded and reported. For most applications there is no traceable record that can be used to correlate performance with coating thickness. Parts are not identified as to source or manufacturing history in most applications. One notable exception to this practice is found in the steam valve test program on the USS William H. Standley (CG 32). Each WSA-coated valve in this program is identified by number and location and detailed production histories are available (Navy, Department of 1981a). Coating thickness has been measured for each valve and is being tracked as a function of time in service. The coating thickness has been measured as a range on each valve and lies between 4 to 7 mil and 6 to 25 mil as extreme values on individual valves. Minimum coating thickness for the 32 valves ranges from 3 to 9 mil, while maximum thickness ranges from 6 to 25 mil. Minimum thickness appears to be more closely controlled than maximum thickness. The average minimum thickness was 6 ± 3 mil. The average maximum thickness was 12.5 + 12.5 or - 6.5 mil.

Very little work has been done on microstructure of coated test panels. Microstructure is not determined as a routine measurement of coating quality, and requirements for structure determination have not been established. As a result, available data on strength and thickness cannot be correlated with coating microstructure.

STATE-OF-THE-ART SUMMARY

Nature of Thermal-Spray Coatings

Those concerned with the selection, manufacture, and use of thermal-spray coatings should be thoroughly familiar with the nature of the process and the characteristics of the coating. A detailed review and discussion of the salient features of the process and its products is presented in the thermal-spray manual (American Welding Society in press). Several of the more critical points with respect to coating characteristics are summarized in the following paragraphs.

During the spray process, molten droplets of the coating metal are formed on leaving the gun, superheated to high temperature, and propelled to the surface being coated at high velocity. Calculation of the heat transfer between a sprayed droplet and a metal surface (Moss 1968) indicates that the droplet cooling rate on striking the surface is of the order of 10^7 °C/sec. Experimental measurement of dendrite spacing in the coating (Wilms and Herman 1976) indicates solidification rates of between 10^6 and 10^8 °C/sec. The coating is comprised of layers of splat-quenched particles. The spray droplets must be molten as they strike the surface in order to form a good particle-to-particle and particle-to-substrate bond. If the gun-to-work distance is too close, the particles will not have time to melt and a weak, porous coating is formed. If the gun-to-work distance is too great, the particles will solidify before reaching the surface, forming again a weak, porous coating. Accurate control of gun-to-work distance is essential to formation of strong, dense deposits that are well bonded to the substrate and in which particles are well-bonded to each other.

Bond Strength

Coatings sprayed in air are a heterogeneous mixture of sprayed metal, oxide inclusions, and pores. The particles are bonded to the substrate and to each other by adhesive forces and cohesion. The strength of a thermal-spray deposit consists of the bond between particles and substrate (adhesion) and interparticle attraction (cohesion). Adherence of the spray to the substrate is of prime concern, and most particle-to-surface interactions are viewed in this relationship. The nature of the bond between the coating and substrate is not fully understood, and in fact, is often a matter of dispute. Regardless, most authorities agree that the bonding mechanisms fall into three categories: mechanical, physical, and metallurgical or chemical. Also, in most instances, deposit adhesion is owed to a combination of the mechanisms. A molten particle impinging a suitably prepared and roughened surface will flatten and conform to the undulating surface and mechanically key itself to the asperities thereon. If diffusion or alloying--that is, the formation of intermetallic compounds--occurs, the adherence mechanism is metallurgical or chemical. The adherence of the particle to the substrate by Van der Waals forces or secondary valence bonds is physical bonding.

Particle-to-substrate adhesion is probably largely mechanical, and this would explain the importance that surface preparation assumes in achieving good bonding. Also, in view of the ultra-rapid quench rate, metallurgical or chemical bonding arising from diffusion across the particle-substrate interface is minimal. A tenacious bond will not generally be obtained between a coating and substrate if the latter is not roughened--that is, grit-blasted, machined, rough-threaded, etc. It is likely that some chemical bonding does occur, but most of the adhesion resides in the mechanical anchoring of the coating by a physically perturbed surface. While tensile tests have shown that coating-substrate adhesion is weaker than the cohesion between coating platelets, it cannot be assumed that the latter will exhibit high strength under the complex stressing conditions that are normally encountered in practice.

Although it is generally assumed that the bond is largely mechanical, the literature commonly cites one spray process or another as producing a stronger bond. Steffens and Crostack (1981) and Stanton (1976) state that arc-wire-sprayed coatings have a higher bond strength than combustion-gas-sprayed coatings under comparable conditions. One manufacturer (private communication, TAFA Metallisation, Inc., Bow, New Hampshire 1981) has reported the following bond strengths for aluminum coatings sprayed on steel by three different processes: arc spray, 6,970 psi; plasma spray, 4,950 psi; combustion-gas spray, 1,030 psi. The higher bond strengths with arc spray are attributed to the higher particle temperature and velocity achieved in that device. However, plasma spray should be at a higher temperature, and combustion gas spray can be at higher velocity than that with arc spray and conventional axial atomizing air flow. The above arc-spray data, however, are for closed nozzles with coaxial atomizing air, which does promote high gas flows.

A recent study by the Puget Sound Naval Shipyard helps to put the tensile test data in a better perspective and clearly points out a major deficiency of this test in terms of providing a useful measure of product quality (Rogers 1982). In this study, pure aluminum was sprayed on suitably prepared steel plates as deposits of different thicknesses by both the arc-wire spray and the combustion gas-wire spray processes. Five studs were then cemented to the surface of each sample and tensile strength determined by standard ASTM procedures. Results are summarized in Table 6.

TABLE 6 Comparison of Tensile Strength of Arc Wire Spray and Combustion Gas Wire Spray Processes

	Average Bond Strength (psi)	
Coating Thickness (mil)	Combustion Gas Wire	Arc Wire
4	7,000	10,700
6	5,400	10,200
8	4,500	7,100
10	3,270	5,340
15	3,700	4,350

The increase in coating strength with decreased thickness is the result of the epoxy glue penetrating pores in the coating and adhering to the substrate. The thinnest coating fails by fracture in the epoxy bond at the stud/coating interface (94 percent of the failure is in the epoxy). The thickest coating fails at the coating/substrate interface (95 percent of the failure is in the interface).

This test, as specified by ASTM, is meaningful only as used to evaluate coatings of 15 mil or greater in thickness. It cannot be used to assess bond strength of thinner coatings unless a glue can be developed that will not penetrate pores in the coating. In addition, it is a test that does not readily lend itself to rapid and inexpensive evaluation as required for routine production control.

The results of the Puget Sound study by Rogers also show that arc wire sprayed coatings are about 50 percent stronger than combustion gas sprayed coatings applied to the same substrate. This could indicate a better overall bond to the substrate. On the other hand, it could indicate a more porous coating in which the epoxy penetrates the coating, adding to bond strength. It was noted that the arc wire sprayed coating at 15 mil thickness failed with 70 percent of the fracture at the bond line and 30 percent in the coating while the gas sprayed coating failed 95 percent at the bond line. This suggests that increased porosity and not increased bonding contribute to the higher strength values for the arc wire sprayed material. The results clearly are not definitive and considerable work is needed to define more clearly the relative characteristics of coatings produced by these different processes.

Calculations and measurements of solidification rates of thermal-spray coatings do not indicate that a sound technical basis exists to support claims that any one process is capable of a higher bond strength than any other (Moss 1968; Wilms and Herman 1976). The quench rate of molten particles on hitting the surface is so rapid (10^7 °C/sec) that any metallurgical or chemical bond from reaction at the interface will be minimal. There are reports, however, that arc spray droplets, being of large mass and at higher temperature, do tend to alloy and bond with the surface (Stanton, 1976; Steffens 1980). These data, however, are not considered to be conclusive. They represent a very limited amount of testing and are not statistically sound. In fact, it can be seen from Figure 9 that 28 percent of the distribution of strength values for the combustion-spray coating deposited on a clean surface would exceed the value of 4,950 psi reported for plasma-coated steel (private communication, TAFA Metallisation, Inc., Bow, New Hampshire, 1981) and less than 1 percent of the distribution has a strength of 2,400 psi, more than double the value reported for a combustion spray coating (private communication, TAFA Metallisation, Inc., Bow, New Hampshire, 1981). Even the lowest strength value of the distribution (Figure 9) for a coating sprayed on a contaminated surface is 1,300 psi.

It must be recognized that bond strength for any process is a variable quantity that for any given distribution ranges between wide extremes. Comparison of test data from single tests or even 5 tests may not be valid, and process capabilities with respect to bond strength should be considered only on the basis of statistical analyses of a large population of data. Unfortunately, few data are available in the literature on which to make such a comparison. One set of strength data obtained from closely controlled plasma-arc studies of sprayed aluminum on steel (Hermanek 1979) has been analyzed using Weibull statistics by R.A. Perkins at Lockheed's Palo Alto Research Laboratory; the results are plotted in Figure 10. The data designated PSAl can be described by the Weibull equation as follows:

	PSAl	Gas WSA (see Figure 9)
γ =	0	0
β =	4.2	6.7
θ =	2.36 ksi	4.80 ksi

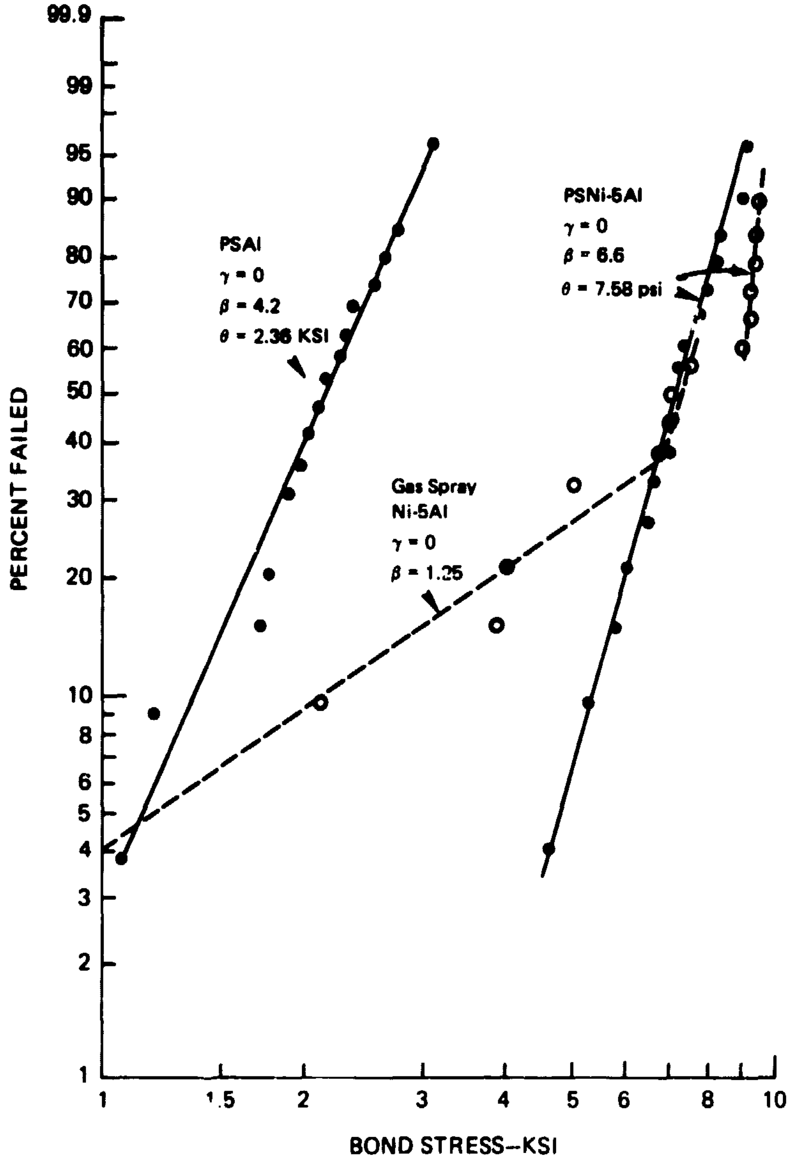


FIGURE 10 Effect of Ni-5Al bond coat on bond tensile strength of plasma spray Al coated steel (Hermanek 1979).

These statistics indicate that the combustion-gas wire-sprayed coating is superior in terms of bond strength, having twice the strength of the plasma sprayed coating as well as a higher value of shape parameter (β).

From the very limited data available it would appear that substrate surface condition, rather than the type of spray process, probably has the greater effect on bond strength. Major increases in bond strength do not necessarily require a change in the basic spray process used, and a change in process from gas-combustion to arc-wire or to plasma spray will not necessarily result in increased bond strength for coatings. This leads to the conclusion that the control of surface cleaning and retention of a meticulously clean surface by processing under controlled temperature and humidity conditions are major requirements for improved coating properties. A high proportion of failures of thermally sprayed coatings can be traced directly to improper surface preparation, regardless of what type of spray process is used (Brown 1979).

The spray process can have an additive effect, however, and under some conditions can result in formation of weak bonds regardless of prior surface condition. Heat from the spray process may oxidize substrate surfaces just before the spray particles arrive. The spray atmosphere thus becomes an important factor. This atmosphere in the case of plasma spray is largely an inert gas (argon or helium) and oxidation should be minimal. With arc-spray, the atmosphere is dry air and will tend to be consistent in its oxidizing potential. With combustion spray, the atmosphere is a complex mixture of oxygen, nitrogen, oxides of carbon (CO, CO_2), water, and possibly unburned hydrocarbons. It can vary considerably in composition from highly oxidizing to reducing, in an uncontrolled and unpredictable manner. The presence of water vapor in the gas could lead to accelerated oxidation of the substrate during spraying. Of the three processes, combustion spray probably has the greatest potential to oxidize surfaces and produce weak bonds if the spray gun is not properly adjusted and controlled. With any spray process, overheating of the work can produce the same effect, and weak bonds can be produced with improper use.

One way to improve coating strength for any coating process is the application of an exothermic alloy bond coat. This group of materials includes but is not limited to molybdenum, columbium, tantalum, iron and to nickel-aluminum alloy mixtures. Each of these materials will adhere to a smooth, clean surface and exhibit bond strengths exceeding 2,500 psi. Hence, these materials are often used as "bond coats" or an intermediate layer onto which a subsequent coating may be overlaid. In this manner overall adhesion of the coating system is improved. The adhesion of self-bonding materials is often explained by (a) localized fusion and alloying with the substrate and (b) diffusion. The heat for reaction comes from the striking molten particle. The degree of fusion and diffusion is governed by the particle quench rate. Metallographically, zones of interaction are located almost solely at the center of the particle of that portion containing the greatest mass.

The most commonly used exothermic bond coat is a Ni-5Al alloy. A nickel-aluminum powder mixture (not prealloyed) must be used to achieve the maximum effect. Bond coats can reduce to some extent the requirements for meticulous surface cleaning and will tend to self-bond to surfaces that are not heavily roughened by grit blasting. A bond coat can be used either to increase the strength of coatings deposited on properly prepared surfaces or to produce coatings of satisfactory strength on less-than-perfect surfaces. The effect is indicated by a Weibull plot of the bond strength of Ni-5Al plasma-coated steel (Figure 10). The median bond strength of 7.58 ksi is more than 3 times that of pure aluminum sprayed directly onto steel. Bond coats work particularly well with arc-wire and plasma-spray equipment. Manufacturers' technical data for Ni-5Al arc-wire-sprayed bond coats indicate a strength of 9,110 psi on a clean, smooth surface and 9,746 psi on a grit-blasted surface (TAFA Metallisation, Inc. 1981). This is in the range of strength reported for gas-combustion and plasma-spray bond coatings (Figure 10). The results obtained by combustion-gas-spray tend to be more variable, probably due to the lower overall temperature of particles in the flame and to a variable atmosphere and/or marginal exothermic reaction. This is illustrated by the Weibull distribution for a gas-sprayed bond coat as shown in Figure 10. A mixed distribution is indicated, with part of the distribution having a random mode of failure ($\beta \sim 1$). The plasma-sprayed bond coat has a uniform distribution with a high value (6.6) of β.

There are a number of confusing and contradictory statements in the literature concerning the suitability of bond coats in WSA preservation systems. In one case it is reported that the nickel-aluminum bond coat is more noble than iron, and the steel would rust beneath the bond coat. In another, it is reported that reactions are incomplete, leaving free aluminum particles in the bond coat that would be corroded preferentially. This should not be a problem in WSA preservation, however, since the bulk coating applied over the bond coat is pure aluminum. Iron-aluminum alloy bond coats have been recommended as more suitable for use with aluminum or zinc coatings (private communication, J. Longo, Metco, Inc., August, 1981). Iron-aluminum alloys should not set up galvanic cells that will promote bond line attack. However, no data are reported on the strength and corrosion behavior of either aluminum or zinc coatings produced with iron-aluminum bond coats. Pure iron bond coats have been evaluated in a number of tests, including the 19-year AWS study (American Welding Society 1974). However, no difference in corrosion resistance and useful life was noted for WSA coatings produced with or without an iron bond coat. No data on coating strength are presented.

Residual Stress

As with other deposition coating processes, thermal-spray coatings often contain residual stresses, produced as a result of contraction during cooling and solidification, that can cause cracking and/or bond separation. The magnitude of the stresses depends upon the thermal expansion coefficients of the substrate and coating materials. In a bimetal strip, longitudinal compressive and tensile forces are in equilibrium as long as the strip is free to deflect, but in sprayed coatings the deposit is entirely under tensile stress. The interface is subject to shear stresses and, for a given adhesive strength, only a certain tensile force can be tolerated in the coating; otherwise, failure of the bond results. This limits the maximum thickness of any deposit, since the tensile force is proportional to the deposit thickness. Stress seldom is a problem with these coatings, but thick deposits may delaminate and spall.

Thickness and Structure

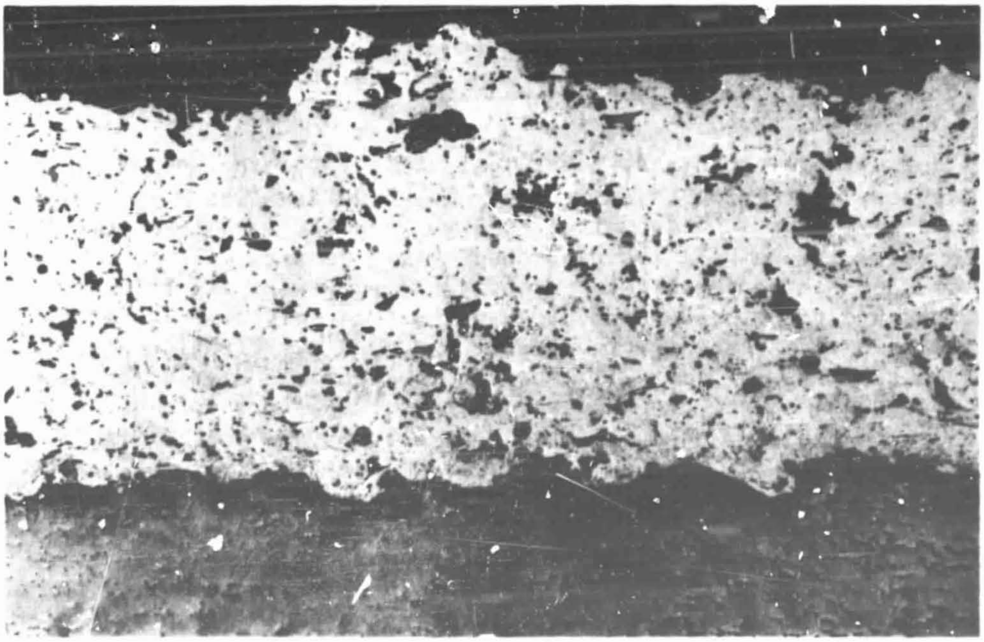
The porosity of thermal-spray coatings can play a major role in coating performance. The primary origins of porosity are (a) shrinkage cavities that form upon rapid solidification of the molten particles and (b) the nonuniformity in contact between the platelets that comprise the coating. The porosity does permit penetration of fluids, which can be beneficial--for example, when one wishes to have a lubricant carried within a cutting tool in machining operations. For purposes of corrosion protection, the porosity is clearly detrimental, and therefore, the pores should be minimized in size and extent, either by spray process control or by thermomechanical treatment after spraying. Alternatively, for many low-temperature uses, the pores may be filled with some inert protective chemical, such as a vinyl-containing sealer. It is important to note, however, that for corrosion protection through cathodic action, the active metal coating (such as zinc and aluminum) has so great a throwing power that the pores are not in fact necessarily detrimental to the protection afforded by the coating. Porosity, however, will accelerate loss and deterioration of the coating by galvanic corrosion. A sealer will give enhanced lifetime by retarding internal corrosion. Sealing of pores is essential to attainment of maximum potential coating life.

All thermal-spray coatings, regardless of the process used, are porous to some degree, containing both open and closed voids. The only exception is plasma-sprayed coatings deposited at high velocity in a low-pressure vacuum chamber. These will approach theoretical density, with less than 2 percent of unconnected porosity. Porosity and pore size are related both to spray method and the process controls used. In any given spray process there will be a wide range in the size, shape, and distribution of pores as the spray parameters are varied. There is considerable overlap between the various processes, and no one process can be cited as producing inherently denser coatings than any other process. In spite of manufacturers' claims, each coating process can produce either very dense or very porous coatings. The one possible exception is combustion-powder spray, in which production of dense coatings is difficult at best, if not impossible. Basically, porosity will be decreased as the temperature and velocity of particles reaching the surface are increased. There is a limit, however, to the increase possible on spraying in air, and even the best air-sprayed coatings will have some interconnected porosity.

This behavior with respect to coating structure is illustrated in Figures 11 and 12. Figure 11 shows typical porosity (black spots are holes) in arc-wire and plasma-sprayed aluminum coatings on steel. These are not representative of the best practice available but may be typical of structures produced with normal shop processes. Figure 12 is an example of what can be accomplished by close process controls. Here a very dense

a. Plasma sprayed Al as deposited by Lockheed Missiles and Space Company

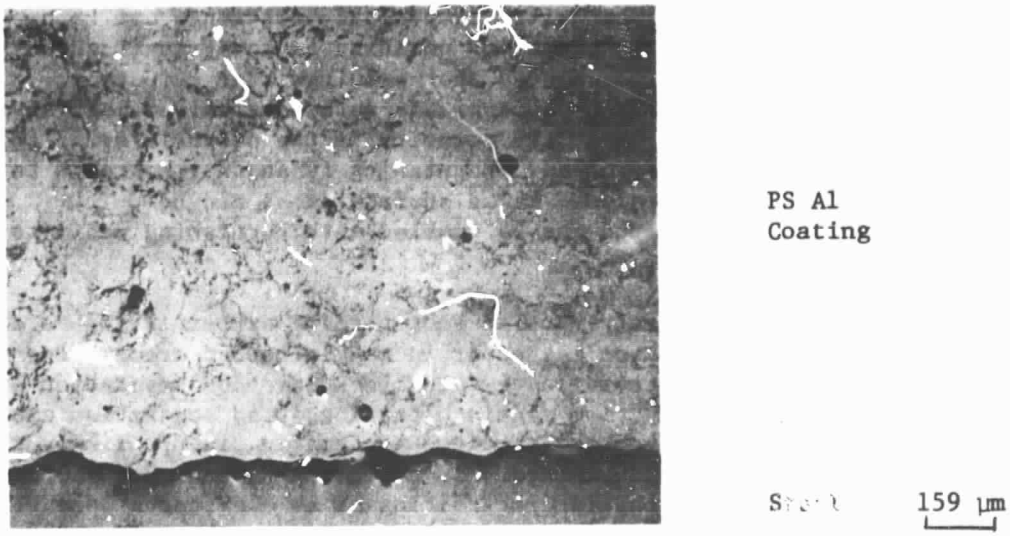
85 μm



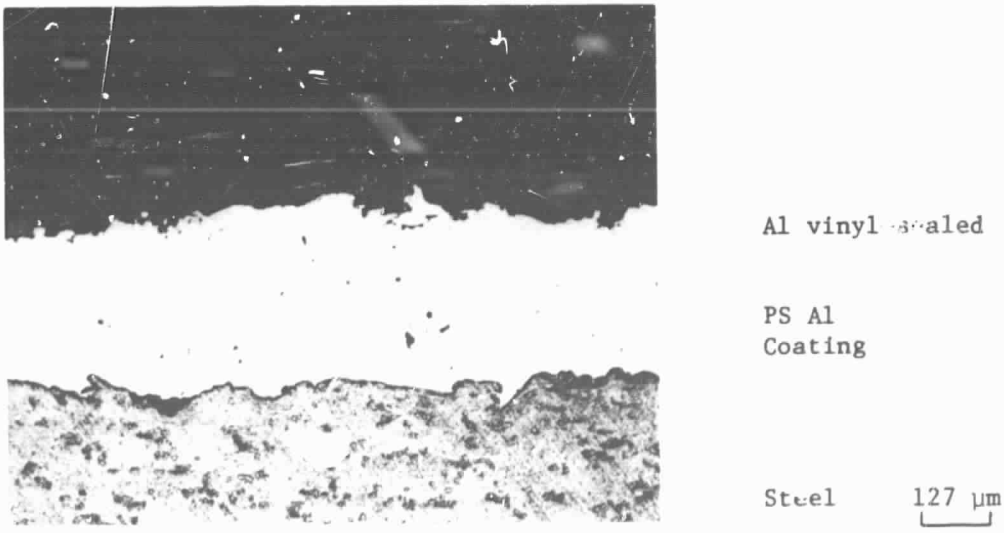
b. Arc wire-sprayed Al as deposited by TAFA Metallisation, Inc.

85 μm

FIGURE 11 Representative microstructure of production quality arc-wire and plasma-spray aluminum coatings on steel (Courtesy Lockheed Missiles and Space Co.).



A. Unsealed



B. Sealed with Al flake pigmented vinyl

FIGURE 12 Microstructure of unsealed and sealed high-quality plasma-sprayed aluminum coatings (Courtesy Metco, Inc.).

plasma sprayed aluminum coating with minimum interconnected porosity has been produced. This may be representative of the best practice possible under carefully controlled process conditions. Figure 12b shows an aluminum-vinyl sealer coat applied to the coating to fill any remaining through-porosities.

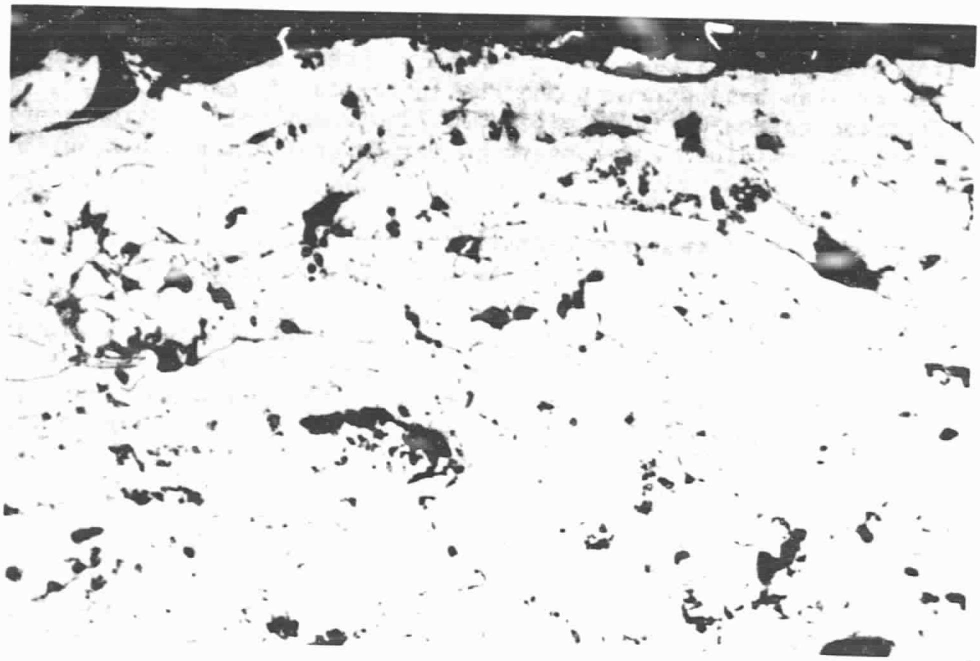
As previously mentioned, thermal or mechanical treatments can be used to further densify and reduce interconnected porosity in spray coatings. The most commonly used method is glass-bead shot-peening. The effect of glass-bead peening on the porosity in a plasma-sprayed aluminum coating on steel is shown in Figure 13. Only the porosity in the outer layer of this rather thick coating has been sealed. Burnishing is another approach to densification of coating surfaces. Large surface areas can be roller-burnished and small parts can be tumbled with burnishing media to close surface pores.

One of the dangers inherent in using shot-peening or burnishing to close porosity is that bond separation may occur in weakly bonded areas. Peening often is used as a quality assurance test to check for bond separation of coatings. However, with a ductile aluminum coating, bond separation caused by peening may not be readily apparent since the coating is not likely to spall unless a very large area is involved. This may have been a factor in the premature failure of a nonskid deck coating on an elevator of the USS Enterprise. A sprayed elevator deck was prime-coated incorrectly and the paint had to be removed. Blasting with glass-bead shot was used to remove the paint (Navy, Department of 1982a). After less than 9 months of service, the nonskid deck coating on this elevator was being undermined by corrosion; the coating was corroding and exfoliating internally as well as at the coating-deck interface (Navy, Department of 1982b). Although the exact cause of failure has yet to be determined, it is considered possible that the internal and interface bond was degraded by shot-blasting to remove the paint.

Coating thickness control is the other approach to coping with coating porosity. In general, thermal-spray coatings more than 35 mil thick will be impervious in spite of high porosity. This is too thick for practical use, since the tendency for spalling will be high. A more useful limit is considered to be 9 mil. Coatings thicker than 9 mil are normally considered not to have through-porosity (to the substrate). Coatings in this thickness range, however, most likely would still require sealing, since a small amount of through-porosity would still exist.

COMMITTEE ASSESSMENT

The structure and characteristics of thermal-spray coatings as produced by gas-combustion, arc-wire, and plasma-spray techniques are similar. There is likely to be more variation in the structure and properties of these coatings as a result of variations in process parameters for a given process and surface cleaning than there is from one process to another, all other conditions being equal. Each process is capable of producing high-quality, dense, well-bonded coatings if properly applied to suitably prepared, clean substrate.



A. AS - sprayed

B. Glass bead shot peened

FIGURE 13 Densification of plasma sprayed aluminum coatings by glass bead shot peening (Courtesy of Lockheed Missiles and Space Company).

The tensile strength of the bond between the coating and the substrate is considered to be the single most important coating characteristic with respect to overall performance. Low bond strength can lead to coating separation from the substrate and underlayer corrosion that can weaken surrounding well-bonded areas. Unfortunately, there is no direct correlation between bond strength and the incidence of coating separation and/or interface corrosion. The minimum bond strength above, which coating integrity will be retained in exposure to marine environments, has not been determined.

The current tensile test for measuring bond strength is not adequate and the majority of available data cannot be used with confidence to characterize or assess the quality of any given coating. Strength values vary with bond coating thickness and porosity and hence cannot be compared unless these parameters are clearly defined. All data should be considered relative, and direct comparisons can be made only for coatings of equal thickness and similar structure. An improved test for bond strength must be developed if this parameter is to be used effectively for either process or product control.

It appears that levels of bond strength of combustion-WSA coatings currently attained are adequate for less severe environments (i.e., below-deck structures, steam valves, etc.). However, variable performance of topside components suggests that strength may be marginal to inadequate for the more severe marine environments. Although it cannot be guaranteed that increased bond strength will increase performance of these components, the conservative approach to design would dictate that the highest attainable bond strength be developed until otherwise proven not necessary. The committee recommends that the Navy take immediate action to increase the bond strength of the coatings on more corrosion-prone topside components commensurate with what is attainable practically with existing equipment and facilities. From a longer range point of view, new processes and/or process controls should be introduced to further increase bond strength. In addition, it is recommended that the Navy initiate a research study to define clearly the relationship between bond strength and coating separation as a result of service. Realistic minimum acceptable values of bond strength for long-term service under a wide range of representative service conditions should be determined.

Porosity is considered to be the second single most important coating characteristic with respect to performance in the marine environments. Excessive interconnected porosity can initiate galvanic corrosion of the coating by providing a direct path for the liquid electrolyte (seawater) to couple the substrate (cathode) and coating (anode). Anodic dissolution of the coating will occur internally as it acts to protect the steel substrate from corrosion. In a short time, however, the coating will be destroyed by corrosion, and the substrate will be attacked. Underlayer corrosion and weakening of the bond in surrounding areas also may occur.

Current levels of porosity in combustion-WSA coatings do not appear to be detrimental to performance in less severe environments (i.e., below-deck structures, steam valves, etc.). Porosity, however, is believed to contribute to accelerated corrosion and premature failure of above-deck components exposed to the more severe marine environments. Again, there is no established direct relation between porosity and corrosion under these conditions, and limiting levels of porosity have not been defined. Although there is no assurance that decreased porosity will improve performance, deductive reasoning indicates that improvement would occur if pores did not exist or were sealed effectively. The committee recommends that the Navy take immediate action to reduce and/or seal off porosity in WSA coatings on the more corrosion-prone topside components. In addition, a research study should be undertaken to determine the exact relation between porosity and performance in marine environments and to establish realistic, acceptable levels of coating porosity.

Porosity is characteristic of all coating processes (except low pressure plasma spray) and no one process has a unique ability to produce dense coatings. Dense coatings can be produced by any process, but necessary controls and process parameters are not clearly defined. It is recommended that a controlled variables study be conducted for both the gas-combustion and arc-wire processes to improve the understanding of the nature and degree of control needed to produce high-density coatings on a consistent basis. Capabilities and limits of each process should be defined more clearly.

The committee also recommends that the Navy take immediate action to reduce porosity in coatings as currently produced. The recommended procedure is to infiltrate the coating after chromate priming with an aluminum-flake vinyl sealer. Manufacturers' procedures for this step should be followed rigorously. This should be adopted as routine practice on all WSA-coated parts and structures.

An analysis of coating characteristics and variations indicates that coating structure and properties do not provide an adequate technical basis for coating process selection. Each of the available spray processes appears to be capable of producing needed coating characteristics for a marine corrosion protection system. Choice of process, therefore, often can be based on economic and operational considerations instead. The potential for mechanization and automation to reduce coating variability should be another consideration in process selection.

Coating thickness is the most difficult coating characteristic to control in thermal-spray processing. Large variations in thickness can be expected in any parts where hand-held guns are used, regardless of how skilled an operator may be. The only solution to this problem is mechanization and automation, preferably with feedback computer control. The operator should be removed from physical control of the process whenever possible in order to produce the most uniform and reproducible coatings. Feedback controls are needed to continually adjust process variables. Within the past few years, techniques have been developed to control these and other important variables in a real-time mode using microcomputers and robotics. It is only a matter of time until this technology expands in the field to upgrade production of all thermal-spray coatings. It is recommended that the Navy act to accelerate this transition by initiating and supporting a manufacturing development program on mechanized and automated wire-thermal-spray processes. Initially, this should include a feasibility study for both gas and arc wire-spray systems. The basic robotic equipment would be similar for both; only the motor control systems will vary. Process development should then proceed with the system that shows the greatest potential for mechanization and automation. If both systems appear to be equal, it is believed that the initial development should concentrate on processes that seem best adapted for high-rate, repetitive production coating of large, simple surfaces. This could be followed by work on more advanced systems for coating smaller and more complex structures and components. The Navy has taken the first step in this direction by mechanization of arc-wire-spray heads for nonskid deck surfacing.

CHAPTER 6

TESTING AND EVALUATION OF COATINGS

CURRENT NAVY PRACTICE

The quality of thermal-spray coatings currently is governed by "process controls," i.e., proper equipment, operating conditions, operator training etc. (Sulit and Vanderveldt 1981). The product quality control employed is minimal, consisting primarily of visual inspection and magnetic permeability thickness measurement. In addition, profile tape is used to measure surface roughness of grit-blasted surfaces prior to coating. Destructive tests of coupons sprayed along with the parts are conducted to determine bond strength and coating adhesion. The bend test is used for day-to-day production control whereas the tensile test is used primarily for qualification testing of operators.

NDE tests and procedures currently available for such important characteristics as bond separation, coating delamination, porosity, coating thickness, and substrate roughness and quality prior to coating are not considered to be applicable to WSA preservation systems. One of the major limitations is the inability to use these processes for inspection of large, complex components, many of which are coated in the field aboard ship and none of which can be removed readily for periodic in-service inspections. Most current NDE techniques for metallic coatings have been developed for use on small components such as aircraft gas turbine blades. The Navy recognizes the need for more extensive use of NDE in quality control and assurance of WSA preservation systems and is pressing for the development of procedures for both production components and in-service parts and structures (Sulit and Vanderveldt 1981).

Corrosion Testing

The Navy uses laboratory, simulated service, and shipboard corrosion tests to assess the performance of WSA preservation systems. Accelerated corrosion tests are performed in the laboratory to assess the relative performance capabilities of different coatings and coating processes in marine environments. The basic test employed is the salt-spray-mist type (Rogus and Vapniarek 1980). Test coupons or simulated components are exposed to alternate cycles of temperature and salt spray. The test for evaluation of steam valve coatings, for example, consists of alternate cycles of heating to 900°F in air and then exposing to salt spray at ambient temperatures (Rogus and Vapniarek 1980). Results of such tests with respect to relative performance of different coatings have been discriminating and in general tend to agree with results in service. Currently, no tests are in progress to study the effect of product and process variables on behavior.

Simulated service tests are conducted by exposure of test samples at shore sites. Large pilings are driven into sand in surf areas, and small samples are exposed in racks suspended from docks or installed on shore (Navy, Department of 1966). Tests of this type were conducted in the past to assess the potential of WSA preservation coatings for shipboard service, although they are not being used today to characterize or study the behavior of WSA coatings or sealants.

The major test program currently in effect is the shipboard corrosion test program. Thousands of coated parts are currently in service on a wide variety of Navy ships in the Pacific fleet. Nearly all major types of naval vessels now have coated components, including carriers, cruisers, destroyers, and LSTs.

The shipboard preservation test program is of two types: controlled tests of components on designated ships and uncontrolled tests of structures and components on normal fleet vessels. Tests of the first category are illustrated by the extensive valve coating evaluation program (Schaper 1979). The test program on the USS Standley (CG 32) consists of evaluation of WSA preservation coating on a statistical sample of 360 propulsion plant valves of all different sizes, shapes, and operating conditions. Each valve is tagged and documented with respect to coating process history and characteristics. The valves are being exposed to actual engine and boiler room operating conditions for a 5-year period while the USS Standley cruises in the Pacific on its normal fleet mission. Each valve is inspected at 6-month intervals and results are reported yearly (Schaper 1979). This study will evaluate coating performance from a life-cycle, cost-effectiveness point of view. It is a comparative study in which other coatings such as Sermetal and aluminum paint are evaluated simultaneously. The program does not include a study of WSA process or product variables.

The major shipboard test of WSA preservation systems is very broad in scope but is largely not controlled in the sense that a materials test program, such as that on the USS Standley, would be. A wide variety of WSA-coated components and structures are being installed on many different naval vessels when they are in port for either routine or major repair and maintenance. Table 7 lists different components that have been authorized for WSA preservation coating and shipboard installation (Navy, Department of 1980a).

These parts are not identified with respect to source or coating history and characteristics. They are coated by what is considered to be the best available practice as defined by WSA preservation system specifications

TABLE 7 Areas and Components Approved for Wire-Sprayed Aluminum (WSA) Preservation Aboard Surface Ships (Navy, Department of 1980a)

Machinery Space Components

- Low-pressure air piping
- Auxiliary exhaust (stacks, mufflers, manifolds)
- Turnstile machinery
- Diesel headers and exhaust systems
- Steam valves, piping, and traps (except safety valves and steam turbine control valves)
- Air ejection valves
- Boiler skirts

Topside Weather Equipment

- Aircraft and cargo tie-downs
- Stanchions and flagstaffs
- Deck machinery castings and foundations
- Pipe hangers
- Rigging fittings-blocks and hooks
- Lighting fixtures, brackets, and signal lamp housing
- Ladders
- Refueling stations
- Intake plenums
- Safety net components
- Weather deck stowage boxes
- Bulkhead pad eyes
- Aluminum helo decks
- Scupper brackets
- Chocks, bits, cleats, and roller chocks
- Capstan/gypsy heads (except wear area)
- Fire-station hardware
- Steel catwalks
- Hangers, brackets and supports
- Steel attached to aluminum bulkheads
- Hatches and scuttles and watertight doors
- Boat davit machinery (components)

Interior Wet Spaces

- Decks in water rooms and water closets
- Fan room decks and equipment support foundations
- Air conditioning room decks and equipment support foundations
- Deck surfaces
- Bilges
- Pump room decks and equipment support foundations
- Water heater room decks and equipment support foundations
- Deck plate supports
- Machinery foundations
- Bulkhead

and process instructions (Department of Defense, 1981; Navy, Department of, 1978). The parts are installed for evaluation of service life testing over a 5-20 year time period. Many, but not all, are inspected periodically as ships return to port. A unified inspection and reporting system to track and document the performance of these components has not been established. The Navy does not have an ongoing shipboard panel test evaluation program designed for long term sea exposure tests of controlled and documented test samples.

STATE-OF-THE-ART SUMMARY

Nondestructive Evaluation

The nondestructive evaluation of thermally sprayed coatings is narrow, primarily confined to thickness, roughness, visual, dye penetrant, ultrasonic, and electroconductive tests. The last two are developmental in nature, whereas the first four are routine, using calipers, micrometers, height gauges, and magnetic gauges; profilometers and replicative techniques; pocket magnifiers and stereoptic microscopes; and dye penetrants with developers. Each measures a particular attribute contributing to the eventual assessment of good or bad. Newer, more sophisticated techniques are, however, currently being evaluated; these involve the use of thermal, light, sound, magnetic, and electrical techniques. A detailed description is given in the thermal-spray manual (American Welding Society, in press).

Much work has been carried out recently to develop NDT procedures based on ultrasound and optics, and these promise to be more suitable for testing thermally sprayed coatings (Steffens and Crostack 1981). The ultrasonic techniques include the application of specific wave modes such as polarized transverse waves, surface waves, and Lamb waves, which are useful for the improved testing of coatings and interfaces. Moreover, interference in sprayed coatings can be exploited for NDT purposes by using special transducer equipment. The use of controlled acoustic signals (the CS technique) is recommended for the examination of coating structures and defects, particularly in describing their type, dimensions, and position, because it allows a frequency-dependent determination of these quantities to be made within wide limits. Evaluation methods such as thermography or the optical visualization of the acoustic field offer further improvements in the detection and description of defects. The limits of the applicability of this technique are demonstrated by means of test results from flame-arc- and plasma-sprayed coatings.

Passive methods such as optical holography and acoustic emission analysis are also suitable for sprayed coatings. Excitation of the test sample--for example, by mechanical or thermal loading--is required in these passive methods. Optical holography can be used to obtain information on defects by visualizing the deformation of the coating.

Applications of these test methods to sprayed steel coatings have given encouraging results. However, both active and passive NDT methods have physical limitations, particularly with respect to size and shape of components. Most available techniques are limited to small, simple shapes.

Destructive Tests

Thermal-sprayed coatings are usually tested destructively--i.e., metallographically or by applying various strength tests. In most cases, the results of NDT procedures, which are of major importance for the inspection and eventual repair of structural components, do not allow satisfactory decisions to be made on component safety.

The single most important property of a thermally-sprayed deposit is its adhesion to the substrate. This property more than any other determines the usefulness and application of coatings. The coatings are usually tested in tension according to applicable ASTM standards. The test initially consists of thermal-coating one face of the substrate and then bonding a loading fixture to the coating with a suitable adhesive. The coating is then ground around the base of the loading fixture so that shear stresses are avoided during the tensile test of the assembly. Simple bend tests are used for rapid, inexpensive evaluation of coating adhesion. There is no ASTM or other standard procedure for conducting bend tests or for evaluation of test results.

The mode of coating failure in tensile or bend testing can be described as either adhesive or cohesive. Adhesive failure takes place when the entire coating separates from the substrate, whereas failure entirely within the coating is cohesive failure. True adhesive failure (also termed interfacial failure) rarely occurs because of the rough nature of the substrate surface, and adhesive failure in this case is defined as taking place near the interface where the fracture surface exhibits areas devoid of the coating.

Many other techniques (American Society for Testing and Materials 1979a; Canadian Government Specification Board n.d.; Deutschen Normen n.d.; Petersen 1969; Hermanek 1978; Pratt and Whitney Aircraft Group 1968; Lyashenko et al. 1969a,b) have been devised that are based on a tensile method of testing a coating; they all suffer from the same disadvantages and have similar limitations:

- If failure occurs within the adhesive only, the area within the coating is considered in the calculation to find the stress at failure. This method is inaccurate because the test result has indicated either defective bonding of the sample or nonnormal loading of the sample.

- The value of the measurements is influenced by the symmetry of the experimental setup and by the penetration of epoxy into pores of the coating.

- The elevated curing temperature of the adhesive may affect the adhesion of the coating, since the residual stress distribution may be altered.

- The fracture surface of a test specimen normally exhibits both adhesive and cohesive failure. The tensile adhesion test finds only an average value when both of these failure modes act together and does not establish which failure mode limits the strength of the coating.

- The mechanism by which the coating structure contributes the adhesion is not readily ascertained without a quantitative assessment of the various modes of adhesion. The tensile adhesion test does not readily permit such mechanistic studies.

- Flaws in the form of microcracks, porosity, and second-phase inclusions within the coating will affect the adhesion of the coating. The role of these microstructural features of the coating cannot be examined by the tensile adhesion test.

Despite all the apparent drawbacks, the tensile test is relatively simple to carry out and is useful for providing a ranking of various types of coatings.

CORROSION TESTING

Three types of corrosion tests are used in the development and characterization of corrosion-resistant alloys and coatings: laboratory tests, simulated field tests, and service tests. Laboratory tests generally are conducted to obtain an understanding of materials behavior as influenced by composition, structure, process variables, etc. These tests are largely investigative in nature and are important to guiding the development and use of new materials. Simulated field corrosion tests can be looked on as a parallel to pilot-plant testing of materials. These tests generally are performed on coupons rather than actual components and may or may not be done in a real service environment. The test environment, however, closely simulates actual service environments. Field tests are used primarily for comparative evaluation of materials behavior and are conducted over a long time span, nominally measured in years for atmospheric corrosion testing. Service tests are conducted with actual operating components and are used primarily to qualify materials for production applications and to establish basic long-term performance characteristics. Information gained from a careful metallurgical evaluation is fed back into laboratory and field-test programs to aid in the modification or further development of materials for improved performance. Service tests also are used to establish the life-cycle costs and cost-effectiveness of new materials.

A comprehensive review of corrosion testing procedures and practices has been prepared by Shrier (1963). A much more detailed compilation of corrosion tests and evaluation procedures in book form has been published by the Electrochemical Society (1971). The majority of the tests are for bulk metals and alloys, but they should be equally applicable to testing of coated metals.

The following tests are widely used to assess corrosion behavior of both coated and uncoated alloys in the laboratory: alternating immersion test, Watts-like test, humidity test, salt spray (salt fog) test, and electrolytic test. Of these, the one which is considered to have good potential use with aluminum coated steel is the electrolytic test. Since the primary mode of protection is galvanic, such a test is ideally suited to evaluate coating behavior. A true accelerated corrosion test can be realized by electrolytic stimulation of the corrosion process.

Potentiostatic methods have been widely used to study the mechanism of corrosion and are very useful for determining relative corrosion resistance of metals. Such measurements may be made on a regular basis on panels exposed aboard ship or on aluminum that is not coated with paint or with an anti-skid material. The environment should be seawater, and it might be retained within an "O" ring or in a cylinder sealed to the aluminum. Vertical surfaces may be tested by means of a porous wick saturated with seawater whose contact area to the aluminum is limited by insulating material. Test procedures and conditions are described in the following ASTM specifications: ASTM G 5, Recommended Practices for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements (Sulit and Vanderveldt 1981); and ASTM G 3, Recommended Practices for Conventions Applicable to Electrochemical Measurements in Corrosion Testing (Steffens 1980).

Simulated Field Tests

Atmospheric Tests--Standardized techniques have been established for testing small samples or coupons mounted on racks exposed to coastal (marine) environments. The normal test panel sizes are 4 x 6, 3 x 6, 4 x 12-3/4, or 3 x 12-3/4 in. Size is not critical, however, and panels of any size can be used. The behavior of panels is assessed by visual examination, weight change, and change in mechanical properties. For WSA-coated panels this also would include coating thickness, porosity, and bond-strength measurements. Pit depth, number, and size also are measured in cases where pitting occurs. Electrolytic (potential) measurements can be used to record continuously the potential or corrosion currents. The procedures and approach to atmospheric testing are covered by the following ASTM specifications: ASTM B 537, Rating of Electroplated Panels Subjected to Atmospheric Exposure (Steffens 1982); ASTM G 33, Recommended Practice for Recording Data from Atmospheric Corrosion Tests of Metallic Coated Specimens (Steffens 1980); and ASTM G 50, Recommended Practices for Atmospheric Corrosion Test of Metals (Steffens 1980).

Tests in Natural Waters--This test is a variation of atmospheric corrosion tests in which samples are immersed or partially immersed in seas, oceans, lakes, or rivers. Details of rack construction and design are given in the corrosion testing handbook (Capp 1914). All specimens to be compared with each other should be exposed at the same depth or range of depths. Isolated samples exposed at different depths will not corrode the same as continuous specimens that extend through a range of depths. Differential aeration and concentration cells have a large effect on behavior. The following ASTM specification is applicable: ASTM G 52, Recommended Practice for Conducting Surface Seawater Exposure Tests on Metals and Alloys (ASTM n.d.).

Service Tests

Since it is often difficult to define and/or simulate actual operating corrosive environments in many applications, it is common practice to expose corrosion test samples in operating equipment. This would be particularly true for WSA preservation systems on naval ships, which cruise over the world's oceans and seas on a year-round basis. Such samples may be either test coupons or actual operating components, i.e., a steam line valve, a deck stanchion, or a deck or bulkhead structure. Where test coupons are used, it is important that they be isolated and electrically insulated from each other and supporting structures to prevent galvanic corrosion. One common form of test rack uses circular large-diameter disk samples mounted on plastic spindles with plastic spacers. Guidance for this type of test is provided by ASTM G 4, Recommended Practices for Conducting Plant Corrosion Tests (Navy, Department of 1966; Steffens 1980).

Evaluation, Analysis, and Data Acquisition

One of the major problems in corrosion testing is in the measurement, analysis, and recording of test results and data. Sample identification and documentation also are potential problem areas. Careful planning at the start of tests and detailed recording of all significant materials, test conditions, and performance data are essential. The following ASTM specifications are a useful guide to conducting meaningful corrosion tests: ASTM G 15, Definition of Terms Relating to Corrosion and Corrosion Testing (Steffens 1980); ASTM G 1, Recommended Practices for Preparing, Cleaning, and Evaluating Corrosion Test Specimens (Steffens 1980); ASTM G 46, Recommended Practice for Examination and Evaluation of Pitting Corrosion (Steffens 1980); and ASTM D 1654, Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments (American Society for Testing and Materials 1979b).

All types of corrosion tests and in particular field and service tests should be conducted on a statistically sound basis. Single, duplicate, or even triplicate tests are not adequate. The Weibull function has been found to be very useful in the analysis of the corrosion behavior and time-to-failure of high-temperature coatings (Wurst 1968) and a reasonable distribution for analysis can be obtained from as few as 10 samples. The following specification furnishes additional guidance: ASTM G 16, Applying Statistics to Analysis of Corrosion Data (Steffens 1980).

Metallographic and materials analyses by Auger (AES), electromicroprobe (EMP), scanning microscope (SEM), transmission microscopy (TEM), and X-ray diffraction (XRD) techniques are used to interpret the results of corrosion tests and aid in the development of mechanistic explanations of behavior. All too often these important scientific tools are not incorporated into corrosion test programs, and only visual observations and weight changes or perhaps changes in mechanical properties are measured and reported. It is important that interpretive metallography and materials analyses using the techniques cited be included in corrosion test programs. Performance of coatings cannot be judged solely on a simple visual and weight-change basis. Reactions within the coating and at the interface with the substrate also must be characterized to assess performance. Metallographic and materials analyses should be used to support all types of corrosion tests--laboratory, field, and service.

COMMITTEE ASSESSMENT

The Navy and its industrial spray coating contractors appear to be utilizing available and proven NDE techniques and mechanical test methods for evaluation of coating quality. Several emerging and developing NDE techniques may be of value in the near future. Two of the most important of these are the modified ultrasonic techniques (CS technique) and optical holography as recently described in detail by Steffens and Crostack (1981). These investigators believe these methods to be most promising for detection of bond separation, cracks, and porosity in thermal-spray coatings. Both methods used separately or in conjunction appear to have the potential for use as effective product control and quality assurance NDE techniques. It is recommended that the Navy undertake a program to further develop and evaluate these procedures for evaluation of WSA preservation coatings and support the development of practical test facilities for both shore and ship-based use.

The Navy's corrosion test and evaluation program for WSA preservation systems has advanced rapidly from minimal laboratory and field test studies (Rogus and Vapniarek 1980; Navy, Department of 1966) to a large, full-scale service evaluation of shipboard components (Schaper 1979; Wurst 1968). Coated structures and components for the most part are considered to be production hardware manufactured by the optimum practices in accordance with applicable specifications. A major effort has not been launched to document, track, and characterize many of the components currently being put into shipboard service. In addition, no plan has been developed and work has not begun on testing and evaluating in laboratory, field, or service the variations of WSA coatings in terms of composition and structure. The committee believes that this is a major deficiency or weakness in the Navy program to put WSA preservation systems into more widespread use. Failure to undertake simultaneously a technically sound supportive corrosion test and evaluation program introduces a fairly high element of risk into the overall program. Whereas it is generally agreed the systems currently used will survive 2 to 5 years in above-deck sea-exposed service, it is considered doubtful that the ultimate goal of 15 to 20 years of service will be realized. The WSA preservation system is capable of providing over 20 years of maintenance-free service under such conditions, but extensive corrosion testing and evaluation is needed to develop the optimum material and production practices and controls.

There is a need for a systematic evaluation of parameters that govern coating performance. These include factors such as coating composition and structure, process parameters and controls, surface sealants, and paints. The number of parameters is large, with many complex interactions. Field or service test corrosion evaluation is precluded for the most part, and laboratory testing is needed to evaluate systematically the effect of various parameters on corrosion resistance. Laboratory tests should include most of those described in the section on service tests. These tests should be supplemented with both field and service tests after sufficient understanding has been obtained to permit planning of realistic long-term controlled tests.

The committee recommends that the Navy sponsor and conduct a comprehensive corrosion test program to support their major investment in WSA preservation systems. It is unlikely that industrial coating sources will on their own conduct any supporting studies because of the fragmented nature of the market. It is recommended that a Navy-sponsored and Navy-directed program be conducted both in-house at naval research facilities and under contract at industrial research organizations.

A historic parallel to such an effort is found in the refractory metal sheet rolling program conducted between 1950 and 1960 (National Materials Advisory Board 1[illegible]). This program was originally established by the Bureau of Naval Weapons to identify the variables and causes responsible for variation of refractory metal sheet and to develop remedies for these difficulties. It was intended to provide comprehensive industrial technology for production of high-quality, reproducible, usable materials. The needs with respect to WSA preservation systems are much the same. The program was expanded through DoD to include the other services and received supplementary funding. The National Materials Advisory Board provided a supporting panel of technical experts who aided in coordination and technical implementation of the program.

The committee recommends that the Navy establish a number of field and shipboard marine corrosion test sites for more extensive field and service testing of large numbers of WSA corrosion test panels. Field sites should consist of more worldwide coastal and/or harbor-based test rack sites. Consideration should be given to large buoys as a possible approach to sea-based test sites. With respect to shipboard sites, it is recommended that corrosion test racks be installed on selected Navy ships for a sea exposure of corrosion test panels. Space between deck stanchions could be used without interfering with ship operations.

With respect to planning and conducting corrosion test programs, it is recommended that a statistical approach be used whenever possible. The Weibull function is recommended as a very useful extreme value function suitable for corrosion test data analyses. ASTM specifications related to corrosion testing should be followed at all times, particularly with respect to procedures for sample preparation, conducting tests, and evaluation of test results. More extensive use should be made of metallographic and materials analyses techniques (AES, EMP, SEM, TEM, and XRD) in the evaluation of coating behavior to develop a needed understanding of factors that control performance and govern coating wear-out.

An analysis of applicable destructive tests for coating adhesion and bond strength indicates that no suitable tests exists for quality control of day to day production. The tensile test is not considered accurate and reliable for coatings less than 15 mil thick due to the effect of epoxy glue penetration in coating pores on measured strength values. In addition the test is costly and often cannot be conducted in a timely fashion. The bend test is well suited to a simple, fast, and effective production control test but has no technical basis for relating results to performance. In addition, the test has not been standardized. A suitable test must be developed and standardized for use as a routine production control. Product quality should be sampled and evaluated on a random basis using technically sound destructive tests.

CHAPTER 7

SAFETY CONSIDERATIONS

CURRENT NAVY PRACTICE

Considerable regard for safety of personnel and equipment used to prepare surfaces and deposit coatings by thermal-spray metallization is incorporated in current Navy practice. Process specifications and instructions and training manuals set forth the major safety concerns and requirements (Navy, Department of 1980c and Schaper 1981). Major factors that are controlled include (a) dust and fume-inhalation, combustion, and explosion hazards; (b) gases combustion and explosion hazards; (c) ultraviolet radiation hazards; (d) noise; and (e) electric shock hazards.

Safety considerations currently in use apply to the deposition of coatings--that is, to the control of coating processes. Current Navy use does not indicate any hazard in the use of WSA coatings, and no safety problems in shipboard use have been identified to date.

STATE-OF-THE-ART SUMMARY

Coating Deposition

The state of the art with regard to personnel protection and safety recognizes all of the hazards listed above (American Welding Society, 1973). There are no additional hazards related to coating deposition and manufacture that need to be mentioned. One recognized hazard, however, often is not fully understood and should be emphasized. This is the explosion hazard that is unique to thermal-spraying of aluminum and zinc. When spraying aluminum wire, 4 to 15 percent of the material sprayed ends up as particles less than 2 microns. This material, if it settles in a duct or other area, can generate enough heat as it oxidizes to burn the paint off a duct wall. Similarly, suspended dust in an area can be ignited if adequate concentrations are present. The solution is good ventilation to extract all dust in the spray area (ventilation velocity of 250 fpm), adequate air flow to dilute dust (5,000 cfm/gun), and duct transport velocities of 4,500 fpm to prevent settling of dust. If the dust is to be collected, a water-wash scrubber is currently the most accepted method. Since hydrogen is evolved when the powder oxidizes in the collector water, provisions should be made to vent any hydrogen in the system before and after spraying.

Coating Use

There are three potential safety hazards in the use of sprayed aluminum and/or zinc coatings on naval ships: sparking, vaporization or atomization, and fire. The first could be encountered in everyday use, whereas the second and third would be encountered only in the event of explosions or fires aboard ships.

Sparking

Aluminum is considered nonsparking; however, on impact with rusty steel, sparks can occur (Van Horn 1967). The tendency to generate sparks depends on composition and hardness of the aluminum. In general, the very soft, pure aluminum used for coatings would have the least tendency to generate sparks. Greatest tendency is for severely deformed, work-hardened surfaces and for aluminum alloys containing over 2 percent magnesium (Van Horn 1967).

Small aluminum particles must be mixed with iron oxide (rust) for sparking to occur. Aluminum alloys dropped from a height of 2 to 4 meters on an inclined rusty iron surface show a 50 percent probability of sparking and igniting a methane-air mixture (Bailey 1978). Sparking occurs only when clean aluminum strikes a rusty steel surface (or vice versa). Sparking does not occur on impact of rusty steel with aluminum paint (Eckart 1970) or with wet or oily surfaces (Starkey 1978). Sparking also does not occur on impact of aluminum with clean steel, stainless steel, and typically used tools (Starkey 1978). There is no known case in industry of aluminum spray-coated steels being the cause of a specific sparking incident in service (Bailey 1978). Sealing and painting of WSA aluminum coatings should reduce the hazard potential to near zero.

Vaporization or Atomization

Explosively induced plane shock waves can produce large volumes of vaporized and atomized (melted) metals (Aherns 1972). The amount of vapor or liquid drops generated for any given shock is a function of the amount of porosity in the metal and increases as porosity increases. Specific volumes of 1.4 to 2.0 times the fully dense volume produce maximum melting and vaporization. For aluminum, a specific volume of 1.2 results in melting and atomization with an induced shock impact of 2 km/sec. A specific volume of 1.4 will vaporize with an impact of 5 km/sec. Fully dense material will melt but not vaporize at the same impact but will not melt at 4 km/sec impact (Aherns 1972).

It is considered likely for sprayed aluminum and zinc or zinc-aluminum alloy coatings to be melted, atomized, and perhaps vaporized as a result of explosions such as might occur under attack conditions or with accidents that create explosions. This in turn can result in additional explosion (metal powder) or fire hazard or in personnel hazard from inhalation of metal vapors. The fire hazard is discussed in the following section. The personnel hazard with respect to toxic fumes is nil for aluminum but may be appreciable for zinc. Aluminum and aluminum oxides are not considered toxic materials (Fassett and Irish 1963). Zinc toxicity is variable and generally considered to be low. Although zinc inherently is not a toxic element (Fassett and Irish 1963), when heated in air, it oxidizes and may burn, evolving zinc oxide fumes. When inhaled fresh, these fumes can cause a disease known as "brass founders ague," "brass chills," or "metal fume fever." This is a malaria-like illness with chills, fever, nausea, cough, fatigue, weakness, and aching of the head and body as major symptoms. Mental confusion and convulsions are possible. The symptoms appear within a few hours after exposure, and the illness lasts about a day (Fassett and Irish, 1963). The maximum concentration of zinc oxide permitted for brief exposure without an effect is 45 mg/m^3 for 20 minutes (Fassett and Irish, 1963).

Fire

Both zinc and aluminum can ignite and burn in air under certain conditions. Aluminum must be heated to the melting point of aluminum oxide (2050°C) for ignition to occur (Merzhanov et al. 1977). Ignition will occur regardless of the oxygen content and pressure of the gas (air) and the particle size of the aluminum (Friedman and Marek 1962). The time for a particle exposed to a gas temperature of 1937-2087°C to ignite increases as a linear function of the particle diameter squared (d^2):

Particle Size	Ignition Time
35 μm diameter	4 m sec
50 μm diameter	6 m sec
67 μm diameter	14 m sec

Once ignited, the burning time also increases with particle size:

Particle Size	Burning Time
23 μm diameter	4 m sec
150 μm diameter	13 m sec

In air with 5.5 percent excess O_2 at 2237°C, the burning time is proportional to $d^{1/2}$. Once ignited, aluminum will continue to burn as long as the gas temperature remains above about 2000°C (Bouriannes 1973). If the gas cools below the melting point of aluminum oxide, combustion will stop in air at normal (atmospheric) pressure.

The combustion of aluminum will be self-sustaining at lower temperatures only if the pressure of oxygen in the atmosphere is above some critical value, p*. At pressures below the critical value, an external source of heat must be supplied to keep the temperature above 2000°C for combustion to be sustained (Bouriannes 1973). The critical pressure is in excess of 50 bar; combusion of aluminum is not self-sustaining in air at atmospheric pressure.

Zinc behaves in a similar manner, requiring external heat to sustain combusion in air at atmospheric pressure. However, the temperature to sustain combustion is comparatively low. Zinc melts at 419°C and the liquid vaporizes rapidly above 500°C; it boils at 907°C at atmospheric pressure. Zinc vapor burns with a characteristic green flame, producing finely divided particles (<1 µm diameter) of zinc oxide. Copious amounts of zinc oxide are formed in heating molten zinc in air at 500°C (Fassett and Irish 1963).

COMMITTEE ASSESSMENT

Safety hazards with respect to thermal-spray coating processes and the manufacture of coated parts or structures are recognized and adequately covered by current Navy process specifications and instructions. There is no new or emerging technology that needs to be considered at this time.

Safety also is not a problem in the use of either aluminum or zinc coated steel in most applications. Spark ignition of combustible gases, which can occur when aluminum is struck with rusty steel, is considered to be a problem in underground mines. An analysis of this behavior, indicates, however, that little if any problem would exist with regard to shipboard applications. WSA preservation systems will be sealed and usually painted, a condition under which sparking is not likely to occur, even with repeated impacts. One possible exception would be the use of aluminum deck coatings where rusty steel objects would be likely to be dropped or dragged on the surface in the presence of volatile fuels (gasoline, jet fuel, etc.). The Navy should recognize this hazard and consider the possibility and probability of spark-initiated explosions in any applications where continued impact of bare aluminum with rusty steel is likely to occur. WSA components should be sealed and painted to reduce the probability for sparking on accidental impact with steels in all applications.

Use of zinc-coated steels can present a unique safety hazard aboard ships under conditions where explosions and/or fire can occur (i.e., under wartime attack or shipboard accidents). Zinc melts, vaporizes, and burns readily, producing zinc oxide vapors that could disable ship personnel temporarily (several days). It is beyond the scope of this committee to analyze the hazard potential with regard to use of zinc under such conditions, but a real threat is considered to exist. The committee recommends that shipboard testing and/or use of steels coated with zinc or zinc-aluminum be minimized until such time that an in-depth hazard analysis can be made by the Navy with respect to zinc oxide toxic effects in case of explosion or fire. Aluminum does not present either fire or personnel hazard, and no safety problems with regard to shipboard use of thermal-spray aluminum coatings under even the most severe conditions of explosion and fire are apparent.

REFERENCES

Aherns, T. J. 1972. Shock melting and vaporization of metals. Journal of Applied Physics 3:2443-2445.

Alloy Metals, Inc. 1981. Computer controlled robotic plasma spray system. Troy, Michigan.

Alumbough, R. L. and A. F. Curry. 1978. Protective coatings for steel piling: additional data on harbor exposure of ten foot simulated piling. Technical Report No. TR711S. Port Hueneme, California: Naval Facilities Engineering Command.

American Society for Testing and Materials. 1979a. Standard method for adhesive or cohesive strength of flame sprayed coatings, C 633. Philadelphia, Pennsylvania.

American Society for Testing and Materials. 1979b. Rockwell hardness and rockwell superficial hardness of metallic materials. ASTME 18. Philadelphia, Pennsylvania.

American Welding Society. 1973. AWS committee on thermal spraying: recommended safe practices for thermal spraying. Report AWS C2.1-73. Miami, Florida.

American Welding Society. 1974. Corrosion tests of flame-sprayed coated steel, 19 year report. AWS C2:14-74. Miami, Florida. (Extended Abstract in Welding Int. 53(1974):363-70.)

American Welding Society. In press. First thermal spray manual. Miami, Florida.

Bailey, J. C. 1976. U. K. experience in protecting large structures by metal spraying, pp. 223. In Proceedings of the 8th International Thermal Spraying Conference. Miami, Florida: American Welding Society.

Bailey, J. C. 1978. Aluminum - coated steels: sparking and the fire hazard. Metal and Materials, October, pp. 26-27.

Ballard, W. E. 1963. Metal spraying and the flame deposition of ceramics and plastics. London, England: Griffin and Company.

Bensimon, R. 1976. Bridges and Large Structures in France, pp. 232. In Proceedings of the 8th International Thermal Spraying Conference. Miami, Florida: American Welding Society.

Bless, M. and L. Moskowitz. 1979. External preservation of steam valves using wire sprayed aluminum coatings. NAVSEA S6435-AE-MNA-010/W Spray CTT, NAVAIR 50-20-1. Lakehurst, New Jersey: Naval Air Engineering Center.

Bouriannes, R. 1973. Experimental investigation of the combustion of aluminum in oxygen - Argon mixtures, nitrogen, and air. Rev. Int. Hautes Temp. Refract. 2:113-124.

British Standards Institution. 1977. Code of practice for protective coating of iron and steel structures against corrosion. BS 5493. London, England.

Brown, R. L. 1979. The thermal spray deposition of metals and ceramics--introductory notes. AMTE (HH)/MZ/MAN 1, Issue 1. Holton Heath, England: Metallurgy and Ceramics Division, Admiralty Marine Technology Establishment.

Canadian Government Specification Board. n.d. Recommended Methods for Inspection of Metallizing 23-GP-8.

Capp, J. A. 1914. Rational test for metallic protective coatings. Proc. American Society of Testing Materials 14:474-78.

Conde, J. F. G., C. S. Dinbylow, R. L. Brown and A. F. Taylor. 1981. Applications of cladding, thermal spray, and advanced coating techniques for marine service. Presented at NATO Defense, Research Group Seminar on Advances in Structural Materials in Relation to Defense Applications, April 1981, Brennen, West Germany. Holton Heath, England: Metallurgy and Ceramics Division, Admiralty Marine Technology Establishment.

Department of Defense. 1981. Metal sprayed coating systems for corrosion protection aboard Naval ships. Report DoD-STD-2138(SH). Washington, D.C.

Deutschen Normen (German standard). n.d. Prufung Termisch Gesprtizler Metallischer Schichten; Ermittlung der Hafz-Zugfestigkeit im Stirnzugversuch DIN 50160.

Eckart, C. 1970. Use of aluminum paints in places where there is an explosion hazard. Fette-Seifen-Anstrichmittel 2:94-97.

Electrochemical Society Inc. 1971. Handbook on Corrosion Testing and Evaluation, p. 873. New York, New York: John Wiley and Sons.

Fassett, D. W. and D. D. Irish. 1963. Industrial Hygiene and Toxicology, Vol. II-Toxicology. New York, New York: Interscience.

Friedman, R. A. and A. Macek. 1962. Ignition and combustion of aluminum particles in hot ambient gases. Comb. and Flame 1:9-19.

Gupta, D. K. and F. J. Pennici. 1981. Manufacturing technology for vacuum plasma spray overlay coatings. Manufacturing Technology Division Report FR 15807, AFWAL/MLTM, Wright Patterson Air Force Base, Ohio: Air Force Wright Aeronautical Lab.

Hermanek, F. J. 1978. Determining the adhesive/cohesive strength of thin thermally sprayed deposits. Welding Journal 57(11):31-35.

Hermanek, F. J. 1979. Manufacturing technology for automated thermal spray processes. Report AFML-TR-79-4186. Wright-Patterson Air Force Base, Ohio: Air Force Wright Aeronautical Laboratory.

Horton, J. B. 1978. Aluminum-zinc alloys as sacrificial coatings, pp 59-73. Corrosion Control by Coating, H. Leidheiser, Jr., Ed. Princeton, New Jersey: Science Press.

Jones, W. D. 1960. Fundamental principles of powder metallurgy. London, England: Edward Arnold Ltd.

Jodoin, N. and M. Nadeau. 1980. The biggest on-site metallizing project: Pierre-Laporte bridge. 9th International Thermal Spray Conference. The Hague, Netherlands: Nederlands Instituut voor Lastechniek, Laan van Meerdervoort.

King, J. R. 1971. Probability charts for decision making, pp 124-133. New York, New York: Industrial Press Inc.

Lyashenko, B. A., et al. 1969a. Strength of adhesion between plasma-sprayed coatings and the base metal. Union of Soviet Socialist Republic: Institute of Mechanical Strength, Academy of Sciences of the Ukranian SSR. (Translated from Porosakovaya Metalluriya No. 4, April 1969.)

Lyashenko, B. A., et al. 1969b. Method for investigating the temperature dependence of cohesion between base and plasma coating. Union of Soviet Socialist Republic: Institute of Material Science, Academy of Science of the Ukranian SSR. (Translated from Zavodskaya, Laboratoriva, Vol. 35, No. 9, September 1969.)

Merzhanov, A. G., Y. M. Gregorjev, and Y. A. Gal'chenko. 1977. Aluminum ignition. Comb. and Flame 1:1-14.

Magome, M., Y. Mimte, and K. Vermo. 1980. Sprayed metals and alloys in a galvanic series based on potential measurements in sea water. 9th International Thermal Spray Conference, The Hague, Netherlands: Nederlands Instituut voor Lastechniek, Laan van Meerdervoort.

Moss, M. 1968. Dispersion hardening in Al-V by plasma-jet spray-quenching. Acta Metallurgia. 16:321-36.

National Bureau of Standards. 1977. Corrosion protection of steel piles in a natural sea water environment. NBS Monograph 158. Washington, D.C.

National Bureau of Standards. 1978. Economic effects of metallic corrosion in the United States. NBS Special Publication 511-2. Washington, D.C.

National Materials Advisory Board. 1966. Final Report of the Refractory Metals Sheet Rolling Panel. Report No. NMAB 212-M. Washington, D.C.: National Academy Press.

Navy, Department of. 1966. Protective coatings for steel piling: results of harbor exposure on ten foot simulated piling. Technical Report No. R490U. Port Hueneme, California: U.S. Naval Civil Engineering Laboratory, Naval Facilities Engineering Command.

Navy, Department of. 1976. Corrosion control for shipboard launch and recovery systems. NAVAIR 51-3-32/NAVSEA 0919-LP-0800-0811. Lakehurst, New Jersey: Naval Air Engineering Center.

Navy, Department of. 1978. Aluminum metallizing for anti-skid surfacing of helicopter landing and hanger deck of USS Fox (CG33). Welding Engineering Report 0168. Bremerton, Washington: Puget Sound Naval Shipyard.

Navy, Department of. 1980a. Shipboard presevation with wire sprayed aluminum (WSA). COMNAVSURFPAC Instruction 9630,1A, Code N43A/WPC 894. San Diego, California: Naval Surface Force, Pacific Fleet.

Navy, Department of. 1980b. Thermal-spray processes for naval machinery and ordnance applications. Report MIL-S-1687(SH). Washington, D.C.: Naval Sea Systems Command.

Navy, Department of. 1980c. Thermal spraying: production qualification quality control. Requirements for Process Instruction 0074-220A. Bremerton, Washington: Puget Sound Naval Shipyard.

Navy, Department of. 1980d. Job performance aid for wire sprayed aluminum preservation. Report NAVSEA-0655-AA-JPA-011. COMNAVSURFPAC, San Diego, California.

Navy, Department of. 1981a. Corrosion control of propulsion plant steam valves on USS William H. Standley (CG-32), Report TM-28-81-09. Bethesda, Maryland. David Taylor Naval Ship R&D Center.

Navy, Department of. 1981b. Naval ships technical manual. NAVSEA 50000-mm-mmm-000, DD 963 Class Corrosion Control Manual.

Navy, Department of. 1981c. Application of anti-corrosion coating technology. AEGIS Guidance and Policy Paper NO. 81-03. Washington, D.C.: Naval Sea Systems Command (PMS-400).

Navy, Department of. In preparation. Corrosion control using wire-sprayed aluminum. CNAVRES IMA-7. New Orleans, Louisiana: Chief of Naval Reserve.

Navy, Department of. 1982a. USS Enterprise elevator nonskid thermal spray report No. 002. Bremerton, Washington: Puget Sound Naval Shipyard.

Navy, Department of. 1982b. Review of electric arc wire sprayed aluminum non-skid program, Memorandum 05E1/HRB, 9631, Ser. 169. Washington, D.C.: Naval Sea Systems Command (SEA 05M1).

Peterson, D. J. 1969. New adhesion test for flame sprayed coatings. Materials Engineering 69(5):80.

Pratt and Whitney Aircraft Group. 1968. Testing standards for plasma deposited coatings, Specification E53 (Revised 01-15-68). Hartford, Connecticut.

Putzier, V., H. Zickler, and F. Kock. 1980. Quality control with thermal spraying. 9th International Thermal Spraying Conference, The Hague, Netherlands: Nederlands Instituut voor Lastechniek Laan van Meerdervoort.

Rogus, B. J. and F. J. Vapniarek. 1980. Testing of external coating systems for the corrosion control of steam values. 053B:BJR: red, 10310 (A-2407) SER 3343. Philadelphia, Pennsylvania: Naval Ships Systems Engineering Station.

Schaper, V. D. 1979. Corrosion controlled production plant steam valves USS William H. Standley (CG-32). Report TM-28-79-308. Bethesda, Maryland: David Taylor Naval Ships R&D Center,

Schaper, V. D. 1981. Thermal spray processes for Naval machinery and ordnance applications. NAVPERO 10531-C. Annapolis, Maryland: David M. Taylor Naval Ship R&D Cwnter.

Sempels, R. E. and M. E. Leclercq. n.d. Properties and anti-corrosion performance of thermal sprayed coatings and related duplex systems. B4900, Angleur, Belgique: Societe Des Mines et Fonderies de Zinc de la Vieille--Montagne S. A.

Shrier, L. L. 1963. Corrosion, vol. 2. Corrosion Control, pp. 20.1-20.106. New York, New York: John Wiley and Sons.

Stanton, W. E. 1976. Sprayed aluminum coatings - why, when, how? Presented at the 8th International Thermal Spraying Conference, Miami, Florida: American Welding Society.

Starkey, W. J. 1970. Mammoth tankship fire safety - falling object friction spark test. San Francisco, California: Standard Oil of California.

Steffens, H. D. and J. Beczkowiak. 1982. Testing and inspection of coatings. In Proceedings of Seminar on Coatings for High Temperature Applications. Joint Researsh Establishment, Petten, The Netherlands.

Steffens, H. D. and H. A. Crostack. 1981. Methods based on ultrasound and optics for the non-destructive inspection on thermally sprayed coatings. Presented at the International Conference on Metallurgical Coatings, San Francisco, California.

Steffens, H. D. 1980. Sprayed coatings, pp. 5.1-5.29. AGARD Lecture Series n. 106. Springfield, Virginia: National Technical Information Service.

Sulit, R. A., H. H. J. Vanderveldt and V. D. Schapiro. 1980. Corrosion control using wire sprayed aluminum in the U. S. Navy. 9th International Thermal Spraying Conference. The Hague, Netherlands: Nederlands Instituut voor Lastechniek Laan van Meerdervoort.

Sulit, R. A. and H. H. J. Vanderveldt. 1981. Thermal spray NDE requirements for production quality assurance in the USN. DARPA/AF Review of Quantitatitve NDE. Ames Laboratory, University of Iowa.

Sulit, R. A., V. D. Schaper, and H. H. J. Vanderveldt. 1981. Thermal-spray applications in the U. S. Navy. Proceedings of the International Conference on Metallurgical Coatings, April 6-10, 1981, San Francisco, California. New York: Elsevier Sequoia, S.A.

TAFA Metallisation, Inc. 1980. A comparison of bonding wires. TAFA Technical Data Bulletin 1.9.1.1.1A. Bow, New Hampshire.

TAFA Metallisation, Inc. 1981. Comparative study--corrosion protection of steel with zinc, aluminum, and thermal sprayed coatings. TAFA Application Data Sheet 2,3.1,6.1. Bow, New Hampshire.

Vanderveldt, H. H. J., R. A. Sulit, and M. Schmeller. 1981. Thermal spray machine element repair applications and procedures during the USS Albert David (FFIOSO) ROH. Presented at 18th Annual Symposium of Association of Scientists and Engineers of the Naval Sea System Command. Washington, D. C.: Department of the Navy, .

Van Horn, K. R. 1967. Aluminum - Vol. 1 and II - Properties, physical metallurgy and phase diagrams, p. 191. and pp. 652-662. Metals Park, Ohio: American Society for Metals.

Wilms, V. and H. Herman. 1976. Crystallography and microstructure of equilibrium and metastable phases resulting from plasma spraying of ceramic coatings. In Proceedings of the Eighth International Thermal Spraying Conference, pp. 236-243. Miami Beach, Florida: American Welding Society.

Wurst, J. C. 1968. Weibull analysis of the oxidation resistance of coated refractory metals. Masters thesis, University of Dayton, Ohio.

Zinc Substitute, Inc. 1971. Zinc: its corrosion resistance, pp. 118-120. New York, New York.

CURRICULA VITAE OF COMMITTEE MEMBERS

ROGER PERKINS is a senior member of the Lockheed Palo Alto Research Laboratory. He received his B.S. and M.S. degrees in metallurgical engineering from Purdue University. Before joining Lockheed in 1960, he worked for Aerojet-General Corporation and for the Union Carbide Metals Co. His principal interest has been in high temperature gas-metal reactions, refractory metals, and protective coatings. He is a fellow of the American Society of Metals.

NEIL N. AULT is Technical Director of the Industrial Ceramics Division of Norton Company in Worcester, Massachusetts. He obtained Bachelors, Masters and Doctors degrees in Ceramic Engineering from Ohio State University. He has been active in industrial research in advanced ceramics and sprayed ceramic coatings for 32 years. A member of ASTM, the American Ceramic Society, and Refractories Institute committees, he received the Distinguished Ceramist of New England Award in 1976.

HERBERT HERMAN is a Professor in the Departments of Materials Science and Marine Sciences. His degrees are from Northwestern and DePaul Universities. He has been a Fullbright Scholar at the University of Paris, and liaison scientist at ONR London. He is currently active in protective coatings technology, ocean technology and other materials science and engineering areas and is chairman of the Marine Materials Committee of the Marine Technical Society.

FRANK J. HERMANEK graduated from Manhattan College and did metallurgical post graduate work at the Polytechnic Institute of Brooklyn. Active in the thermal spray field for over 20 years, Mr. Hermanek served as Manager, Thermal Spray Coatings at General Electric's Aircraft Engine Group facility in Cincinnati, Ohio. In 1980 Mr. Hermanek joined Alloy Metals, Inc., a manufacturer of dry atomized powders for brazing, thermal spray surfacing and other high technology applications. He is a member of the American Society for Metals and the American Welding Society.

HENRY LEIDHEISER, JR., Professor of Chemistry and Director, Center for Surface and Coatings Research, Lehigh University, received his undergraduate and graduate degrees from the University of Virginia. He joined the Virginia Institute for Scientific Research in Richmond, Virginia at the time of its founding in 1949 and held the position of Director during the period, 1960-68, at which latter date he joined the faculty of Lehigh University. He has been active in the fields of corrosion and protective coatings and his research has been honored by awards from the Virginia Academy of Sciences, the Oak Ridge Institute of Nuclear Studies, the Electrochemical Society, the Institute of Metal Finishing, the Society of Automotive Engineers, and the American Electroplaters' Society.

FRANK LONGO, Manager, Materials Engineering at Metco, has worked for that company since graduation from the Polytechnic Institute of New York where he received his B.S. degree in 1960 and his M.S. in 1969. He is a member of American Society for Metals and the American Welding Society; he owns eight patents developed at Metco.

WHITNEY G. SMITH received a Bachelor of Sciences Degree in Physical Metallurgy from Washington State University in 1954. He served three years with the U.S. Navy as a Carrier Aircraft Maintenance Officer, during which time he developed an appreciation for the corrosion potential of the marine environments. Mr. Smith joined The Boeing Aerospace Company in 1958 and has been closely associated with Materials Technology development and application since that time. He served as the Materials and Process Technology Manager on the Saturn-Apollo Launch Vehicle Program, and was subsequently assigned as Materials Technology Manager for the Boeing Aerospace Company. He became Manager of Materials Technology for Boeing Marine Systems upon its inception in 1975. Mr. Smith has since been involved in the study, laboratory and field evaluation, and production use of cathodic metallized coatings in applications on both commercial and military craft involving a variety of worldwide environments. He is a member of the National Association of Corrosion Engineers (NACE), and The American Society for Metals (ASM).

ROBERT SUMMITT, Professor of Metallurgy, Mechanics, and Materials Science at Michigan State University, received his B.S. degree at the University of Michigan and his Ph.D. degree at Purdue University. Before joining the MSU faculty, where he was department chairman from 1971 to 1978, he was a Research Chemist at Corning Glass Works. From 1974-1975 he was an NRC Research Associate at the USAF Materials Laboratory. Dr. Summitt's research spans a broad spectrum from molecular spectroscopy to color science, metallurgy, corrosion, and materials science. He is a member of the American Chemical Society, the American Physical Society, the American Society for Metals, and the National Association of Corrosion Engineers. He is also a consultant in corrosion and failure analysis.

MERLE L. THORPE has been president of TAFA since 1961. He has been an innovator in high temperature technology for the past 25 years, having founded and developed numerous companies in that field. Since 1970 TAFA has been active in the sprayed metal tooling field. In addition to his industrial activity, he has been a Professor and Assistant Dean at the Dartmouth College Engineering School. Mr. Thorpe holds an A.B. and M.S. in Engineering Science from Dartmouth College. He is a member of numerous technical societies and committees including the American Welding Society Thermal Spray Committee.