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FORMATION, ADHESION AND MECHANICAL/CHEMICAL
PROPERTIES OF PROTECTIVE COATINGS*

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ABSTRACT

Some general considerations for protective coatings are discussed. It is suggested that ceramic coatings may provide a class of coatings applicable to high temperature turbine blades for use in a corrosive/erosive environment. In particular, the ceramic glass materials would seem to hold promise, but little or nothing has been done on depositing these materials by vacuum processes.

INTRODUCTION

(but usually by sand)

Coatings may be defined as near-surface regions having properties differing from the bulk material. Coatings are technologically useful in that they allow the surface and near surface region to be tailored for specific properties independent of the substrate material. This may be useful for economic reasons, or for engineering flexibility. Coating materials may be desirable for their own properties or to protect the underlying substrate materials either as barrier layers, sacrificial layers or electrochemical modifiers. For high technology applications, the coating and substrate requirements may be very stringent. For instance, in high temperature - high stress - corrosive environments, the substrate material must have good strength, fatigue, and creep properties and such materials usually have poor corrosion resistance. In this case, the coating material must provide environmental protection to the substrate material without degrading the metallurgical properties of the substrate material.

Coatings may be formed in a variety of ways each of which have their advantages and disadvantages. Coatings may be categorized as diffusion/reaction coatings, deposited coatings or surface modification coatings. Diffusion/reaction coatings rely on a component of the structural material to form the coating by either reacting with the environment (anodizing, boriding, oxidizing, nitriding, etc.), or by segregating to the surface and then forming a passive film usually by reacting with the environment (Be in BeCu, Al in steels, etc.). Deposited coatings may be classed as atomically deposited (physical vapor deposition, chemical vapor deposition, electroplating, etc.), or particulate deposited (plasma spraying, flame spraying, electrophoretic coating, etc.). In a broad sense surface modification treatments such as laser quenching, shot peening, ion implantation, cladding and other such surface modification techniques may be considered to be coating techniques. In all the coating processes the properties of the resulting coating depend on the process and process parameters utilized.

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Coatings may function to protect the substrate from a number of threats but the major threats in energy applications may be considered to be wear/erosion and corrosion. Wear may be considered to be the loss or disruption of material by solid bodies in contact. Erosion is the loss or disruption of material by impact (physical), by chemical reaction (chemical) or by vaporization (thermal). Corrosion may take many forms. Massive corrosion can remove material in depth. More subtle corrosion such as internal oxidation, grain boundary oxidation, or pitting corrosion may affect the physical or failure properties of the materials without obvious loss of material. Interfacial corrosion can destroy the adhesion of a coating-substrate system.

Coatings for wear and physical erosion should be hard and tough and often there is a trade-off necessary between the two properties. In particulate erosion, the rule of thumb is that the surface should have a hardness greater than that of the impinging particle. Failure in coatings for particulate erosion resistance generally start at coating defects such as cracks, nodules or pores. Coatings for chemical protection (corrosion, chemical erosion) should be nonreactive, or should form coherent surface layers which do not allow progressive chemical reaction. The coatings should have low diffusivity for the corroding atoms and atoms of the substrate material. Low diffusivity generally implies a low point defect concentration (stoichiometric composition) and an absence of short circuiting defects such as cracks and pores. Grain boundaries may provide a high diffusivity path in some systems. Coatings for high temperature environments should be refractory in nature in order to avoid thermal erosion. In addition, thermal effects on the coating and interface microstructure and composition must be known and controlled. Thermal fatigue may be a problem for some coating systems.

In gas-turbine engines coated components which operate at high temperatures are subjected to corrosion (oxidation and sulfidation), particulate erosion, thermal fatigue, mechanical stressing and fatigue, and elevated temperatures (1). The coating-substrate system must survive these threats. Generally, this requires that the coating have chemical compatibility, low defect concentration, thermal and mechanical fatigue resistance, high creep strength, and a high hot hardness. In order to extend the temperature range of protective coatings to greater than that achieved by the oxidation resistant metal superalloy coatings will probably require development of new classes of coatings. With the possible exception of the chemically stable intermetallic compounds ($ZrPt$, Mo_5Ru_3 , W_3Ru_2) it would seem that ceramic coatings hold the greatest promise. In this paper the author would like to discuss selected aspects of coatings in general and ceramic coatings in particular.

ADHESION

The adhesion of a coating to a surface is determined by a number of factors including, 1) chemical bonding, 2) intrinsic stress distribution, 3) interfacial defects, 4) distribution of applied stresses and, 5) failure modes (2). In ceramic systems it is generally considered that for an adherent bond to be formed that there should be interfacial reaction to either form a complex compound region or to alloy (dissolve) substrate atoms into the coating material. In oxide metallization or metal enameling this interfacial reaction region may be a complex metal oxide. In many cases the metal surface is oxidized before

glassing in order to facilitate solution and reaction. In addition to the forming of the desirable interfacial compound solution it is desirable to eliminate interfacial defects such as voids which lead to stress concentration and easy fracture modes. In solid-liquid systems these defects can be minimized by wetting and spreading of the liquid phase over the solid surface. This wetting and spreading is enhanced by surface layers which will be dissolved in the liquid phase and thus acts as a flux as well as partake in the interface formation. Intrinsic stress due to a mismatch in the coefficients of thermal expansion of the coating and substrate should be minimized though a residual compressive stress will tend to retard crack propagation.

CERAMIC COATING TECHNIQUES

Ceramics are materials which fail by brittle fracture processes and are generally ionically bound compounds. Compounds of borides and carbides are hard but often do not demonstrate high temperature chemical compatibility with oxygen as do the oxides. To form a stable high temperature coating-substrate system, the coating material must have limited reaction with the underlying substrate material. This requires that the oxide material have a free energy of formation much more negative than that of the oxides of the base materials. This may mean that an intermediate "barrier" layer must be formed in the coating system in order to isolate the coating materials from the substrate materials. A potential problem with ceramic coating systems is their thermal shock sensitivity. Thermal shock sensitivity depends on the coefficient of thermal expansion. Thermal shock resistance of a given system can be enhanced by internal and surface compressive stresses and an internal microstructure such that stresses are not transmitted (internal microcracks, etc).

Ceramic oxide coatings may be formed in a number of ways. Protective oxide layers may form on alloys such as Hf (15-30)Ta or Hf (10-15)Nb at high temperatures. The progressive oxidation of the alloy may be substantially modified by the addition of Al, Cr, Si, B, Ir, or Pt. In this case, the coating could be formed by metal alloy deposition followed by high temperature thermal oxidation. Oxide coatings may also be formed by the diffusion of a substrate constituent (Al, Si) to the surface and thermal oxidation of the surface layer. The oxide thus formed is thin but is self healing under the proper conditions. Oxide layers may also be formed by the mass transport of oxygen or metal ions through the oxide layer under an impressed electric field (anodization of Al, Ti, Ta, etc). Barrier layers may be formed if the oxide is coherent or thicker layers may be formed if the oxide is rather porous. Each of these formation techniques requires mass transport through the oxide layer and hence will probably provide limited corrosion protection at elevated temperatures.

Oxide coatings may also be formed by plasma spraying of powders or sintering or melting of powders deposited by slurry techniques or electrophoretic deposition. Plasma spraying results in a porous coating which is difficult to densify. The sintering of crystalline powders is difficult and in coating form have a great deal of porosity. These coatings generally require significant amounts of a glassy phase to generate a coherent material. Melting and flowing of glass powders to form coatings is well developed in such applications as enameling. Chemical vapor deposition of glass layers for encapsulation is well developed in the semiconductor industry.

POROSITY/VOID FORMATION

In order to be protective, a coating must be coherent and in ceramic coating systems obtaining a fully dense structure is often a problem. For particulate deposition of crystalline refractory oxides consolidation is difficult. For particulate deposition of glassy oxides consolidation can be obtained by post heat treatment which flows the material. In atomistic deposition processes, porosity, and voids may form due to the influence of foreign particles, surface defects or geometrical shadowing giving low density regions. For glassy deposits the porosity/voids may be healed by post thermal treatments. For crystalline materials this would be ineffective. Some improvement in the porosity of deposited oxides can be obtained by mechanically disturbing the surface during deposition or between successive layer depositions.

POINT DEFECTS/STOICHIOMETRY

Atomistically deposited oxides are difficult to form in stoichiometric compositions and even when formed they probably have a high point defect concentration. This is evident in the very low initial strain point of sputter deposited glasses films compared to bulk glass and annealed glass films. Stoichiometry often can be achieved by the addition of oxygen to the discharge in sputter deposition of glasses and possibly by the use of sputtering during deposition to remove loosely bound atoms from the growing deposit. Glass films deposited by chemical vapor deposition processes are probably more defect free than are the physically vapor deposited films. Very little has been done on the diffusion properties of atomically deposited glass coatings. Most glassy coatings should be expected to creep at elevated temperatures. The addition of a crystalline phase in the form of dispersed particles will reduce this tendency. An example of such a system is the ceraming glasses where the material is formed in the glassy state and then partially crystallized by thermal treatments. This formulation uses nucleating agents in the glass to initiate crystallization and control the amounts, size, and dispersion of the crystalline phase.

SUMMARY

It would seem that coherent protective films of ceramic materials would be highly useful. Coherent films of glasses can probably be formed by various deposition processes possibly followed by thermal flowing of the coating: These glass films would probably not be stable under the conditions of a high temperature gas turbine environment. Crystalline ceramic coatings would be more stable, but it is improbable that a coherent film of a crystalline ceramic coating can be deposited by vacuum processes.

A possible solution to the problem might be the use of ceraming glasses which can be fabricated in the form of a glass and then crystallized by subsequent heat treatment. Ceraming glass has been formulated which match the coefficient of expansion of metals ranging from aluminum to stainless steel. Coatings of the ceraming glasses have been produced by particulate deposition followed by flowing then ceraming. Nothing seems to have been done with vacuum deposited ceraming glass formulations.

coherent implies a match in lattice positions

It would be highly desirable to have a self-healing coating system. In a ceramic material formed by ceramizing, the strength and fracture properties are dependent on the microstructure and the relative phase composition of the crystalline and glassy phases. Cracks which form in ceramic coatings may be healed by the formation of a glassy phase formed by the interaction of some component of the substrate material with the environment (oxygen, sodium, etc). Glass forming elements include boron silicon.

REFERENCES

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