CORROSION RESISTANT COATINGS FOR HIGH TEMPERATURE APPLICATIONS

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ABSTRACT

Efforts to increase efficiency of energy conversion devices have required their operation at ever higher temperatures. This will force the substitution of higher-temperature structural ceramics for lower temperature materials, largely metals. Yet, many of these ceramics will require protection from high temperature corrosion caused by combustion gases, atmospheric contaminants, or the operating medium. This paper discusses examples of the initial development of such coatings and materials for potential application in combustion, aluminum smelting, and other harsh environments.

INTRODUCTION

Existing power conversion systems can obtain increased energy efficiency either through the addition of topping and bottoming cycles or through increased operating temperatures. Typically, operating temperatures are limited by materials capabilities, which in practice means the metallic alloy temperature limitation. Thus, any thrust toward higher operating temperatures involves the use of new materials for that application, with ceramic materials generally selected because of their superior high temperature stability and corrosion resistance.

The Si-based ceramics are of particular interest for energy conversion because of their excellent mechanical and physical properties. New Si_3N_4 ceramics have high toughness and excellent thermomechanical stability. They are also stable in purely oxidizing environments. Silicon carbide has been an attractive material because of its high thermal conductivity, and when in the form of a continuous fiber ceramic composite (CFCC) it is tough, thermal shock resistant, and thermomechanically stable.

The use of silicon-based ceramics has been somewhat limited because of their high temperature corrosion behavior in the presence of impurities and steam.^{1,2,3} A particularly severe example is seen in the rapid, catastrophic failure of a SiC CFCC tube in a coal slag environment (Fig. 1). The issue in most combustion systems is the attack by alkali metal compounds and/or steam. Alkali's can react with the native silica surface scale, which protects the Si_3N_4 or SiC in an oxidizing environment, to form a low-melting, soda-silica glass that allows active corrosion of the ceramic. In static steam environments the protective silica cracks and becomes non-protective, and under high gas velocities there is even significant recession through the formation of volatile hydroxides from the protective scale. The current approach to allowing the use of Si-based ceramics in these environments is to protect them with oxide ceramic overcoat systems.

Another important area for chemically stable, high-temperature materials is in the electrochemical smelting of aluminum. Structural materials, including thermocouples and other probe sheaths, must be stable in molten aluminum or cryolite. These are particularly reactive systems, and thus, there has been little progress in developing usable

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Fig.1. Silicon carbide composite corroded by impingement of molten coal slag.

materials. Boron nitride, however, has historically been observed to be relatively stable in cryolite, and this has recently been more closely evaluated.

This paper will review some recent work originating at ORNL that has made progress in developing systems for allowing ceramics to be effectively used in high temperature corrosive environments. These include development of protective coatings for Si_3N_4 and SiC -based CFCCs. Efforts to develop BN materials for use in the cryolite environment of aluminum smelting will also be discussed.

HIGH TEMPERATURE PROTECTIVE COATING REQUIREMENTS

In order to afford adequate, long-term protection, high temperature protective coatings must meet a number of requirements. Basically, they must be hermetic, remain adherent to the surface, and, of course, protect against the corrodant. These requirements thus raise a range of issues with regard to coatings, including thermomechanical stability, thermochemical stability, and interfacial adhesion. Since almost all solutions will by necessity be imperfect, compromise among these various properties is inevitable. The properties of protective coatings can thus be categorized as having differing degrees of:

- High temperature stability and chemical compatibility
- Adhesion and strain tolerance
- Corrosion and oxidation resistance
- Hermeticity
- Manufacturability, reliability, and cost (materials and processing)
- Tolerant failure mode (graceful vs. catastrophic)

COATING FABRICATION PROCESSES

There are a wide variety of coating processes that deposit materials with varying structures. Some of these are listed below with their potential advantages and disadvantages:

- Solution-deposited coatings
 - Advantages: Inexpensive, rapid, flexible process, can coat complex geometries
 - Disadvantages: Poor microstructural control, residual porosity, variable adhesion, impurities difficult to control
- Plasma spraying: Atmospheric plasma spray (APS) and vacuum plasma spray (VPS)
 - Advantages: Flexible processing, moderate cost, good uniformity
 - Disadvantages: Surface heating, surface preparation, high porosity, line-of-sight process, high impurities, can require substrate heating
- Chemical vapor deposition (CVD)
 - Advantages: High throwing power, high density coating, microstructural control, high purity
 - Disadvantages: High temperature, low deposition rate, uniformity in scale-up, difficult (reactive) precursors
- Electron-beam physical vapor deposition (EBPVD)
 - Advantages: Rapid deposition, uniform microstructures, minimal surface preparation, good strain tolerance
 - Disadvantages: Very expensive, problematic stoichiometry control, requires ingots, line-of-sight process, porous coatings, complex apparatus

PROTECTING Si-BASED CERAMICS FROM ALKALI ATTACK

As noted above, Si-based ceramics are susceptible to relatively low-temperature ($< 1000^{\circ}\text{C}$) corrosive attack by alkali compounds in a high ambient oxygen potential. In Fig. 2, a glassy phase is evident due to such corrosive attack of the ceramic material. In this case, aqueous Na_2SO_4 solution was applied to the surface of Si_3N_4 (AS800, AlliedSignal, Phoenix, AZ) with the sample held at 1000°C for 100 h in flowing oxygen.

Fig. 2. An AS800 Si_3N_4 sample corroded for 100h by Na_2SO_4 at 1000°C in oxygen.

Designing a Protective Coating

One of the major issues in choosing a protective coating for a ceramic material is compatibility with regard to thermal expansion coefficient. The poor strain tolerance of ceramics require that the thermal expansion coefficient of the coating and substrate be close in value. Any mismatch, however, should at least cause the coating to be somewhat in compression since that tends to increase its thermomechanical stability. Figure 3 is a plot of thermal expansion coefficients showing the relationship between SiC and Si₃N₄ and a number of potential protective coatings.⁴ Alumina has been found to be particularly protective of Si-based ceramics from alkali metals, however, the thermal expansion difference is excessive. Mullite, despite its SiO₂ content, is a likely candidate with an expansion curve substantially closer to SiC and Si₃N₄ than that of alumina.^{5,6,7}

Fig. 3. Thermal expansion versus temperature for selected materials (reprinted courtesy of Marcel-Dekker).⁴

Another approach has been to utilize low-expansion oxides that would have coefficients of expansion in the range of SiC and Si₃N₄. Thirty years ago, a new family of ceramic materials was developed based on the crystal structure of sodium zirconium phosphate NaZr₂(PO₄)₃ (NZP).^{8,9} Ca_{0.6}Mg_{0.4}Zr₄(PO₄)₆ (CMZP)^{10,11} and

$\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4(\text{PO}_4)_6$ (CS-50)¹² have been derived from this family and possess a near-zero thermal expansion coefficient, low thermal conductivity, and good thermal stability up to 1500°C, which makes them excellent candidates for high temperature applications. Additionally, these oxides have shown great promise for operating in alkali environments. CMZP coatings produced by sol-gel techniques on SiC and Si_3N_4 have provided protection to alkali exposure at 1000°C.¹³ The interaction between plasma-sprayed CS-50 coatings, as well as bulk CS-50, and sodium sulfite at high temperature has been studied, and CS-50 remained unaffected after exposure to alkali salts.^{14,15}

It is possible to utilize multilayer coatings to take advantage of the thermomechanical properties of one material and the thermochemical properties of another which together form a protective coating system. A series of possible combinations of coatings are seen in Fig. 4. A CVD SiC seal coat applied to a SiC-based composite will prevent ingress of corrodants into the residual pores of the composite, and a native silica layer will provide a good oxygen barrier. The high-density mullite coating also acts as a barrier to oxygen as well as protects against alkali attack. Grading the mullite to alumina allows distribution of the thermal expansion mismatch between alumina and SiC and can allow a highly protective alumina outer layer to be used. Finally, APS coatings of yttria-stabilized zirconia (YSZ) or low expansion materials of the NZP-type can improve resistance to attack by alkali metal compounds and steam.

CVD Mullite

Efforts on CVD mullite as a protective coating have been reported at both Boston University and ORNL.^{5,16} The coatings are deposited at ~1000°C via the reaction:

A high density, conformal coating 3-4 μm thick, typical of CVD, has been deposited. The material was exposed to Na_2SO_4 as described above and experienced no apparent attack of the coating or the underlying Si_3N_4 (Fig. 5).

Fig. 5. An AS800 Si_3N_4 sample coated with mullite corroded for 100h by Na_2SO_4 at 1000°C in oxygen remained unaffected. The coating has a uniform, dense layer with nodules and particle having grown above that layer.

Fig. 4. Strategies for protective coating systems

Solution-Deposited NZPs

A CS-50 slurry and CMZP slip were prepared according to a proprietary composition. The addition of ZnO as a sintering aide was necessary in order to get the coating to flow during firing so as to fully protect the substrate. Coatings were applied by either dipping or by the use of a doctor blade for SiC-matrix, NicalonTM-fiber composites. Corrosion testing was again performed using applied Na₂SO₄ with the samples heated to 1000°C for 100h in flowing oxygen. Examples of surfaces of an uncoated specimen, one that was corroded, and a CS-50 coated and corroded specimen are seen in Fig. 6. The protective ability of the NZP formulation is apparent with similar results seen for the CMZP composition.

Fig. 6. A SiC/NicalonTM composite (a) as fabricated, (b) corroded by Na₂SO₄ in air, (c) and protected by CS-50 coating and corroded.

CORROSION RESISTANT MATERIALS FOR ALUMINUM SMELTING

Commercial hexagonal-BN samples (Advanced Ceramics, Cleveland, OH) were provided to Kaiser Aluminum Materials Laboratory (Spokane, WA) for testing in an electrolytic cell. Post-exposure electron microprobe analysis of a polished cross-section of the surface revealed that the hex-BN, which suffered some recession but did survive the exposure, was covered by an $\sim 15\text{ }\mu\text{m}$ thick carbon-rich layer which may have been produced prior to or during exposure to the cryolite.¹⁷

Hexagonal-BN was prepared at ORNL via low-pressure CVD from BCl_3 and NH_3 on silica and sapphire substrates.¹⁷ Samples of these materials were tested by partially submerging them in molten cryolite ($3\text{NaF}\cdot\text{AlF}_3\text{-}12\%\text{Al}_2\text{O}_3\text{-}5\%\text{CaF}_2$) at 943°C in air or CO_2 atmosphere. After cooling to room temperature, samples were easily removed from the cryolite bath. Unprotected silica or sapphire rapidly dissolved in the cryolite.

The coatings deposited on the silica substrates were largely transparent. After several days, however, the silica windows ($\sim 3\text{ mm}$ dia. $\times$ $\sim 1\text{ mm}$ thick) developed cracks that initiated at the coating-silica interface. Eventually, the windows fractured into several pieces. In addition, even very short-term exposure of the coatings to a cryolite melt resulted in their dissolution. In order to determine if an intentionally deposited carbon coating, mimicking what was seen with the cell tested material, would protect the low-temperature hex-BN from dissolution in cryolite, a sample was prepared of CVD hex-BN overcoated with carbon with sapphire as the substrate. Figure 7 is an electron back-scatter image of a carbon-coated, low-temperature CVD hex-BN after exposure to cryolite for 52 h. The sapphire substrate is seen at the bottom of the image and appears unaffected by the exposure.

Fig. 7. Electron back-scatter image of hexagonal-BN coated sapphire with a top coat of carbon after exposure to cryolite.

CONCLUSIONS

There has been substantial progress in dealing with some very challenging high-temperature corrosion protection problems. Protecting Si-based ceramics for use in combustion environments is obviously a tremendously difficult problem. Mullite-based protective coatings, however, have demonstrated encouraging resistance to alkali attack serving to protect the ceramic substrate. Specific NZP compositions also appear promising, and the ease of their application warrants substantial further investigation of these materials.

The problem of materials survivability in aluminum smelting has been an issue since commercial production began in 1888. The remarkable ability of hexagonal-BN to remain intact in cryolite should be studied in some depth. The role of the carbon layer is particularly intriguing since carbon should not be stable in cryolite.

Finally, it is likely that successful corrosion protection systems will consist of multiple coating layers that are mechanistically synergistic. An example of that can be seen in the intrinsic silica-mullite layer on silicon-based ceramics and the carbon layer on hexagonal-BN.

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