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FABRICATION AND TESTING OF CORROSION RESISTANT COATINGS

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ABSTRACT

The susceptibility of SiC and Si₃N₄ to sodium corrosion mandates that corrosion resistant coatings be developed to protect silicon-based turbine engine components. Materials with good corrosion resistance and thermal expansions that nearly match SiC and Si₃N₄ have been identified. Corrosion testing of hot-pressed pellets of these compounds has identified the most promising materials. Development of chemical vapor deposition systems to apply these materials has been initiated.

INTRODUCTION

SiC and Si₃N₄ are currently prime candidates for turbine engine applications because of their high retained strength to 1400°C, excellent oxidation resistance, good thermal shock resistance, and light weight. Unfortunately, sodium, potassium, and steam have been shown to cause degradation of SiC and Si₃N₄ at temperatures above ≈1200°C.[1-4] However, corrosion has not been recognized as a significant problem in engine testing because current components can survive only several hundred hours due to thermal and mechanical stresses. After improved designs and materials permit tests of longer duration, the severity of the corrosion problem will become more evident.

The outer surfaces of SiC and Si₃N₄ components oxidize at high temperatures to form a silica layer that inhibits further oxidation.[5] However, sodium ingested into turbine engines from the environment or impurities present in the fuel can react with this silica layer, such that it is no longer protective.[6,7] The primary corrosion mechanism is the formation of a sodium-silicate liquid phase at temperatures above ≈800°C, the eutectic temperature in the sodium-silicate system.[8] The objective of the reported research is to develop a coating that will protect the SiC or Si₃N₄ components or coatings from sodium corrosion as well as provide oxidation protection.

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BACKGROUND

In 1986, GTE Laboratories initiated a program to develop coating systems to protect silicon-based ceramics from contact stress damage. Development of a protective coating for SiC or Si₃N₄ is difficult because the coatings crack due to the mismatch in coefficient of thermal expansion (CTE) between the substrate (low CTE) and the coating (high CTE). A coating system was therefore designed to accommodate the stresses caused by the difference in CTE.[9] (Fig. 1) An AlN coating is initially deposited onto the SiC or Si₃N₄ substrates to promote adherence via reaction (formation of a SiAlON compound) at the substrate/coating interface. The coating is then compositionally graded from AlN to Al₂O₃ + ZrO₂. Residual stresses within the graded layer are minimized through the absence of sharp interfaces and the gradual increase in thermal expansion from the interface to the outer protective coating.

Figure 1. GTE's Protective Coating

The use of the GTE Laboratories' coating system appeared very promising for several years.[10,11] Application of the coatings at about 1000°C produced adherent crack-free coatings. Repeated thermal cycling between room temperature and ≈1100°C produced no apparent effect on the coatings. However, heating the coatings to temperatures above 1200°C produced disastrous results, with the CTE mismatch causing the outer Al₂O₃ + ZrO₂ coating to crack. Penetration of oxygen through the cracks oxidized the AlN interfacial coating resulting in blistering of the outer coating. In an attempt to reduce the stresses at high temperatures, coatings were deposited at 1200°C. However, these coatings spalled on cooling to room temperature. Developers of this coating system concluded that the difference in thermal expansion between SiC or Si₃N₄ and Al₂O₃ + ZrO₂ is too great to develop an adherent, crack free coating.

CANDIDATE PROTECTIVE COATINGS

The list of potential materials for corrosion protection of SiC and Si₃N₄ is very limited because the material must be an oxide (for oxidation resistance) with a CTE significantly less than that of Al₂O₃ (for adherence). A carbon/carbon composite (C/C) is a material with a very low thermal expansion (≈ 0) that must be protected from oxidation in high-temperature aerospace applications. However, after 20 years of investigation no oxidation resistant coatings have been found that can survive the dramatic thermal cycles, although several materials with low CTEs were identified that might be useful for the higher CTE heat engine components. (Table 1).

TABLE 1
Refractory Oxides with Potential for Oxidation/Corrosion Protection

Compound	Density (g/cm ³)	CTE ($\times 10^{-6}/^{\circ}\text{C}$)
Al ₂ O ₃ *	3.97	8.0
3Al ₂ O ₃ •2SiO ₂	2.8	5.7
SiC*	3.21	5.5
ZrTiO ₄	≈ 5	≈ 4
HfTiO ₄	≈ 5	≈ 4
Ta ₂ O ₅ •6ZrO ₂	≈ 6	≈ 4
Ta ₂ O ₅ •6HfO ₂	≈ 6	≈ 4
Ta ₂ O ₅	8.02	3.6
Si ₃ N ₄ *	3.19	3.0
Al ₂ TiO ₅	3.68	2.2
carbon/carbon*	1.9	≈ 0

*Included only as a reference and not as a potential coating.

Mullite (3Al₂O₃•2SiO₂) is a material with a CTE very close to that of SiC and has performed reasonably well in corrosion tests, corroding somewhat more severely than Al₂O₃, but surviving significantly better than SiC.[4] Corrosion resistance is dependent on the formation of stoichiometric mullite with no free SiO₂, since free SiO₂ is readily attacked. Because of its corrosion resistance and low CTE, mullite is also being investigated as a material for high-temperature particulate filters that are exposed to sodium contaminants.[12]

Not very much is known about the materials ZrTiO₄, HfTiO₄, Ta₂O₅•6ZrO₂, or Ta₂O₅•6HfO₂, however, investigations have shown their thermal expansions to be quite low.[13-15] The structures formed by the titanate phases provide significant advantages over the destructive phase transformations of monoclinic ZrO₂ or HfO₂. Stabilization of

the cubic structure of ZrO_2 with yttria, ceria, etc., is impractical because of their high thermal expansion ($13 \times 10^{-6}/^\circ\text{C}$) and because the stabilizers would be leached out of the structure. ZrTiO_4 and HfTiO_4 , however, crystallize in an orthorhombic structure that does not undergo polymorphic transformations.[16] (Fig. 2) Even less is known about $\text{Ta}_2\text{O}_5 \cdot 6\text{ZrO}_2$ and $\text{Ta}_2\text{O}_5 \cdot 6\text{HfO}_2$, although the reported[13] low thermal expansion and the potential for good corrosion resistance make the materials promising candidates.

Figure 2. Phase equilibria in the ZrO_2 - TiO_2 system.

An additional material of interest is Ta_2O_5 , in part because of the ease of chemical vapor deposition.[17,18] Phase equilibria studies have shown that no liquid phases are present below 1625 $^\circ\text{C}$.[19] Formation of either of the sodium tantalate phases at turbine application temperatures that are more than 300 $^\circ\text{C}$ below the liquidus temperature would seem unlikely. Furthermore, the formation of these phases would not be catastrophic unless volume changes would cause spallation of the coatings.

One final material that shows promise is Al_2TiO_5 , which has been investigated as a protective coating for C/C and as a corrosion resistant material for high-temperature particulate filters.[20] However, obvious problems do exist for this material. First, because the CTE of the material is very anisotropic the material exhibits significant microcracking and could become permeable to oxygen and sodium. Second, the material tends to absorb water and could degrade significantly when exposed to an environment containing as little as 10% moisture at high temperatures.

To adequately protect SiC and Si₃N₄ components, the candidate protective coating must prevent oxygen present in the combustion environment from diffusing through the coatings to the substrate. Since oxygen will diffuse through most oxide coatings at a significant rate, an additional barrier to oxygen must be established. The native SiO₂ layer that coats SiC and Si₃N₄ is impermeable to oxygen and prevents further oxidation; however, reaction with or diffusion into the corrosion resistant oxide coating would likely destroy the oxygen barrier. Therefore, testing will need to be performed to insure that the SiO₂ layer is stable with respect to the candidate protective coatings.

DESCRIPTION OF MATERIALS AND EXPERIMENTS

Development of processes to chemically vapor deposit all of the potential materials described above would be very costly and time consuming. Therefore, relatively easy to prepare hot-pressed samples of these materials are being exposed to sodium-containing combustion environments to assess their corrosion resistance. Chemical vapor deposition processes will then be developed for the most promising materials.

The starting materials for all hot-pressed samples are high purity powders which are combined and ball milled for 24 h. The mixtures are then loaded into 38mm-diam graphite dies, and hot-pressed using appropriate conditions for each composition. Powder X-ray diffraction of each sample verified the material to be the compound of interest.

Processes for the chemical vapor deposition of Ta₂O₅ have already been developed at this laboratory. The system consists of an inductively heated substrate within a quartz tube sealed on each end by threaded stainless steel end caps. Chlorine and argon gas are introduced into a tantalum chlorinator electrically heated to 600°C. TaCl₅ exiting the chlorinator is mixed with oxygen flowing through a separate inlet tube. The deposition temperature (1100-1300°C) is measured by an optical pyrometer sighting through a window in the end cap directly on the substrate. Ta₂O₅ coatings were applied to SiC coated graphite substrates to simulate a heat engine material system.

Corrosion tests are performed in a horizontal alumina tube furnace with an inner diameter of 60 mm. Hot-pressed pellets of each material are sectioned and tested at ≈1000°C. A combustion environment is simulated by flowing methane into the furnace at 685 cm³/min along with air at 7,600 cm³/min. The sodium level is controlled by the position, and hence the temperature, of the Na₂CO₃ source. Based on the measured weight loss of the Na₂CO₃ source, the sodium concentration in the system varied from 20 to 110 ppm. Sodium concentrations that are an order of magnitude lower and exposure times that are an order of magnitude higher are more realistic for many combustion applications. The total amount of sodium that the samples were exposed to was therefore similar to that projected for many applications, thus the experimental results that have been obtained provide a reasonable basis for approximating the performance of these materials. The sodium levels, however, may have been subject to some variation during each run, primarily because the exposed surface area of the sodium carbonate powder was not constant.

CORROSION TESTING

Specimens of Al_2TiO_5 , ZrTiO_4 , and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ were successfully hot pressed for corrosion testing. Evaluation of these materials by X-ray diffraction revealed that the desired crystalline compounds had been produced. The initial hot-pressing conditions selected for the Al_2TiO_5 produced a porous pellet, therefore, a dense specimen was obtained from a commercial source. X-ray diffraction of the commercial material showed that the outer surface was predominantly Al_2O_3 , whereas the interior of the pellet was Al_2TiO_5 . The hot-pressed pellets of ZrTiO_4 and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ were fine grained, but the former contained approximately 20% porosity.

After exposing each of the candidate materials plus a sintered α -SiC specimen to a combustion environment at 1000°C , the pellets were examined metallographically. The α -SiC had a surface layer of glass about $20\mu\text{m}$ thick. Significantly better corrosion resistance, which is consistent with the published results of Federer [4], was exhibited by $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ which had a $10\mu\text{m}$ glass layer. Further improvements in corrosion resistance are seen by ZrTiO_4 and Al_2TiO_5 since the reaction layers were $\approx 4\mu\text{m}$ and $< 2\mu\text{m}$ thick, respectively. Al_2O_3 grains were observed on the surface of the polished Al_2TiO_5 sample, thus verifying the X-ray diffraction results discussed previously.

SiC-coated graphite substrates overcoated with Ta_2O_5 were also corrosion tested. During coating in an oxidizing environment, the SiC formed a relatively thick crystalline SiO_2 protective layer. The Ta_2O_5 coating nucleated onto the SiO_2 with small equiaxed grains that grew into large columnar ones normal to the surface (Fig. 3). Corrosion testing left the Ta_2O_5 coating and the crystalline SiO_2 sublayer unaffected.

Figure 3. Fracture surface of a Ta_2O_5 coated substrate after corrosion testing.

Successful hot-pressing conditions have not yet been determined for HfTiO_4 , $\text{Ta}_2\text{O}_5 \cdot 6\text{ZrO}_2$, and $\text{Ta}_2\text{O}_5 \cdot 6\text{HfO}_2$. Analysis of the pellets produced to date by X-ray diffraction have indicated unidentified phases. Additional process development will be required before corrosion testing can be initiated.

CONCLUSIONS

Corrosion testing of various oxides revealed a considerable improvement over SiC. Mullite exhibited a glass reaction layer that was only about half as thick as the layer formed on a SiC specimen. Still better corrosion resistance was exhibited by Al_2TiO_5 and ZrTiO_4 . Chemically vapor deposited Ta_2O_5 exhibited excellent corrosion resistance. Further tests of much longer duration will be required to identify the most corrosion resistant oxides for overcoating SiC or Si_3N_4 components. After the most promising materials have been identified chemical vapor deposition processes will be developed for application of coatings.

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