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Summary Report
High Temperature Oxidation Resistant Coatings

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SUMMARY REPORT

HIGH TEMPERATURE OXIDATION RESISTANT COATINGS

Prepared by the

COMMITTEE ON COATINGS

NATIONAL MATERIALS ADVISORY BOARD

Division of Engineering - National Research Council

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ABSTRACT

Coatings for superalloys, refractory metals, and graphite are described from the points of view of fundamental principles, specific substrate, and application. This report constitutes a summary of a larger volume which describes these areas in detail. General and specific conclusions were reached, followed by recommendations for upgrading coating capabilities.

I. CONCLUSIONS

1a. Based on the performance of simple shapes and test coupons, the current generation of coatings for superalloys and refractory metals meets the basic requirements for existing applications. These applications have been designed, however, to operate within the limitations of the available coatings. For example, reusability may not be required, and the operational envelope restricted so as not to exceed the coatings temperature capabilities. At the hardware stage, characterization and evaluation of existing refractory metal coating systems are not adequate. In addition, improvements in the processing of large or complex shapes may be required.

1b. The current generation of coating systems is not adequate for advanced applications that are predicted to evolve within the next five to fifteen years. Major advances will be required in oxidation behavior, microstructural stability, manufacturing technology, and overall system reliability. The prospect of developing adequate systems is not favorable, and a reappraisal of design concepts and performance requirements is therefore indicated.

2. There is a dearth of sound approaches to the development of new or improved coating systems. Current technology depends solely on the formation of Al_2O_3 or SiO_2 as the protective oxide. Coatings which form complex oxides, spinels, or dense glasses are needed to provide a major advance in performance capabilities. These coatings also must possess a self-healing mechanism for reliability in service. Coatings of the fused slurry type are regarded to have the best potential for meeting future needs.

3. A fundamental understanding of the factors that govern the performance of existing coatings is needed to provide a sound basis for the development of advanced coating systems. To date, only a minimum understanding of a

few very simple systems has been attained, and significant advances are required in this area. It is known that the useful life of most coatings is a small fraction of the maximum attainable under ideal conditions. Performance of most coatings is established and controlled by random defects. In the absence of defects, coating life is limited by diffusional processes at low temperature and by vaporization or melting at high temperature.

4. Specific conclusions related to general areas of application are as follows:

a. Gas Turbines

(1) Coated alloys in advanced engines must have a 2-3 fold increase in useful life and 200°F increase in maximum temperature capability, i.e., to 2200°F maximum.

(2) The ability to coat small internal passages is not adequate and manufacturing improvements are required.

(3) Recoating processes result in excessive substrate attack and improved methods are required.

(4) The current techniques for nondestructive testing are not satisfactory and improved methods are needed.

b. Chemical Propulsion

(1) Available coating systems are adequate for existing applications.

(2) Currently, there is no need for major advances in this area.

c. Hypersonic Vehicles

(1) The current generation of coatings is adequate for existing and near-term future applications.

(2) The re-use capability of coated parts will extend to 1 or 2 flights. Current test and performance data are inadequate for making a better assessment of re-use capability.

(3) Coated columbium alloys are limited to a 2500°F maximum operating temperature (coating lifetime of 150-200 hours) by creep properties. Inadequate creep resistance, not coating technology, limits the use of these materials.

(4) Satisfactory coatings do not exist for use on molybdenum or tantalum alloys above 3000°F and on tungsten above 3300°F. Further work on silicide-base coatings to extend the service temperatures on these alloys is not warranted, and a new approach to coating must be taken.

d. Energy Conversion Systems

(1) Oxidation-resistant coatings generally are not needed. One exception is the platinum coating on RTG systems. Current technology is satisfactory for this application.

e. Industrial

(1) Use of coated metals is limited, and current technology appears to be adequate.

II. RECOMMENDATIONS

1. The minimum performance capabilities and reliability of existing coatings for superalloys and refractory metals should be upgraded by means of processing improvements. Specifically:

a. The mitigation and control of defects should be studied.

b. New coating deposition processes, particularly suited to large surfaces and complex shapes, should be developed.

c. Field repair techniques should be devised.

d. Recoating processes that reduce substrate loss should be developed.

e. Processes for the coating of small internal passages should be improved.

f. Automated manufacturing processes should be considered.

2. New approaches to the development of oxidation-resistant coatings should be explored. Specifically:

a. Compositions that form complex oxides, perovskites, or spinels on oxidation should be investigated as coating materials.

b. Preference should be given to single-layer coatings applied by slurry processes.

3. A basic understanding of the mechanisms that govern coating behavior should be obtained for current systems. Specifically:

a. The origin of critical defects should be determined. Factors governing the nature, size, and distribution of defects must be defined.

b. Layer growth and diffusion studies should be made with existing systems to establish basic levels of stability and kinetics of compositional changes.

c. Phase diagrams (equilibrium), thermodynamics, and kinetics of oxidation processes should be established for representative coating systems.

d. The physical chemistry of deposition (cementation) processes should be studied for silicide and aluminide coatings.

4. Existing coating systems should be more fully characterized and evaluated at the hardware stage. Specifically:

a. A statistical analysis of performance (and failure) in relation to coating defects should be made.

b. Nondestructive test procedures should be perfected for process control and prediction of coating behavior.

c. Flight environment tests of hardware should be conducted.

d. Accelerated coating-life tests for prediction of long term performance should be developed.

e. Mechanical and oxidation test methods should be standardized.

f. Comprehensive hardware studies should be made to establish the basic levels of quality, reproducibility, and performance for existing coating systems.

III. INTRODUCTION

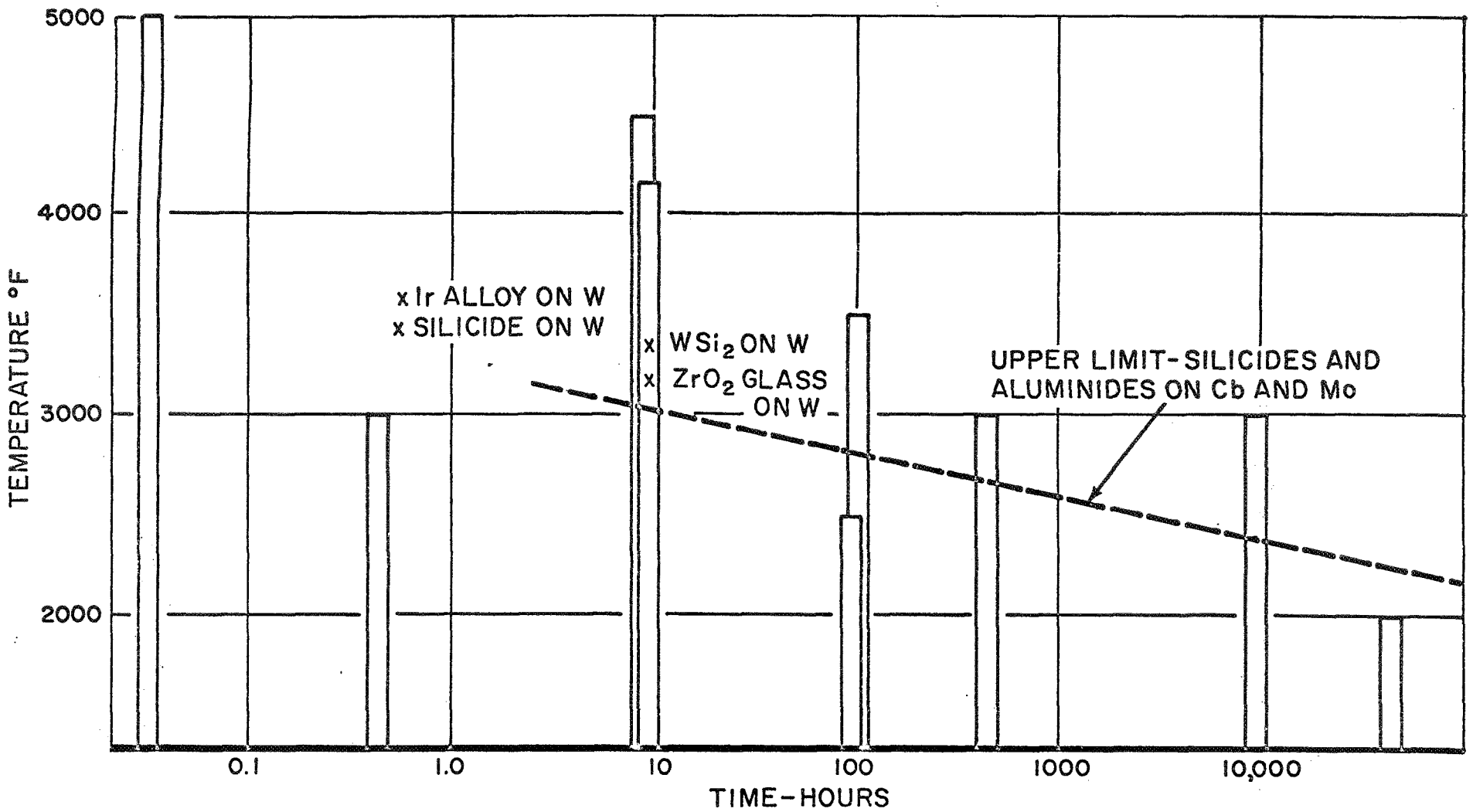
Coatings to protect structural materials against oxidation at elevated temperature have become important only in recent years. In the past, superalloys based on nickel or cobalt containing about 20% chromium were used where both strength and oxidation resistance were required, such as in the turbine section of aircraft jet engines. In these alloys, strength falls off at elevated temperatures somewhat more rapidly than oxidation resistance. Thus, the turbine inlet temperature was maintained below about 1600°F, where strength fell off. High-temperature oxidation is not a matter of concern at this temperature, and superalloys could be used in gas turbines for thousands of hours without incurring significant oxidation or sulfidation damage.

In recent years, stronger superalloys have been developed based on increasing the aluminum and titanium content needed to form strengthening γ' precipitates at the expense of chromium content. This has resulted in a new generation of strong superalloys containing about 10% chromium. These alloys can be used at higher temperatures without losing strength. Unfortunately, they have significantly poorer hot corrosion resistance than the former 20% chromium alloys. To combat this problem, coatings were developed, largely based on monoaluminides produced by diffusion with the substrate alloys. These coatings provide improved oxidation and sulfidation resistance and have been remarkably successful in some applications even with the increased turbine inlet temperatures (up to 2200°F) which have been made possible through the use of bypass air cooling of the hot components.

Other developments which have prompted increased consideration of high-temperature coatings are glide reentry and hypersonic vehicles. These advanced aerospace systems have only become of serious interest in recent years, starting in the early 1960's. Aerodynamic heating of lift and control surfaces required structural materials which could operate for short periods of time (minutes to hours) at 2500-3000°F, depending upon the reentry corridor of the vehicle. Refractory metals afford an excellent basis for fabrication of such advanced structures. During the early 1960's until recently a national capacity was developed in the United States to produce mill products of strong refractory metal alloys based on columbium, tantalum, molybdenum, and tungsten. In a remarkably short time, mill products of aircraft quality and size were produced. The Materials Advisory Board provided guidance during this effort through the MAB Refractory Metal Sheet Rolling Panel (MAB Report 212M, March, 1966). Coatings based on disilicides and monoaluminides were developed concurrently, which were capable of protecting refractory metal alloy structures during typical glide reentry environments.

In future aerospace systems, the projected requirements for coatings for refractory metals will be much more severe than was the case for the early reentry vehicles of the Dyna Soar and ASSET classes. In 1965, the Materials Advisory Board Aerospace Applications Requirements Panel forecast that future aerospace vehicles would require coatings for refractory metals that would operate in an oxidizing environment at temperatures and times given by the vertical bars shown in Figure 1. As in the presently used intermetallic coatings, the future coatings would be thin (< 0.005 inch thick) and would have to withstand thermal cycling. On the same figure are plotted the capabilities of oxidation protective coatings as they stood in 1965. The diagonal line represents the best performance of thin disilicide or monoaluminide coatings on columbium or molybdenum

Fig. 1 - REQUIREMENTS AND PERFORMANCE OF THIN COATINGS ON REFRACTORY METALS



tested under laboratory conditions in still air. In addition, a few points on the figure give laboratory performance data for a number of coatings on tungsten. These fall in line with the performance line for coated columbium and molybdenum. Compared with future systems requirements in aerospace vehicles, the performance of state-of-the-art coatings falls considerably short, even under the maximum performance conditions found in the laboratory.

It is apparent that coatings for high-temperature materials will become of increasing importance as time passes. The National Aeronautics and Space Administration, therefore, requested that the Materials Advisory Board convene a committee to review the status of coatings for high-temperature materials including superalloys, refractory metals, and graphite, to consider the present research and development underway and to recommend modifications or changes in scope and emphasis.

IV. OBJECTIVE OF THE PROGRAM

The Coating Subpanel of the Refractory Metal Sheet Rolling Panel recommended in 1966 (MAB-212-M) that a new Panel on Oxidation Resistant Coatings be established. In line with their recommendations, amplified by later experience, the following objectives were established to guide this panel study:

(1) Define current and future applications for coated superalloys, refractory metals, and graphites.

(2) Define the performance requirements for these applications.

(3) Review basic coating concepts and current status.

(4) Define key technical problem areas in performance, manufacture, and testing in the light of current and future requirements.

(5) Define possible approaches to the solution of key problems.

(6) Indicate the nature or direction of research and development studies for producing major advances in coating technology.

V. METHOD OF OPERATION

Work of the Panel on High Temperature Oxidation Resistant Coatings was divided into two major phases:

Phase I - Review of the current status and future requirements for coatings on superalloys, refractory metals, and graphite.

Phase II - Detailed analysis of coating concepts, methods of protection and failure, applications technology, manufacturing processes, testing, and inspection.

In Phase I, individual members of the main Panel and DOD liaison representatives, in accord with their special interests or abilities, conducted a cursory review of various aspects of coating technology as shown in Table 1. The results of this study were published as a first progress report in 1968 (MAB-234).

The analysis of Phase I studies indicated the areas in which more detailed studies would be required to satisfy program objectives. Subpanels were organized, as shown in Table 2, to implement the studies. Leading experts in related fields from industry, Government, and education were appointed to the subpanels. Each subpanel met at least once to establish individual assignments for study and analysis. The sections of each subpanel report were submitted to the Subpanel Chairmen, who prepared the final input for the main Panel report.

The main Panel met periodically to review the Subpanel reports and conclusions. Each Subpanel was requested to submit to the main Panel for consideration five recommendations (primary) related to key technical problems in their respective areas and any additional recommendations (secondary). These were reviewed and discussed at the last Panel meeting. Draft copies of each Subpanel report were reviewed and discussed also by the main Panel at its last meeting.

TABLE 1. Phase I Study Assignments

Coating Concepts	L. L. Seigle
Testing and Standards	J. C. Wurst
Coatings for Superalloys	J. R. Myers
Coatings for Chromium	S. J. Grisaffe
Coatings for Columbium	J. D. Gadd
Coatings for Molybdenum	R. A. Perkins
Coatings for Tantalum and Tungsten	L. Sama
Coatings for Graphite	H. Volk
Requirements for Hypersonic Aircraft	E. E. Mathauser
Glide Reentry Requirements	L. Sama
Requirements for Ramjets	I. Machlin
Requirements in Energy Conversion Systems	R. I. Jaffee
Requirements for Rocket Nozzles	S. J. Grisaffe

TABLE 2. Phase II Subpanels

Subpanel	Chairman
Fundamentals of Coating Systems	L. L. Seigle
Coatings for Gas Turbines	J. R. Myers
Coatings for Chemical Propulsion	H. Volk
Coatings for Hypersonic Vehicles	D. L. Kummer
Coatings for Energy Conversion Systems	R. I. Jaffee
Coatings for Industrial Applications	J. C. Wurst
Manufacturing Technology	J. D. Gadd
Testing and Inspection	J. C. Wurst

An editorial Subpanel was commissioned to assemble the final report and to prepare the over-all conclusions and recommendations. G. M. Pound, R. I. Jaffee, and R. A. Perkins served in this capacity.

The results of the Phase II Subpanel studies and the final conclusions and recommendations are set forth in this summary report. The detailed Subpanel studies and results of the Phase I analysis are presented in a separate bound volume, "Coatings for Protection from Oxidation of Superalloys, Refractory Metals, and Graphite."

The documents which have been generated under this program provide a very broad and comprehensive review of technology for high-temperature oxidation-resistant coatings. The information should be of great value to NASA, DOD, and industry representatives who are charged with the responsibility of applying coating technology to the design and manufacture of a wide range of devices, structures, power plants, and vehicles. The method of operation selected by the Panel to meet its objectives proved to be extremely effective. All members of the Panel and all Subpanels are to be commended for the thoroughness in which they carried out their respective assignments. The wealth of information that has been assembled, analyzed, and correlated attests to the sincerity of their efforts and the over-all effectiveness and worth of this study.

VI. SUBPANEL SUMMARIES

A. Fundamentals of Coating Systems

1. Summary and Conclusions

Coatings developed for protecting refractory metals against oxidation may be classified as (a) intermetallic compounds which form compact or glassy oxide layers, (b) alloys which form compact oxide layers, (c) noble metals which resist oxidation, and (d) stable oxides which provide a physical barrier to the penetration of oxygen. Successful coatings exhibit certain characteristics among which the following are important:

1. Low growth rate of the protective oxide layer.
2. Resistance to cracking.
3. Low evaporation rates of the protective oxide and other coating constituents.
4. Low rates of coating-substrate reaction.
5. Self-healing ability.

It may be stated as a general principle that due to higher activation energies, vaporization processes tend to predominate over diffusion processes at very high temperatures, and, conversely, diffusion processes tend to predominate at lower temperatures. This applies to the silicide and aluminide coatings as well as ThO_2. For example, at temperatures above approximately 3000°F, the evaporation rate of SiO_2 becomes significant as well as the vapor pressures of SiO in equilibrium with Si + SiO_2 and of Si in equilibrium with the higher silicides. With aluminide coatings the vapor pressure of Al is appreciable at higher temperatures. The role of vaporization in coating degradation is also enhanced by low ambient pressures, which not only allow more rapid vaporization, but may even lead to circumstances under which a protective oxide layer does not form at all.

The occurrence of defects in coating systems makes lifetimes in practice fall far short of those theoretically achievable with a flawless coating. In silicide and aluminide coatings cracks are seemingly always introduced during application of the coating, or formed during exposure. Thermal cycling enlarges these cracks until they penetrate through the coating to the substrate, causing localized failures in a fraction of the time required for the coating as a whole to deteriorate. Different susceptibilities to cracking exist in different systems. Silicide coatings are prone to the formation of such defects, while aluminide coatings on superalloys are more resistant to cracking. Methods to ameliorate the influence of cracking upon coating lifetimes have been developed, such as the use of a liquid Sn-Al phase to seal cracks, or the use of complex silicides, fused to the surface, which resist or tolerate cracking. In general, however, not enough is known about the nature and distribution of cracks in various coating systems and the mechanisms of crack propagation and crack healing.

From experience gained in practical coating development, as well as theoretical analysis of coating behavior, it is possible to draw some conclusions about the concepts which underlie or may lead to the development of successful coatings. For an oxide to be protective it must resist transport of both metal and oxygen ions. This implies not only low intrinsic diffusivities of the ions, but a composition which remains close to stoichiometric and a minimum of lattice defects. Oxides other than SiO_2 and Al_2O_3 which possess these characteristics are known, such as MgO, CaO, and BeO, although they may be unsuitable for other reasons. Complex oxides with a spinel or perovskite structure may exhibit low diffusivities. These are largely unexplored.

The ideal protective oxide would form a sound and coherent layer over the substrate. Preservation of such a layer is aided by the glass-forming ability of the oxide, as with SiO_2, since glassy oxides can flow and accommodate

mechanical strain and heal defects. Other glass-forming oxides, such as B_2O_3, may prove useful. The known procedures for enamel-coating development may be of assistance in developing glassy oxide coatings which resist cracking.

Since it is difficult to form a protective oxide which remains absolutely sound under all conditions, the self-healing capacity, i.e., the ability of a coating to regenerate its protective oxide layer in case of surface cracking, has proven to be of great importance. This capability is related to the preservation of an active reservoir of protective-oxide-forming substance (e.g., disilicide or dialuminide) in the coating. The minimization of diffusion into the substrate is an important step in preserving this layer, and hence diffusion barriers are a useful concept in coating development. The reservoir layer, however, is often short-circuited by the penetration of cracks formed during processing or exposure, and hence the ability of this layer itself to resist cracking is of the greatest importance. Such crack resistance may be obtained by raising the fracture strength of the layer through development of a fine-grained structure, or increasing the plasticity of the layer by the introduction of fluid or plastic constituents.

The concept of employing oxidation-resistant, nonstructural alloys such as Hf-Ta, or Nb-Ti-Al-Cr to coat refractory metals has had some success. Such coatings can deform without cracking, and afford a means of protection against foreign object damage.

a. Intermetallic compounds

The penetration of cracks is a most important factor in determining the lifetime of a coating, but even in the absence of cracking a protective coating would ultimately fail due to the inevitable progress of oxidation, diffusion, and evaporation reactions at high temperatures. Analysis of these mechanisms of deterioration indicates that different processes are important in different coating systems at different temperatures. In simple silicide and aluminide coatings used at or near 2500°F, it appears that coating-substrate interdiffusion is the important degradation process in air at 1 atm. pressure. This occurs more rapidly

than either growth or evaporation of the oxide film, and leads to a theoretical coating lifetime in the absence of cracking, of the order of 1000 hrs., more or less, depending upon the specific system,* for a thin ($\sim$ 5 mil) coating. It would take about this long for a 5 mil disilicide or aluminide layer to be converted to lower silicides or aluminides. Observed coating lifetimes under test conditions are, of course, much less than the theoretical lifetimes due to cracks which develop during processing or testing, and penetrate the silicide or aluminide layers resulting in local failures before a large fraction of these layers has reacted with the substrates.

b. Oxidation resistant alloys

Although the data are incomplete, it is believed that interdiffusion between coating and substrate is a major factor in the degradation of Ni-and-Co-based superalloy coatings on the refractory metals. In any event, these coatings are limited to temperatures below about 2100°F, due to the possible occurrence of low-melting constituents in the diffusion zones.

c. Noble metals

From the available data, particularly that for Ir on W, it appears that at temperatures in the vicinity of 2000°C, evaporation of the noble (Pt group) metals is an important deterioration process since this seems to occur, at least for Ir on W, much more rapidly than interdiffusion with the substrate. A 10 mil coating, for example, would evaporate in of the order of 10 hrs. in low pressure air at 2000°C, while it would require hundreds of hours to diffuse into the substrate.

d. Stable oxides

Evaporation also becomes important for stable oxides such as ThO_2 on W at the very high use temperatures contemplated for such coatings.

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*Theoretical lifetimes are greater for silicide than for aluminum coatings.

Calculations indicate that it would require only minutes for evaporation of a 10 mil ThO_2 layer at 2500°C, while the rate of reaction of ThO_2 with W is negligible at this temperature. On the other hand, at elevated temperatures, the diffusion of oxygen is, surprisingly, many times more rapid in ThO_2 than in SiO_2 or Al_2O_3, and diffusion of oxygen through even a coherent layer of ThO_2 could be a life-limiting factor in a certain temperature range, perhaps just below 2500°C. At higher temperatures, however, it is clear that evaporation theoretically becomes predominant.

2. Recommendations

The five recommendations of this Subpanel of greatest importance are as follows:

1. A thorough study should be made of the origin and control of defects during the formation of coatings and during their use in service.

2. The influence of defects on coating lifetimes should be defined quantitatively by the use of statistical analysis.

3. Layer growth studies and diffusion measurements in successful complex coating systems should be made, in order to identify the reasons for superior performance.

4. New oxides, around which to design new coatings, should be sought. Complex oxides with the spinel or perovskite structures are particularly recommended for investigation.

5. Further information should be obtained about the phase diagrams, thermodynamic properties, and kinetics of reactions of coating constituents with substrates and oxygen, including the substrate oxide-coating oxide system.

A striking fact which emerges from this study is the serious lack of phase diagram, thermodynamic, and/or diffusion data for the systems of interest, necessary for a complete understanding of coating behavior at high temperatures. This is particularly true when the combination oxygen-coating-substrate represents a ternary or higher order system. While sporadic attempts are made from time to time to obtain portions of this information, it is clear that a fairly large and sustained effort is needed to do the job more rapidly and completely. Since data of this type are often lacking in fields of materials technology, it is felt that attention should be given by federal agencies to the organization of a sufficiently large and systematic effort to obtain such data on a continuing basis. It is clear that information of this type is not now being obtained quickly enough. It is also clear that there is little hope of changing the situation without an effort such as that recommended.

For protective coatings, even in the absence of complete diffusion, etc., data, it seems clear that much useful information can be obtained by careful studies of the behavior of practical coatings, using metallographic, X-ray diffraction, microprobe and other techniques, to investigate the reactions occurring and structures developed in the coating system, and to relate these to the success or failure of the coating. Among others, it would be particularly valuable, for example, to ascertain the reasons for the superior performance of the fused silicide coatings. Work of this type should be included more often as part of the coating evaluation process.

Finally, certain approaches to improving existing coatings, as well as developing new types of coatings, are indicated. These include the development of means to eliminate or inhibit cracking in silicide and aluminide coatings and of means to prevent diffusion into the substrate. New oxide systems should be sought, around which to design new coatings. The possibilities in complex oxides merit further investigation, as well as the development of means to decrease the

point defect concentrations in refractory oxides, such as ZrO_2 and ThO_2. Glass-forming oxides, such as B_2O_3, may be worth further study. Further consideration of the use of oxidation-resistant alloys as coatings or parts of coatings also seems to be indicated.

B. Applications of Coating Systems

1. Gas Turbines

a. Summary and conclusions

1) Applications and environment. Gas-turbine engines are being developed for numerous industrial, marine, and vehicular applications. Industrial engines, already providing some primary electrical power generation and stand-by power for larger electric-generating facilities, will be used more frequently in future years for a variety of purposes. Marine engines are being and will continue to be used to power high-speed boats and ships, including relatively large vessels in the submarine-chase and in transportation classifications. Efficient and economical engines will be developed for large commercial and military trucks and military tanks. Gas turbines may also be used to power high-speed, ground-transportation systems. These newer applications and increased demand for improved performance commercial and military aircraft engines will result in unprecented growth in gas-turbine engine technology and production during the next fifteen years.

The requirements for increased performance undoubtedly will be manifested in higher turbine inlet temperatures. These temperatures are expected to reach 2400°F to 2700°F, as compared to 2100°F to 2300°F maximum currently reached. However, air cooling schemes will maintain turbine blades in the 1800°F regime and turbine vanes at 2000°F maximum. This metal temperature level indicates that superalloys will continue to be used for some time for turbine hardware.

The phenomena which contribute to the deterioration and failure of hot-section components in gas-turbine engines are:

(1) Oxidation and sulfidation (hot corrosion) - sulfidation is an accelerated form of high-temperature corrosion associated with the presence of Na_2SO_4. Sulfur from the fuel reacts during combustion with ingested sodium chloride from the air to form the Na_2SO_4.

(2) Creep - centrifugal loading at high temperatures can cause extension of rotating blades; gas pressure differentials can cause bowing of stationary vanes.

(3) Thermal fatigue - a form of low cycle fatigue; grain boundary oxidation can contribute to the initiation of thermal fatigue cracks.

(4) Erosion - carbon particles, dust, and other ingested particulate matter can cause premature removal of engine components.

(5) Foreign object damage (FOD) - damage from debris ingested by the engine, or failure of upstream components, is a major reason for replacing turbine blades and vanes.

(6) Overtemperature - re-solution of alloy constituents and incipient melting seriously affect the structural integrity of the components.

Cooling techniques are and will be necessary to lower metal temperature of many components as turbine-inlet temperatures exceed about 1900°F. It is not believed that refractory metal alloys of Mo, Cb, W, or Ta will be used to any large extent in near-future engines because sufficiently reliable, oxidation-

resistant coatings for these materials are not available. The same would be true of chromium-base alloys in the event a suitable alloy were available. Therefore, in order to achieve the long-life expectancies required for future engines, high-temperature corrosion must be minimized, and protective coatings appear to be the most promising approach. In addition to minimizing the hot corrosion problem, advanced coating systems may also be beneficial in reducing thermal and mechanical fatigue and improving erosion and FOD resistance.

2) Performance and reliability. The basic requirements of a coating for superalloy substrates in gas-turbine engines dictate that: (1) it must resist the thermal environment, (2) it must be metallurgically bonded to the substrate, (3) it should be thin, uniform, light in weight, reasonably low in cost, and relatively easy to apply, (4) it should have some self-healing characteristics, (5) it should be ductile, (6) it should not adversely affect the mechanical properties of the substrate, and (7) it should exhibit diffusional stability.

A number of organizations have developed high temperature protective coatings for superalloys and many of these coatings have been used effectively in gas-turbine engines to extend the life expectancies of hot-section components. All of the currently important coatings are based upon the use of aluminum as the primary coating constituent. Processes used to obtain these aluminum-rich coatings are: (1) pack cementation, (2) hot-dipping, (3) slurry, and (4) electrophoresis. However, regardless of processing techniques, basic similarities exist among the current coatings in that they are predominantly composed of NiAl (nickel-base alloys) or CoAl (cobalt-base alloys) with minor additions of an alloying element, usually chromium.

Although the current coatings do not satisfy all the aforementioned basic performance requirements, aluminide-type coatings successfully extend the life expectancies of gas-turbine engine blades and vanes. Because the advantages obtained by using coatings outweigh the disadvantages, several hundreds of

thousands of superalloy blades and vanes for military and commercial aircraft gas-turbine engines are coated by the engine manufacturers and coating vendors in the United States each month.

However, future coatings for superalloy, hot-section components will have to exhibit performance capabilities superior to those of the currently available aluminide coatings. With improved coatings, blade and vane life expectancies hopefully will exceed 12,000 hours at metal temperatures of 1700°F and 1850°F, respectively. A two- to three-fold improvement in life may be expected in the higher temperature military gas-turbine engines.

To achieve these goals, future coatings should possess the following characteristics: (1) improved diffusional stability, (2) improved resistance to oxidation, sulfidation, and hot-gas erosion, (3) improved ductility, (4) a 200°F increase in operating temperature capability, (5) improved resistance to thermal and mechanical fatigue, (6) improved resistance to thermal shock, (7) minimum adverse effect of the mechanical properties of the substrate, (8) some self-healing capability, and (9) compatibility with brazing alloys.

3) Manufacturing technology. Large-scale coating production for superalloy substrates has been limited primarily to individual turbine blades and vanes, varying in size from about 1.5 to 6-inches in length. A variety of nickel-base and cobalt-base alloys are involved, as well as the various coating processes previously mentioned.

Engine hardware often requires certain specialized coating techniques, often difficult to achieve. Blade root sections generally are not coated and so require suitable masking techniques. Coating of internal cooling passages is difficult, particularly with certain coating processes. Recoating of engine-operated hardware is another requirement. Large hot-section components, up to 48 inches in diameter and 10 inches deep, have been coated experimentally but exhibit processing difficulties.

Future needs indicate that, in addition to an increased production capacity requirement, a capability to coat engine components other than turbine blades and vanes will be needed. Several production problems must be solved including processing of large and very small components, adaptation of process to more and newer alloys, recoating, coating of internal passages, better process control, and newer coating techniques. Nondestructive test and inspection procedures must also be included.

b. Recommendations for advancing the state-of-the-art

It is believed that a number of research and development programs can be outlined that will greatly assist in the development of advanced coating systems for superalloys to be used in future gas-turbine engines. The primary recommendations of the Subcommittee are as follows:

1. Conduct studies to thoroughly evaluate the potential (i.e., determine advantages and limitations) of newer coating techniques for depositing advanced coatings on superalloy components used in gas-turbine engines. Processes to be considered should include: (1) cladding, (2) electrodeposition from fused salts, (3) pyrolytic deposition from organometallic vapors or solutions, and (4) physical vapor deposition, especially as applied to alloys. Successful research results in developing new coating processes probably will be necessary in order to permit deposition of advantageous coating alloys.

2. Develop a recoating capability that will minimize (or eliminate) substrate-metal loss.

3. Develop nondestructive testing methods for process control and for predicting the useful remaining life of coated turbine-engine components. Techniques should measure or identify defects, corrosion damage, coating thickness, extent of coating-substrate interdiffusion, fatigue damage, and wall thicknesses of cooled components.

4. Develop manufacturing techniques for the reliable coating of extremely small diameter internal cooling passages used in convection and transpiration cooling.

5. Develop automated manufacturing processes in order to improve coating reproducibility and reliability.

In addition, a number of secondary recommendations are made to point out areas of study on a more specific basis:

1. Conduct research to statistically define the effect of modifier elements (e.g., rare earths) on the oxidation and sulfidation resistance of aluminide coatings.

2. Determine the effect of alloying elements on the compositional range of NiAl (CoAl). If certain elements can be added that will increase the aluminum content of this intermediate phase, the larger reservoir of available aluminum could increase coating life expectancies.

3. Oxidation and sulfidation kinetics (using both kinetic and static tests) should be determined for promising binary, ternary, and quaternary alloys in order to find a replacement coating for the basic, currently-used aluminides. These alloys should have some inherent ductility in order to be considered for use as future coatings.

4. Attempts should be made to raise the melting point of the nickel (cobalt)-poor, aluminum-rich diffusion zone in currently-used aluminide-coating systems. Modifier elements may prove to be effective in satisfying this necessity for future aluminide coatings.

5. Additional research to develop a coating for dispersion-strengthened alloys that will function for long times at temperatures above 2000°F is recommended.

6. Continue the preliminary studies of adding discrete particles (e.g., Al_2O_3) to the coating in order to improve oxidation and sulfidation resistance of aluminide coatings.

7. Develop a simplified procedure for coating turbine-blade tips in order to provide for oxidation and sulfidation resistance at this location after minor blade-length modifications have been made to coated blades during engine fit-up.

8. Determine the effect of coating-process variables, coating chemistry, and post-coating heat treatments on (aluminide-type) coating ductility.

9. Establish the effect of long-time service on the mechanical properties of coated components, especially thin sections.

10. Continue research on the use of diffusion barriers (or elements added to the coating to reduce thermodynamic activities of diffusing species) to minimize interdiffusion between the coating and the substrate.

11. Obtain a more comprehensive and fundamental understanding of the degradation phenomena for coated components.

12. Continue research on the development of protective coatings for columbium- and chromium-base alloys.

2. Chemical Propulsion

a. Summary

1) Launch engines. In almost every case, propulsion rocket engines in present use are regeneratively cooled and uncoated. One exception is the transtage of the Titan II, which employs a thermal insulation coating consisting of a proprietary metal-oxide mixture plasma sprayed onto the nozzle tubes. Another engine employing regenerative cooling supplemented by an insulative coating is the XLR-99, which powered the X-15 experimental aircraft. In this engine the stainless steel nozzle tubes, cooled with ammonia fuel, were further protected by a plasma sprayed graded zirconia-nickel chromium alloy deposited on a plasma sprayed molybdenum undercoating.

Thermal lag coatings are used in liquid- and solid-fueled rocket engines, providing the firing times are very short (frequently less than 5 seconds), so that the heat from combustion does not degrade the mechanical properties of the light-weight structural alloys. The Bullpup missile employs flame-sprayed zirconia on both the aluminum combustion chamber and on the nickel-chromium alloy precoated copper nozzle. The solid fueled Scout missile uses a flame-sprayed zirconia coating to protect its ZTA graphite nozzle. The Lance surface-to-surface missile uses a metal graded zirconia thermal lag coating.

In contrast to current practice, many of the advanced, regeneratively-cooled rocket engine concepts incorporate thermal insulation coatings. In such concepts, gas temperatures, chamber pressures, and heat transfer rates are higher than those now encountered. Thus, higher heat fluxes to the structure

and the coolant can be expected. These heat fluxes must be reduced if nickel alloys, Type 347 stainless steel, and Inconel-X are continued to be used as structural materials. Thermal barrier coatings may include refractory oxides, refractory metals, or mixtures, or graded layers of both, as well as the refractory metal carbides, nitrides, and borides. These coatings may be applied by plasma spraying or slurry application. Undercoatings of intermediate melting point may also be used to relieve thermal shock and improve coating adherence.

Examples of regeneratively cooled nozzle conditions for which coatings will be required are hydrogen/oxygen and Flox/propane engines. For nozzles ranging from 3 in. in diameter to very large boosters, H_2-O_2 combustion will develop environments containing H, H_2, O, O_2, and OH with gas temperatures of about 5900°F (approx. 3250°C) and chamber pressures from 1000 to 2000 psia. Coating surfaces may reach 4000°F (2200°C). Coatings having thermal resistances of from 120 to 250 in.^{2} sec-°R/BTU will be expected to drop heat fluxes to the nozzle from 60 BTU/sec-in.^{2} (for uncoated nozzles) to 20 BTU/sec-in.^{2} for a coated nozzle. The latter heat flux will allow the liquid hydrogen to keep the tube surfaces under the coating cooler than 1600°F (approx. 870°C) and thus structurally sound.

For small second stage engines (3" to 5" in diameter), the use of Flox (liquid oxygen containing 76 weight percent fluorine) and liquified gases, such as propane, is attractive. The highly reactive combustion products will include H, HF, F, F_2, O_2, etc. Gas temperatures will be about 7000°F (approx. 3900°C), while coating surface temperature will reach 4000°F (approx. 2200°C). Chamber pressures will be around 100 psia. Here coatings with thermal resistances to 1400 in.^{2}-sec-°R/BTU will be needed to decrease heat fluxes from 6 to 3 BTU/sec-in.^{2}.

Large solid-rocket boosters do not need coatings on either the graphite nozzles or on the carbon-phenolic or silica-phenolic exit cones, because any given loss of nozzle material results in a relatively small percentage increase in nozzle diameter. For rockets with smaller nozzle diameters, the same loss of nozzle material has a much larger effect on performance. Here, tungsten or carbide coatings are needed. For example, the Polaris A3 (lst stage) has tungsten in the throat and a tungsten liner below.

2) Engines for space maneuver capability and attitude control. Rocket engines for space propulsion use a wide variety of refractory materials. However, only engines made from molybdenum, columbium alloys, and, in some instances, polycrystalline graphite are customarily coated. Rocket motors of up to 300 lb thrust incorporating Cb alloy nozzles or nozzle extensions are now in use or under advanced evaluation. The lunar excursion module utilizes a C-103 alloy nozzle with an aluminide coating and ablative throat nozzles. The Apollo service module has ablative throat engines with a C-103 extension nozzle, coated with a modified aluminide slurry. A 100-lb thrust C-103 nozzle, coated with a (Ti, Cr, Si) slurry coating, forms the backup system to a similar molybdenum engine for the Apollo command module. Engines of up to 300 lb thrust made from C-103 have been tested without failure for 15,000 seconds at 2500°F (approx. 1370°C). Maximum operating temperature was 2800°F (1540°C) with rapid failure occurring at 3000°F (1650°C). Recent work has shown the feasibility to protect columbium alloys to 3600°F (approx. 1980°C), but a substantial amount of fabrication development and testing still remains to be done before these recent developments can be translated into improved coatings for columbium rocket nozzles.

The Apollo program also utilizes molybdenum engines of 50-100 lbs thrust for attitude control on the command module and for the LEM module. Similar engines of 100 and 22 lbs thrust were envisioned for the MOL program. The coating for these engines consisted of pure $MoSi_2$ and was applied by pack

cementation. Coating life is limited more by abrasion during handling than by oxidation. Earlier spalling problems have been solved by improvements in coating technique. Molybdenum engines have performed well so far, and future engines will probably use the same pure $MoSi_2$ coating. The principal reservation to the use of molybdenum nozzles centers on the inherent brittleness of the metal, not on coating performance.

Graphite is generally used uncoated in rocket engines. Exceptions are the Scout and Lance missiles, which use a flame-sprayed zirconia coating on polycrystalline graphite. This coating is thermodynamically unstable and functions only because of the short firing times. Graphite engines with a SiC coating have also been evaluated, but the performance of this coating is limited to approx. 3000°F (1650°C). This very limited use of coated graphite is due to the fact that, at present, there are no operational coating systems that can protect graphite from oxidation in the 4200-4700°F (2300-2600°C) temperature region, where graphite reaches its highest strength. Iridium coatings may potentially protect graphite up to the eutectic temperature of 4140°F (2280°C), and an Ir-30% Re alloy may offer protection to 4500°F (2480°C). Substantial efforts have been made to develop tungsten coatings for graphite for use in solid fuel engines, although none of these coatings appear yet to be in use.

Future coating requirements for maneuvering and attitude control engines are probably somewhat limited. Some use of coatings may be made with hybrid engines and tactical system engines. Attitude control may in the future be achieved by monopropellant hydrazine engines, which operate most efficiently at approx. 1800°F (980°C). Uncoated superalloys, e.g., cobalt based L605, perform successfully in this application. Alternatively, coated molybdenum or columbium engines, or the uncoated beryllium engine, could also serve future attitude control requirements.

Increased maneuverability requirements, i.e., capability to throttle and re-start in the future may require the use of storable liquids, hybrids or re-start solids as fuel for tactical missiles. For these advanced requirements, pyrolytic graphite coatings on polycrystalline graphite have shown promise in the laboratory. Some designers favor a 'hard' throat for high performance missiles. Tungsten is a candidate metal especially if it could form a protective coating with some metal that had been infiltrated into it, e.g., possibly zirconium or hafnium. Such 'hard' throat should be useful with fluorine or Flox oxidizers, perhaps with hybrid rockets.

b. Conclusions and recommendations

Present regeneratively cooled liquid-fueled booster engines do not require coatings. Future booster engines still in the conceptual design stage will operate at much higher exhaust gas temperatures and will require thermal insulation coatings. Coated hardware requirements for these engines are still several years in the future. NASA is at present funding work on oxide (ZrO_2, ThO_2)-based thermal insulation coatings for superalloys. Eventual operational requirements envisioned are a gas temperature of 6000°F (3310°C), coating surface temperature of 4000°F (2200°C), coating-metal interface temperature of 1800°F (980°C) and metal backface temperature between 0° and -200°F.

A number of liquid-fueled space maneuver engines utilize coated molybdenum or columbium throats. The $MoSi_2$ coatings for Mo-engines are adequate, and reservations to the use of these engines are based on the brittleness of the metal, not on coating performance. The modified silicide coatings for columbium also perform well, with a present operational limit at approximately 2800°F (1540°C). The development of improved silicide coatings for columbium alloy engines is largely dependent on the "fall-out" from similar coating work for reentry protection and/or jet engine blades. This is unfortunate because the trade-off considerations are different in these cases.

The Scout and Lance missiles use polycrystalline graphite engines with flame sprayed zirconia coatings. These coatings appear to perform well, principally because of their low thermal conductivity and short firing times. Other graphite engines are used uncoated, because at present there is no operational coating system that can protect graphite for an adequate time period in the 4200°-4700°F (2300-2600°C) temperature region, where graphite reaches its highest strength. Iridium coatings may eventually protect graphite up to 4140°F (2280°C), and iridium-rhenium coatings could extend the protection to 4500°F (2480°C). However, the high price and limited availability of these metals will likely restrict their use to the most critical applications.

3. Hypersonic Vehicles

a. Summary and conclusions

The hypersonic vehicles and related propulsion systems that will require the use of high temperature coatings are:

a) Manned hypersonic aircraft

b) Lifting reentry vehicles

c) Hypersonic missiles

d) Air-breathing propulsion systems

Manned hypersonic vehicles will require modest amounts (relative to superalloys) of coated refractory metal for use as radiative-cooled heat-shields and as structure. The coated refractory metals will operate at peak temperatures in the range of 2000 to 3000°F and must have as long life as possible for cost effectiveness. This class of vehicle will be reflown many times. Superalloys will be used to a greater extent for heat-shields and structures. However, the payoff for coating the superalloys is not obvious because present day coatings are not generally weight effective. That is, the oxidation rate of the superalloy is sufficiently low so that it can be used without a coating. In many cases, the amount of metal

that is oxidized will not equal the coating weight until after 50 to 150 flights. The manned hypersonic vehicle is not likely to become a flight system before the turn of the century.

Lifting reentry vehicles are likely to become operational in the near future. Coated refractory metals and superalloys will be used for the same purposes as previously mentioned for the manned hypersonic vehicles. The maximum temperatures are likely to be somewhat higher for lifting reentry vehicles (3200°F); however, the vehicle life is considerably shorter. Therefore, it is less likely that superalloys will require oxidation-protective coatings. However, the lifting reentry vehicle life (50 to 100 flights) probably exceeds the capabilities of current coating systems for refractory metals.

Hypersonic missiles are currently under development. Although their environment is more hostile than that encountered by manned hypersonic aircraft, service time is shorter (up to a few minutes), in a single flight. Present day silicides have potential for service to about 3200°F, and hafnium-tantalum coatings or claddings to 4000°F. Higher temperature capability is desired, particularly for propulsion systems where flame temperatures exceed 6000°F.

Air-breathing propulsion systems (scramjet) generally would be used for the manned hypersonic vehicles. Very high heat rates are attained in the inlet area so that regenerative cooling is required. Thus, the most likely coating need is for thermal insulation to reduce the coolant requirement.

Currently, the superior oxidation-protective coatings for refractory metals for use on hypersonic vehicles are the silicides. This class of coating is most likely to be used in the near future for coating all refractory metal alloys. The aluminides have received considerable use to date because of their processing advantages. However, they are not competitive with the silicides for long life and, in some cases, for maximum temperature resistance. Also the

recently developed fused-slurry silicides have essentially the same processing advantages as the slurry applied aluminides.

A reasonably good coating capability exists for columbium, molybdenum, and tantalum alloys for use up to about 2800 to 3000°F. There is no doubt about the current ability to satisfactorily and reliably coat most hypersonic vehicle heat-shields and structures for one or two flights. The real questions are how many flights will the coating survive, what are the part design constraints, and what is the cost effectiveness of coated refractory metals compared to other heat shielding approaches such as ablators. Of course, answers to these questions are highly dependent upon the mission requirements for the flight vehicle.

The life of the present-day coatings on hypersonic vehicle components most likely will be determined by the coating defects or thinly coated areas present. The state-of-the-art coatings generally fail by defects or thin spots, with the defect or thin spot induced failure time being considerably less than the intrinsic life of the coating. Hypersonic vehicle components fabricated from refractory metals will tend to be relatively large, of complex geometry, and made from thin gage material. Therefore, the probability of a coating defect or thin spot, or a number of defects or thin spots, is much greater than for the typical test coupon normally used for coating life determinations. In spite of this probability of coating defects or thin spots, the chances of a coated refractory metal part surviving one or two flights in a hypersonic airframe application are extremely good because an early coating defect or thin spot failure is not likely to cause functional or structural failure of a part until after one or two additional flights. After the local coating failure occurs, it is more readily detected and repair or replacement may take place as appropriate. The fused-slurry silicide coatings have been prone to thinly-coated areas, but have not indicated a tendency for the classical defects such as variable composition, holes, or large edge crevices.

An accurate determination of the reuse capabilities of the better present-day coatings has not yet been accomplished. The coatings must be applied to representative flight hardware and tested at simulated flight conditions where the important environmental factors including temperature, pressure stress/strain, and time are simultaneously duplicated. Such testing will also reveal the effects of manufacturing processes and part design on coating/part life. Furthermore, it will establish the defect tolerance of coated refractory metal parts.

Because coating defects are likely to be the factor that controls the life of coated refractory metal parts, coating compositions and processes that are less prone to defects should be emphasized for future development. The fused-slurry silicides are considered the most promising coatings currently available for meeting all the requirements for hypersonic vehicle applications. This tendency for defects or thin spots to generally govern the useful life of state-of-the-art coatings makes nondestructive testing (NDT) very important. Detection of these defects and thin spots prior to flight and detection of early local failures after flight is necessary for maximum utility of these coatings.

b. Recommendations

The five major recommendations for research on coatings for hypersonic and reentry vehicles are as follows:

1) Determine the capabilities of the most promising currently available coating systems for refractory metals by testing representative hardware to the flight environmental conditions that have the greatest influence on coating performance. Accurate hypersonic flight simulation is required.

2) Improve the reproducibility and reliability of the most promising coating systems when applied to representative hardware. The deficiencies to be corrected will be identified by the testing performed in recommendation No. 1. Improvements shall include all influencing aspects of manufacturing technology and processing as well as design considerations.

3) Improve NDT methods for use in process control, inspection after coating application, and inspection in service.

4) Future development should emphasize simple (nonmultilayer) coatings applied by a fused-slurry method because they are considered to have the greatest potential for meeting the majority of future needs for oxidation-protective coating of refractory metals. Fused-slurry silicide coatings for use to 3200°F should be further developed for tantalum and molybdenum alloys. Exploratory research on new coating systems, inherently more reliable than silicides, should be encouraged. Desired characteristics include coating ductility at ambient and elevated temperatures, and diffusional stability in contact with substrates.

5) For coating applications to large surface areas, weight usually is a critical factor; therefore, thin coatings ($\sim$ 1 mil) that have a long service life ($\sim$ 1000 hrs for superalloys) are needed.

The following is a discussion of specific recommendations for selected coating systems:

1) Diffusion coatings for refractory metals. Before undertaking any further coating development effort, the present coating capabilities should be clearly defined in terms of their ability to reliably and reproducibly protect representative prototype flight hardware. This evaluation must be at thermal and mechanical environments which correspond to service use. It is only quite recently, after significant progress has been demonstrated by conventional laboratory specimen testing (such as furnace, "slow cyclic," and low-pressure oxidation exposures), that such advanced simulated service environmental testing has become warranted. But intensive testing under mission-oriented, vehicle-design constrained test parameters is now appropriate. This will permit a clear picture of current coating limitations to emerge before embarking on any ambitious coating/processing improvement programs. This recommendation is generally applicable to all categories of diffusion coatings considered for hypersonic vehicles.

Future developments should primarily involve efforts to advance the practicality and reliability of the better coatings already developed. Specifically, it is recommended that efforts be concentrated on improving the reliable cyclic life of fused-slurry silicide coatings for fabricated columbium components for use in the temperature range up to 2500°F. Any work toward improving higher temperature capabilities for columbium coatings should be deferred until higher creep-strength columbium sheet alloy is available. At temperatures above about 2500°F, creep of the columbium appears more limiting than the coating for long-life, multi-mission vehicles.

Similarly, more effort is required to establish and improve the reliability of reusable fused-slurry coatings for tantalum and molybdenum alloys for use to 3200°F. Work should be done to adapt the more refractory silicide compositions as fused coatings for these substrates. Processing times and

temperatures need to be minimized for coating molybdenum to avoid ductile-brittle transition problems. Significant improvements in coating emittance compared to available pack silicides appear feasible by slurry composition adjustments for molybdenum.

For vehicle structure and heat-shield applications, the emphasis should continue to be on fused-slurry coatings, because of inherent advantages in coating large parts or complex geometries. To minimize the likelihood of incurring localized coating defects on parts where reusability is critical, pack or sintered coatings should be avoided, if possible; and multi-layer (multiple process) coatings should be considered only as a last resort, with simple one-step coatings accorded priority.

In the processing area, further work is needed to obtain uniform coating thickness on simple and complex parts and assemblies. Process specifications incorporating good quality assurance provisions are also required. It is essential to define the scope of applicability for available NDT methods and to devise apparatus and techniques amenable to the field inspection of "flight" hardware. Techniques for reliably and quickly detecting small local coating failures after flight exposures is desired. Special attention must be given to the inspection of the interior surfaces of complex fabrications, such as closed corrugations.

Specific effort should be directed to the problems of field repair of coatings. Feasibility for coating repair has been established in the laboratory, but more work is needed to define the limits of repairability and the degree of confidence merited by repaired coatings—i. e., how large and what type of defect can be repaired and how long will it be protective. Research on quality control and inspection methods for "patch" coatings is required.

No truly satisfactory diffusion (silicide) coating is available for the protection of molybdenum or tantalum at temperatures much beyond 3000°F, or for tungsten beyond about 3300°F. Moreover, based on considerable past effort, it does not appear that any additional work along the silicide coating approach is warranted for these very high temperatures unless the operation time is short. It is therefore recommended that no further work be undertaken on diffusion coatings for the protection of refractory alloys at 3500°F (or above). Other concepts for very high temperature protection are needed.

2) Superalloys. Since there is a definite need for improved protective coatings for superalloys used in gas-turbine engines, it is recommended that research and development efforts for satisfying this objective precede coating technology for hypersonic flight and reentry vehicles. This approach is considered most logical because much of the information that would be gained in developing protective coatings for gas-turbine engines will be directly applicable to the other application if the need occurred.

It is also recommended that improved oxidation-resistant alloys having adequate high-temperature properties be developed. (This would significantly reduce the need for protective coatings on hypersonic flight and reentry vehicles.) An approach for obtaining these alloys is through minor compositional modifications of existing superalloys and TD-Ni alloys. For example, rare-earth metal additions are known to improve the oxidation resistance of several superalloys and additional progress can be anticipated if this area of research would be more completely exploited.

3) Platinum-group metal coatings. No advanced development studies are recommended for Pt group metal protective coatings unless a specific need occurs, or if no other coating system can be used.

If it is found necessary to further the development of Pt group metal coatings, the following research areas should be considered:

a. Future research should be limited to Ir and Rh and alloys of these metals.

b. Additional research on diffusion barriers (particularly oxides) is recommended.

c. Research on metallic substrates should be limited to those that will not oxidize catastrophically in the event of localized coating failure.

d. Additional research is recommended on applying Ir- and Rh-base coatings by pyrolytic deposition from organometallic vapors and solutions, or by fugitive vehicle slurries.

e. Continued research on Ir-base coatings for protecting non-metallic materials (e.g., graphite) is believed to be worthy of additional consideration.

f. Any of the above recommended-research should be limited to relatively low monetary expenditures.

4) Hafnium-tantalum coatings. Hf-Ta and Hf-Cb alloys should be extensively studied to develop their full potential both for short-time and multi-hundred hour service as coatings and claddings, as well as free-standing bodies in oxidizing environments. Detailed understanding should be obtained of: (1) oxidation and degradation mechanisms, (2) alloying for combined oxidation resistance, ductility, and strength; (3) properties of optimum coatings and claddings on Cb alloys, Ta alloys, and graphite substrates; and (4) component design, fabrication, performance, reliability, and design allowables.

5) Coatings for graphite. Practical coatings, having a temperature capability comparable to graphite, are required if graphite materials are to be utilized to any extent for hypersonic vehicles.

6) Oxide coatings. New ideas and approaches are required for the reliable utilization of oxide ceramic coatings as thermal insulations for hypersonic vehicle structures.

4. Energy Conversion Systems

a. Summary

1) Background. Energy conversion systems are used to convert heat or chemical energy into electrical energy. Their efficiency depends on the maximum temperature of the heat source and the lowest temperature at which heat may be rejected. A considerable advantage is associated with the use of high temperatures, which may be translated into weight saving in the energy conversion devices. Efficient energy conversion systems requiring high-temperature materials are needed for auxiliary power units (APU's) for orbital and space vehicles. Nuclear APU's are designated by the acronym SNAP (systems for nuclear auxiliary power), and are of two types: odd number SNAP systems use radioactive isotopes as the heat source and thermoelectric generators as the energy conversion systems and are designated RTG systems; and even number SNAP systems employ turbine-alternators, and operate as a gas Brayton cycle or as a vapor-liquid Rankine cycle system. The coating requirements in these various energy conversion systems are summarized below.

2) Nuclear reactors. Fuel elements for high-temperature nuclear reactors employ coatings to isolate the fuel elements from the heat-transfer fluid and to retain gaseous fission products that are released. Coatings for fuel elements have received a great deal of concentrated attention from the Atomic Energy Commission and its contractors. They are not considered as coming under the scope of oxidation-resistant coatings for energy conversion systems.

3) Radioisotope thermal generators (RTG's). These devices are fueled by radioactive isotopes of plutonium, polonium, curium, etc., the amount of which used per capsule is selected to produce a suitable operating temperature for a thermoelectric converter, about 700°C for PbTe and 1000°C for SiGe. The radioisotope containment capsule is generally multilayered for high-temperature

applications, with tungsten inside, an intermediate layer of high-strength tantalum alloy, an outer layer of oxidation-protection material, either superalloy or platinum-base alloy. Lower temperature radioisotope sources are contained in a shell of high-strength, oxidation resistant superalloys. Another coating requirement in RTG's is coatings that enhance thermal emissivity from the nuclear heat source to a dynamic system.

The chief safety hazards in the operational cycle of an RTG occur in ground handling, launch, space operation, and during and after reentry from orbital flight. It is imperative to provide oxidation protection to maintain fuel container integrity and not disperse fuel into the atmosphere. Requirements include stability against interaction with the fuel during its lifetime, which can be as much as hundreds of years.

4) Thermoelectric systems. Thermoelectric generators have secondary applications for coatings, including insulation and diffusion barrier coatings.

5) Turbine-alternator systems. High-temperature turbines intended for space power will not have to be protected against oxidation, since they operate in the vacuum of space. It is considered too risky to use oxidation-resistant coatings for ground testing in air, and such systems are tested in large vacuum chambers.

Coatings in turbine-alternator converters are used chiefly in the radiator section to enhance heat loss by radiation. Thus, they must have high emittance.

6) Thermionic diodes. Coatings would be needed in thermionic diode systems for improving electronic emission and for insulation purposes. However, they are not considered as critical as the many other problems associated with these devices.

b. Conclusions and recommendations.

Coatings are important to achieve long life and high efficiency in energy conversion systems. However, they are used principally for secondary purposes such as maintenance of stability of thermoelectric materials, electrical insulation, barriers against diffusion, and thermal emissivity on radiator surfaces. RTG systems have a critical coating requirement for protecting the radioisotope core during launch and space operation and during and after reentry into the earth's atmosphere. The heavy sheathings of oxidation-resistant alloys are probably the best coating system that could be used for this purpose. Coating of nuclear fuel elements was considered to be a special case, not within the scope of the Committee.

The task group had no recommendations for future research and development, since the main coating requirements are for secondary purposes, and the only oxidation-resistant coating appeared to be as good as could be developed.

5. Industrial

Coatings for high temperature service must clearly offer improvements in process or component performance before their additional cost can be justified by an industrial user. Coatings are most widely used in the metal- and glass-producing industries where they frequently offer the only way to operate economically and successfully. For example, glass and metal producers must protect their molten product against contamination from the crucible and their control thermocouples from corrosion. In metal forging and extrusion, coatings provide thermal insulation which prevents heat loss from the work piece and so insures optimum fabricability. Such coatings also protect the hot metal against atmospheric contamination.

Elsewhere, high-temperature coatings are used to extend the lives of critical components of a wide variety of products. Home furnace burners, automotive exhaust control devices, and parts of petroleum cracking plants are just a few of the many applications for these protection systems.

While the industrial application of high temperature coatings is not presently extensive, their use by selected industries was found to be more widespread than expected. As more industries increase processing temperatures, the use of the coating technology base established by defense and space research can be expected to expand considerably.

C. Manufacturing Technology

1. Summary and Conclusions

A very thorough survey was made of all industrial and laboratory organizations in this country, active in the application and development of high-temperature, corrosion-resistant coatings. Each organization was requested to provide information relative to their coating processes, substrates protected, coating designations and chemistries, coating facility sizes, and process status (production or development). About 80% of the organizations responded to the questionnaire. The principal coating organizations did reply, and the information collated does represent a good summary of the manufacturing capabilities available for the application of coatings to high temperature materials.

Nine basic coating processes were defined. Comments pertinent to each of these processing categories are summarized below.

a. Pack processing

Pack coating involves immersion of the material to be coated in a granular pack media, and a thermal cycle which is performed in a non-oxidizing environment. The coating is formed by vapor transport and diffusion. For the

refractory metals, several promising coating systems are pack applied; and, for the limited requirements for coated refractory metals, adequate coating facilities are generally available. Only experimental or low production quantities of coated aerospace and aircraft gas turbine components have been required, consequently little impetus has been provided for establishing reproducible and reliable production coating methods. Should the demand for production coating of refractory metal components arise, a major effort would be required to advance current processes to the required technological level. Silicides are the principal coatings that are pack applied to refractory metals. An unresolved problem is reliable repair methods for pack applied silicide coatings.

Pack-aluminizing of nickel and cobalt alloy turbine airfoils is a large-scale manufacturing activity in the gas turbine industry; and the major pack-coating requirement for high-temperature-nonrefractory alloys. At present, adequate facilities are available in the industry for processing the hundreds-of-thousands of airfoils processed each month. The manufacturing problems related to coating nonrefractory metal alloys are principally: (a) coating of component air-cooling passages and internal holes, (b) masking during coating, (c) processing of large-size components such as gas turbine transition ducts, (d) processing capability for coating dispersion-strengthened alloys, and (e) processes and facilities for aluminide recoating of service operated gas turbine components. The industry has directed its efforts primarily to the aluminizing of non-air cooled blades and vanes; consequently, the problem areas outlined above will require substantial attention in future R&D efforts. A significant need for pack coating capabilities outside those required by the aerospace and gas turbines industries was not identified in this survey.

b. Slurry processes

Slurry coating entails the application of a slurry mixture containing the coating elements on a substrate surface, generally by dipping or spraying, followed by a thermal treatment in a protective environment. Coating formation

is achieved by vapor transport, liquid reaction, or solid state sintering. Slurry processes have been widely used for the formation of high temperature coatings to refractory metals, e.g., aluminides, silicides, noble metals, and others. A major problem with slurry-applied coatings has been thickness control. From a manufacturing standpoint, the lack of significant requirements for coated refractory metals precludes the need for expanded manufacturing capabilities. Laboratory development of improved coatings and improved slurry application methods is recommended.

Slurry application of aluminide coatings to superalloy blades and vanes is a large-scale production activity in the gas turbine industry. Automation of the slurry approach to aluminizing blades and vanes would be required to make this method economically competitive with pack processing. For the aluminide coating of large nickel alloy AGT components, such as combustors and transition ducts, the slurry approach may offer advantages over pack processing. In this event, development of methods for applying uniform slurry coatings to large-complex shapes will be required.

c. Chemical vapor deposition

Chemical vapor deposition (CVD) is an entirely gaseous process, where the coating elements are transported to the substrate surface in vapor form, and are deposited upon the surface by chemical or pyrolitic reduction of the gaseous compound. CVD has been successfully employed to apply many high temperature protective coatings; however, the available facilities are predominately laboratory scale. Substantial problems are encountered in depositing uniform coatings on complex shapes by CVD. Until a demand exists, and significant advantages are defined for CVD deposition of certain coatings, a specific effort aimed at developing expanded CVD manufacturing capabilities is not warranted.

An immediate problem in the aerospace field where CVD may be applicable is the deposition of a tungsten barrier layer coating on tantalum alloys. Additional R&D effort in this area is recommended.

d. Electrolytic deposition

Electrolytic deposition includes conventional aqueous electroplating, electrolytic deposition from fused salt baths, and electrophoresis. The latter technique involves deposition of charged particles from a liquid suspension onto an oppositely charged substrate. Aqueous electroplating is not widely used for forming high-temperature coatings, and specific development efforts in this area are not recommended. Electrolytic deposition from fused salts has been successfully employed on a laboratory scale for depositing many high-temperature coatings. However, owing to the problems associated with scaling-up fused salt coating methods, and the absence of clearly defined advantages for this method, manufacturing development in this area is not recommended.

Electrophoresis provides an excellent means of applying uniform slurry coatings to complex shapes. Electrophoresis is the most promising approach to resolving the problem of uniformly, reproducibly, and economically applying slurry coatings to high-temperature materials. Fused-silicide coatings can be electrophoretically deposited, and consideration should be given to this coating method in future programs.

e. Fluidized bed

Fluidized bed processing involves immersion of the material to be coated in a fluidized granular media of the coating elements or inert materials. Fluidization is accomplished with an inert or reducing gas, and/or a gas containing a halide form of the coating species. The process is a variation of chemical vapor deposition. Expensive facilities and high operating costs are disadvantages to fluidized bed processing. No immediate need for process development exists for the fluidized bed coating method.

f. Plasma and flame spray processes

Coating deposition with the arc plasma or gaseous fuel/oxygen flame torches has proved extremely successful for the application of hardfacing and wear-resistant materials. These techniques have not been used extensively for applying high-temperature protective coatings, owing to problems such as density, bonding, thickness control, cost, etc. Although the expansion of manufacturing capabilities in these areas is not warranted currently, the use of these techniques for the deposition of coatings not easily formed by diffusion methods should be explored.

g. Hot dipping

Hot-dip coatings are formed by immersion of the part to be coated in a molten bath which contains the coating elements. Hot dipping has been widely used for the application of coatings to ferrous and nickel-base alloys; however, the family of high-temperature coatings applicable to these materials have been better formed by other methods. Adequate hot-dip manufacturing capabilities are available for current high-temperature coating needs.

h. Cladding

Cladding entails sandwiching of a structural high-temperature material between surface layers of a protective high-temperature alloy. Edge closure is a major problem associated with the cladding application of high-temperature coatings, consequently little effort has been directed to utilizing this approach to high-temperature coating development. For the refractory metals, only very few protective systems are amenable to cladding application, therefore manufacturing development in this area is not warranted. In the case of superalloys, heat-resistant coatings not easily formed by diffusion-controlled processes may be applied by cladding, and this approach should be considered.

i. Vacuum vapor deposition

Vacuum vapor deposition encompasses all methods associated with the physical vaporization and deposition of coating materials. This process has been widely used for the deposition of thin-film coatings on mirrors, ornaments, reflectors, etc. Recent methods have been developed for the deposition of 3.5-mil thick high-temperature coatings on superalloys and refractory metal substrates. The flexibility of this method for depositing coatings not amenable to formation by nonconventional diffusion processes makes it attractive for further development. Since relatively expensive facilities are required, laboratory demonstration of the capabilities of this technique must be provided.

2. Primary Recommendations regarding Manufacturing Technology

(1) Demonstrate the reliability and reproducibility of available protective coating systems on refractory metal hardware.

(2) Develop reliable and reproducible methods for refurbishing service operated— aluminized superalloy hardware; and assess the influence of coatings and recoating operations on the mechanical properties of these hardware materials.

(3) Develop reliable methods for applying coatings to the internal passageways of air-cooled gas turbine hardware.

(4) Study the physical chemistry of current coating processes to provide a sound basis for process control and improvement.

(5) Develop field repair methods for diffusion coated refractory metals and superalloys.

3. Secondary Recommendations

(1) Establish manufacturing methods for applying Cr-Al protective coatings to large dispersion strengthened (TDNi and TDNiC) components.

(2) Develop reproducible processing technique for depositing tungsten-barrier layer coating to complex tantalum alloy shapes.

(3) Establish improved electrophoretic techniques for depositing a wide range of slurry coatings to complex refractory metal and superalloy hardware.

(4) Develop vacuum vapor deposition methods for applying complex, heat-resistant alloy coatings to nickel- and cobalt-based superalloys.

(5) Introduce automation into high volume coating activities, such as the aluminizing of superalloy turbine blades and vanes, for cost reduction and improved process reproducibility.

(6) Promote communication between hardware designers and coating suppliers to assure the design and fabrication of coatable components.

D. Testing and Inspection

1. Summary and Conclusions

The successful development of an effective high-temperature protective coating depends, to a great extent, upon the proper application and interpretation of tests at critical stages during the development phase and in the final evaluation

of the finished product. The technology of testing and inspection is broad and interdisciplinary. This discussion is concerned with only one aspect of this technology, that which pertains to the evaluation of high-temperature protective coatings for service above 1800°F. Consideration of only those applications above 1800°F virtually eliminates all industrial coatings. Aerospace and propulsion systems are the primary areas where such high service temperatures are normally encountered. In reviewing current testing procedures for this temperature range, it is not surprising to find them profoundly influenced by the data requirements that lead directly or indirectly to the design of coated components for aerospace and propulsion systems.

Coating evaluation procedures fall into four general classes: standard characterization, nondestructive-testing, screening, and environmental simulation. Standard characterization tests are those that measure basic characteristics of a coating and/or the coating-substrate composite. This would include the measurement of such properties as: hardness, thickness, density, melting point, emittance, thermal conductivity, tensile and creep strength, elastic modulus, and fatigue strength. Many of these measurements are routine procedures for which there are ASTM standard tests. Nondestructive-testing (NDT) includes any inspection or measurement technique that neither disturbs nor alters the physical or chemical characteristics of a coating system. NDT is frequently employed in process control to measure coating thickness and to detect nonvisible coating flaws. NDT techniques employ dye penetrants, ultrasonic transmission or emission, eddy-current emission, radiography, infrared emission, and thermoelective response. The technology of NDT is advancing rapidly and will have a significant influence upon the character of future testing and inspection techniques.

Screening tests are generally designed to provide a preliminary evaluation of the capability and potential of a coating system for a given application. Usually the data derived from such tests are of a comparative or relative nature.

The test environment ordinarily includes only one or two independent variables, and the emphasis is on high volume-high rate testing rather than environmental simulation. While screening tests normally involve a minimum of equipment, some facilities, notably those which are used to screen gas turbine coatings, may represent capital investments exceeding $50,000. Perhaps the most common screening test for high-temperature coatings is the so-called cyclic oxidation test in which small coated tabs are subjected to a series of isothermal air exposures until the original lot of specimens has failed. This test, like other screening tests, can be quite effective in eliminating from further consideration ineffective coatings, thereby minimizing the number of candidate coatings which must be carried into advanced proof testing. Simulated environmental tests are those in which the use-environment is simulated in the laboratory. This classification is somewhat of a misnomer since most aerospace and propulsion environments are either too severe or of too long duration to be realistically simulated. Most "simulated environments" are abbreviated representations of the real environment, and frequently significant parameters must be omitted because the physical capacity to simulate them is nonexistent.

When evaluating coatings for a certain class of applications, for example, gas turbine hardware, laboratories are in general agreement regarding the performance requirements. However, with respect to the tests employed and the significance of data obtained from these tests, there is almost total disunity. This lack of agreement stems principally from the independent evolution of testing procedures by different laboratories in an atmosphere of limited communication. It is virtually impossible to compare test results from different laboratories. This has been the cause of substantial duplication of testing efforts. The procedural difficulties of high-temperature testing have contributed to the nonuniformity of evaluation techniques. At elevated temperatures, even simple measurements of temperature and strain are difficult and none of the several techniques now

employed are completely satisfactory. Problems with high temperature reactions between coatings and specimen support media and the unavailability of simple inexpensive furnaces for long-term operation in air above 3000°F have further complicated the situation.

Another elusive factor which complicates interlaboratory data comparisons is failure criteria. The appearance of substrate oxide has been generally regarded as evidence of coating failure. However, the amount of oxide which accumulate to constitute a failure is a subjective quantity and will vary from laboratory to laboratory. Moreover, this failure criterion is strictly artificial and may have no relevance to what would constitute a service failure.

The first step toward elimination of the current confusion in evaluation of coatings would be establishment of meaningful test standards. An effort of this nature was the subject of an earlier NMAB study. The establishment of test standards for high-temperature protective coatings is currently being investigated by ASTM Committee C-22. The NMAB test procedures have received only limited acceptance; the progress of ASTM C-22 has been relatively slow. This due, in part, to the reluctance of laboratories to discard self-developed test procedures in favor of new and unfamiliar routines. Eventually standardized tests will be established, but not in the near future.

The confusion and inefficiencies produced by the current lack of test uniformity can only worsen as coating requirements become more stringent. Higher operating temperatures, longer service life, and greater reliability will be demanded of future coatings. Improved measurement techniques, refined reliability analyses, and more effective NDT must be developed so that the ability of coated parts to provide satisfactory performance for extended periods in hostile environments can be demonstrated with a high degree of confidence. Unified test standards must be cooperatively evolved by testing laboratories to minimize unnecessary duplication of effort. Furthermore, as service lives

increase, meaningful accelerated tests which can be accurately interpreted in terms of service life will be required.

2. Recommendations on Testing and Inspection

In anticipation of these future requirements, the following recommendations are made:

(1) Standardization of test methods must be effected—including standard characterization, nondestructive inspection, screening, and simulated environmental tests. In the interim, cooperation among coating vendors and evaluation groups must be encouraged for the purpose of unifying current testing procedures and eventually standardizing all tests.

(2) New and improved NDT methods which yield quantitative data must be developed. Exploitation of reliability analyses and nondestructive characterization techniques should proceed as an integral part of new coating development programs.

(3) Meaningful, accelerated coating-life tests which are thoroughly correlated with service performance must be developed.

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