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Plasma-Sprayed Ceramic Coatings for SiAlON Ceramics

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Abstract

Plasma-sprayed coatings of yttria-stabilized ZrO_2 *and* $Al_2O_3.TiO_2$ *used as a protective barrier on* β*-*Si_3N_4*-based sialon ceramics were investigated. The coatings showed better cohesion with the pre-oxidized surfaces due to the reaction between the* SiO_2*-rich oxidation layer and the coating materials. Formation of low thermal expansion zircon and aluminium titanate on the pre-oxidized ceramic was studied using scanning electron microscopy and X-ray diffraction. Preliminary experiments on oxidation and molten metal immersion, showed that the coatings provide significant protection against oxidation and molten metal attack. © 1996 Elsevier Science Limited.*

1 Introduction

Si_3N_4-based sialon ceramics are possible candidate materials for a number of advanced heat engine applications, molten metal containment, wear-resistant applications, etc. However, oxidation, hot salt corrosion and molten metal attack are some of the major limitations for high-temperature applications of these ceramics. These effects are more pronounced in pressureless-sintered sialon ceramics due to the presence of intergranular glass phases.[1] The problem of oxidation, above 1200°C, of pressureless-sintered sialon ceramics has been partially solved by stabilizing the metallic ions by the crystallization of the residual intergranular glass phase.[2] However, this improves oxidation resistance only up to 1300°C. Above this temperature, the crystalline intergranular phase becomes a liquid silicate due to its reaction with oxidation products on the surface (mainly SiO_2) and the problem of oxidation becomes severe.

Protective coatings are widely used to improve the corrosion, oxidation and wear resistance of high-temperature components.[3–5] The main objective of this work was to explore the feasibility of using plasma-spraying to produce a protective diffusion or corrosion barrier on sialon ceramics. Plasma-spraying has several advantages over other surface coating techniques such as chemical vapour deposition (CVD). Spraying of plasma coatings is simple, relatively inexpensive and can be carried out in a short time in a controlled manner. However, plasma-spraying at ambient pressure in moderately oxidizing conditions restricts the sprayed powders to the oxides. In addition, the availability of powders having suitable particle size for plasma-spraying imposes further restrictions. The major problem associated with ceramic oxide coatings is the mismatch in thermal expansion coefficient, α, with the substrate ceramics (α for oxides is typically 6–10 $\times 10^{-6}$ K^{-1} and α for sialon ceramics 3×10^{-6} K^{-1}). However, the use of intermediate layers of mid-range thermal expansion may alleviate the problem of layer cracking or spalling on thermal cycling. The intermediate layers may be formed by pre-oxidation of the substrate ceramic or prior deposition of silicate films of selected composition. These silicate films are reactive with the plasma-sprayed coating and are expected to provide good cohesion. In this work, zirconia (ZrO_2) and aluminium titanate (Al_2TiO_5) were chosen for plasma-spraying on the sialon ceramics.

It is known that pure ZrO_2 undergoes a volume expansion when it transforms from the tetragonal phase to the monoclinic phase[6,7] during cooling below 1200°C. This could lead to extensive microcracking and hence reduction in the protective properties of the coating. However, the addition of about 15 mol% Y_2O_3 results in the formation of a stabilized cubic phase which does not transform[7] into the monoclinic phase. ZrO_2 in all its polymorphic forms has a high thermal expansion coefficient (α) compared with sialon. However, its reaction product with SiO_2, believed to be zircon, has a value of α (4×10^{-6} K^{-1}) comparable to that of sialon ceramics (3×10^{-6} K^{-1}).

Al_2TiO_5 has a very low thermal expansion coefficient and should help alleviate the problem of spalling during thermal cycling. The low thermal expansion property is due to the expansion anisotropy of individual orthorhombic Al_2TiO_5 crystals[8] giving rise to a stable microcracked structure[9,10] in the polycrystalline state. However, due to the non-availability of a suitable pre-reacted aluminium titanate powder, a powder mixture of Al_2O_3 and TiO_2 was sprayed on the sialon ceramics. A reaction between Al_2O_3 and TiO_2 to form Al_2TiO_5 could be expected during plasma-spraying, due to the very high temperature of the plasma.

2 Materials and Spraying Conditions

2.1 Substrate ceramic

Pressureless-sintered, diphasic sialon samples of dimensions 3 mm × 3 mm × 50 mm were used as the substrate ceramic. The two phases of this material are β' (Al-substituted β-Si_3N_4) and an Y/Al-rich silicate matrix (YAG).[2] One side of the substrate ceramic was exposed to the plasma in various surface conditions:

(i) diamond cut and lapped to 1 μm grit;
(ii) similar surface finish to (i) and pre-oxidized at 1220°C to form a SiO_2-rich layer;
(iii) diamond cut and lapped to ~30 μm grit; and
(iv) similar surface finish to (iii) and pre-oxidized at 1220°C.

2.2 Spraying powders

A 13 wt% yttria-stabilized ZrO_2 (YSZ) powder (Plasmatex 1081), of particle size in the range 20–75 μm, was sprayed via a H_2/argon plasma at a distance of 110 mm from the ceramic substrate. Different layer thicknesses of YSZ were sprayed on ceramic substrates having pre-oxidized layers of thicknesses in the range of 5–30 μm. The thickness of the plasma layer was preselected to match the oxide layer in order to obtain complete growth of a low thermal expansion zircon ($ZrSiO_4$) film during post-spraying heat treatment.

A powder mixture of 60 wt% Al_2O_3 and 40 wt% TiO_2 (Plasmatex 1021), of particle size in the range 5–25 μm, was sprayed under similar conditions. However, to form a complete aluminium titanate (Al_2TiO_5) coating, it is necessary to use an equimolar (56·1 wt% Al_2O_3 and 43·9 wt.% TiO_2) mixture of powders in plasma-spraying. The phase diagram of Al_2O_3/TiO_2 shows that the powder mixture (Plasmatex 1021) is very slightly away from the eutectic composition. Hence the coating should have a diphasic structure (Al_2O_3 and Al_2TiO_5).

3 Microstructural Analysis

3.1. As-sprayed coatings

There was limited adhesion of both YSZ and $Al_2O_3.TiO_2$ films on the polished surfaces of the substrate. The adhesion of coatings was improved with pre-oxidation of the substrate surface. This is due to the reaction between the SiO_2 layer and the coating materials. In addition, the presence of the SiO_2 layer is necessary in ZrO_2 coatings to produce the low thermal expansion reaction product, zircon. In the case of aluminium titanate, it has been reported that addition of SiO_2 up to 20% does not influence the thermal expansion coefficient of Al_2TiO_5.[11,12] This is probably due to the substitution of some Si atoms for Ti atoms without changing the expansion anisotropy of individual orthorhombic Al_2TiO_5 crystals. Addition of a small quantity of Si to Al_2TiO_5 to form a solid solution is also advantageous in controlling the thermal decomposition below 1300°C of Al_2TiO_5 into Al_2O_3 and TiO_2.[13,14] However, some investigators,[15] have observed that the Al_2TiO_5 samples containing SiO_2 underwent decomposition at 1370°C under reducing conditions.

The coatings were extensively craze-cracked (Fig. 1), especially in the thinner areas, due to the rapid cooling of droplets after striking the cold substrate. Heating the substrate ceramic during plasma-spraying may prevent craze-cracking by reducing microstresses.[16] It is also clear that the molten or semi-molten particles from the plasma gun have flattened and spread on the substrate in the diameter range 30–60 μm, after striking it (Fig. 2). The YSZ coatings were 15–60 μm thick and the $Al_2O_3.TiO_2$ coatings were 50–100 μm thick. The laminated appearance of the cross-section of $Al_2O_3.TiO_2$ coatings [Fig. 2(b)] is a result of the lateral spreading of molten particles. Energy dispersive X-ray analysis (EDAX) revealed that the light areas were TiO_2 and the dark areas were Al_2O_3. The small amount of ZrO_2 occasionally detected was probably due to contamination of the spraying equipment. There was no indication of reaction between Al_2O_3 and TiO_2 during plasma-spraying.

The X-ray diffraction (XRD) studies of YSZ coatings confirmed that ZrO_2 was in cubic stabilized form. The XRD studies of $Al_2O_3.TiO_2$ coatings revealed that α-Al_2O_3 in the initial plasma powder mixture of Al_2O_3 and TiO_2 has been transformed to a metastable, face-centred cubic γ-phase. This transformation has been reported earlier[17] in Al_2O_3 plasma coatings on metal substrates. The formation of the metastable γ-phase is due to the rapid cooling of molten particles, thus limiting the subsequent diffusion of oxygen

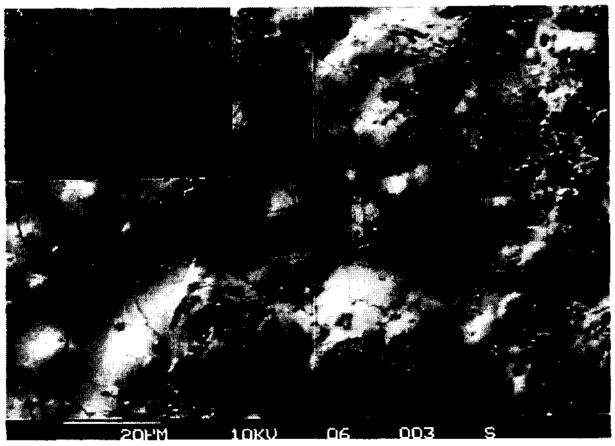

Fig. 1. SEM micrograph showing craze-cracking in as-sprayed coatings (ZrO_2) due to rapid cooling of droplets after striking the cold substrate. The insert shows an extensively craze-cracked thinner area.

Fig. 2. Backscattered SEM micrographs showing the spreading and flattening of molten droplets ($Al_2O_3.TiO_2$) on the substrate after striking it. (a) View of the coating surface and (b) laminated structure of a cross-section of the coating. The dark and the light contrast represent Al_2O_3 and TiO_2 droplets, respectively.

and aluminium atoms necessary for the formation of the stable α-phase.

Although the outer surface of the coatings was mainly crystalline, in the interface region of the as-sprayed coatings some amorphous material is likely to be present, due to the relatively rapid cooling expected to occur in this region during plasma-spraying. The volume shrinkage experienced during crystallization of the interface region can give rise to buckling of the coating. It has been proposed[18] that buckling is prerequisite to spalling of coatings.

3.2 Heat-treated coatings

Since there was no reaction between ZrO_2 and SiO_2 or Al_2O_3 and TiO_2 during plasma-spraying as expected, various post-spraying heat treatments were conducted between 1200 and 1400°C to promote reaction. Heat treatments below 1300°C in air resulted in partially reacted zones in both coatings (Figs 3 and 4). Lengthy heat treatments (1220°C for 600 h), however, showed a little improvement in achieving a complete reaction layer. The partially reacted zone in $Al_2O_3.TiO_2$ coatings was identified by XRD as orthorhombic aluminium titanate (Al_2TiO_5). Coatings of both materials had poor adhesion to the substrate ceramic and were also found to be brittle after heat treatments. However, many coatings spalled from the substrate during heat treatments as a result of thermal expansion mismatch between the substrate and the high thermal expansion unreacted initial powders.

In order to accelerate the reaction to form low thermal expansion products on the substrate, heat treatments were conducted at a higher temperature range (1350–1400°C). However, severe oxidation reactions of the substrate ceramic at this temperature range inhibited the growth of low thermal expansion products and hence heat treatments were carried out in an argon atmosphere and in vacuum (10^{-5} torr). These higher temperature treatments resulted in the formation of larger regions of $ZrSiO_4$ and Al_2TiO_5. However, as expected, a small amount of Al_2O_3 was present in the reacted products of Al_2TiO_5 coatings. This is due to the presence of excess Al_2O_3 (8·9%) in the starting plasma powder. The XRD studies also showed that the γ-Al_2O_3 present in the as-sprayed coatings of $Al_2O_3.TiO_2$ was transformed to α-phase via θ-Al_2O_3. It is worth noting that an equimolar $Al_2O_3.TiO_2$ pellet sintered at 1450°C did not show the Al_2O_3 peaks in XRD.

Heat treatments in non-oxidizing environments reduced coating spalling due to the formation of low thermal expansion products. The coatings of $Al_2O_3.TiO_2$ exhibited a volume expansion on formation to Al_2TiO_5. This gave rise to a curling effect of the coatings. This was clearly evident in long and thicker coatings (Fig. 5). The formation of Al_2TiO_5 is accompanied by an 11% increase in molar volume.[19] This volume expansion may be partly responsible for the spalling of the coatings. The curling effect was reduced by coating thinner layers on the substrates. However, very thin coatings were porous and detrimental to protective properties. A denser thin coating may be obtained by optimizing the spraying parameters such as powder particle size, power level and spraying distance. Since there was no reaction between Al_2O_3 and TiO_2 during plasma-spraying, it would be worth exploring the possibility of plasma-spraying of pre-alloyed aluminium titanate powder. This will avoid the unnecessary post-spraying heat treatments and hence the curling effect.

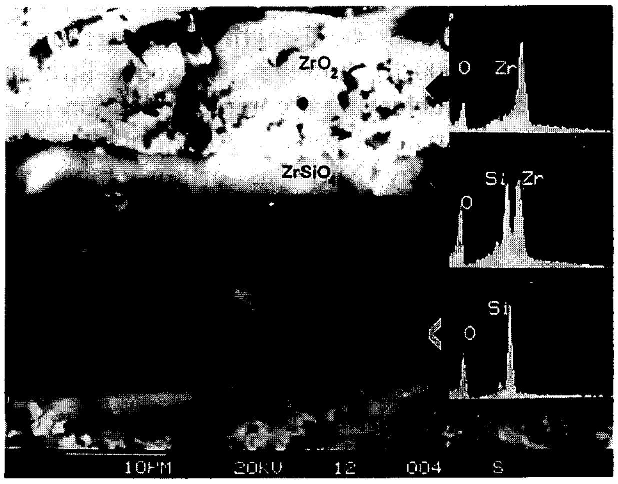

Fig. 3. Backscattered SEM micrograph and EDAX spectra (inserts) of a heat-treated (1300°C) ZrO_2 coating showing a partially formed $ZrSiO_4$ layer between SiO_2 and ZrO_2.

4 Preliminary Study of Oxidation Resistance and Protection of Heat-treated Coatings from Molten Metal Attack

The samples were ultrasonically cleaned in methanol prior to the oxidation and molten metal immersion experiments. The extent of oxidation and the effect of molten metal attack was studied on the transversely cut cross-sections in a scanning electron microscope (SEM). The conventional ceramic polishing techniques were employed to prepare the SEM specimens. However, a very good surface finish could not be achieved particularly in the molten metal immersion samples because of the differences in hardness between the metal and the ceramic.

4.1 Oxidation

Oxidation experiments were conducted in static air, in an open alumina tube furnace at 1200 to 1400°C for 50 h. The test samples were kept in an alumina boat supported by pure platinum mesh to avoid contact with the alumina boat. The SEM study showed that the exposed surfaces of the samples had undergone extensive oxidation at 1400°C (Fig. 6) compared with the coated surfaces. The oxidation reaction in sialon ceramic forms an yttrium-rich aluminosilicate with evolution of N_2 gas (visible in Fig. 6). The mechanism of oxidation of sialon ceramics has been discussed elsewhere.[1] It is clearly evident from the micrographs that both $ZrSiO_4$ and Al_2TiO_5 coatings provide sufficient protection against oxidation by preventing oxygen diffusion into the substrate ceramic. Furthermore, EDAX analysis of the coatings showed no evidence of the diffusion of metal atoms from the substrate ceramic to the coatings during oxidation. However, it can also be seen in the micrographs that the coatings have lifted off slightly from the substrate surface. The lack of oxidation on the substrate ceramic surface where the coating has lifted, suggests that this probably has occurred during cooling or preparation (cutting or polishing) of cross-sections for the SEM observation.

Fig. 4. Backscattered SEM micrograph of a heat-treated (1300°C) $Al_2O_3.TiO_2$ coating showing partial formation of Al_2TiO_5.

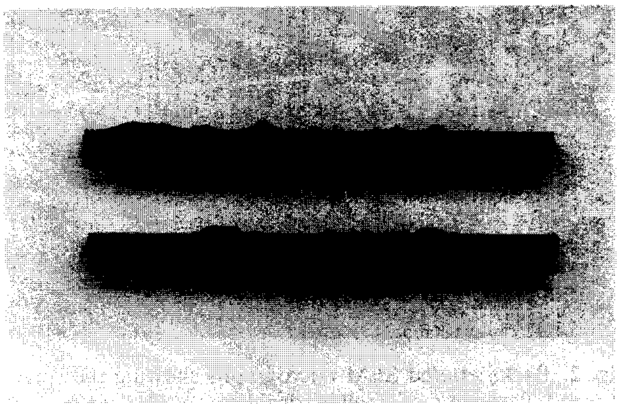

Fig. 5. Photograph showing the curling effect of the $Al_2O_3.TiO_2$ coatings due to volume expansion during the formation of Al_2TiO_5.

4.2 Molten metal attack

Ferrous metals are more reactive with sialon ceramics[20–22] and therefore low melting cast iron was chosen to study the effect of molten metals on plasma coatings. Cast iron (carbon equivalent 4·3 and liquidus 1150°C) was heated in an alumina crucible above its melting temperature (1300°C) and the ceramic samples with one side plasma-coated were gradually dipped into the crucible. The crucible was kept in a box furnace in static air and the sample was introduced into the cru-

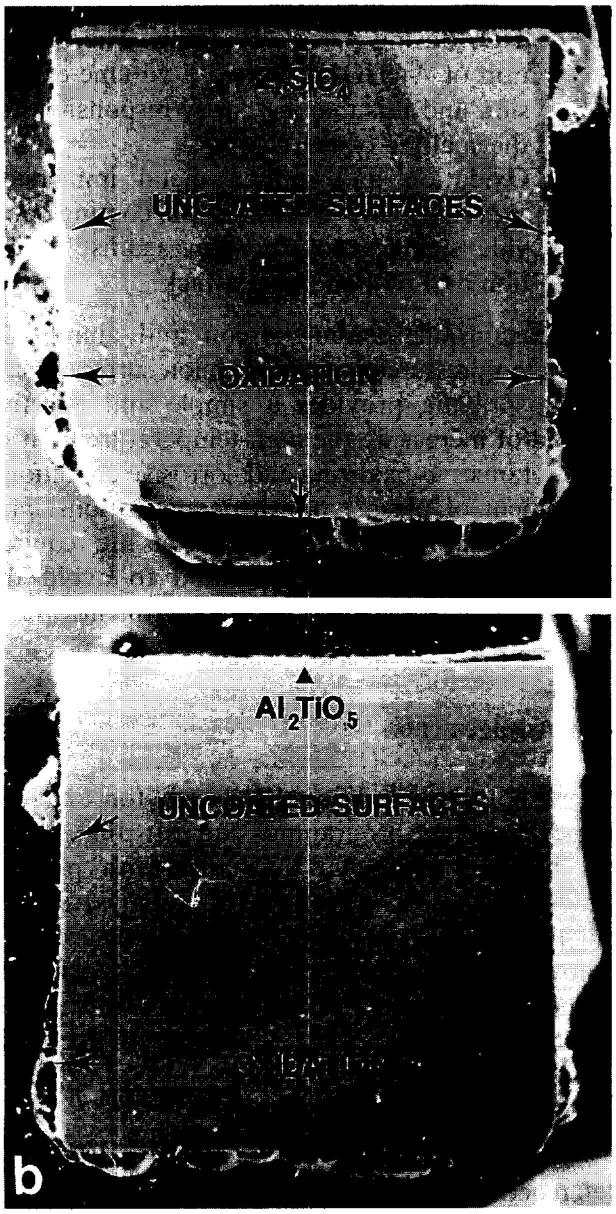

Fig. 6. Backscattered SEM micrographs showing oxidation resistance of (a) the $ZrSiO_4$ coating and (b) the Al_2TiO_5 coating compared with the uncoated surfaces.

cible from the top by means of a support alumina rod. The immersed samples were withdrawn from the molten cast iron after leaving them in the melt for different time durations.

It was observed (Fig. 7) that a vigorous reaction of molten cast iron with the uncoated surfaces occurred, with a strong pitting corrosion after leaving the samples in the metal for about 1 h. It was also observed that the molten cast iron attack was significantly aggravated with increasing temperature of the melt as well as the duration of the immersion. In contrast, both the coatings showed excellent protection against molten cast iron (Fig. 8). Although the molten metal had wetted the $ZrSiO_4$ coatings and penetrated surface irregularities, there was no evidence of either iron diffusion into the plasma layer or metal ions from the plasma layer diffusing into the cast iron melt.

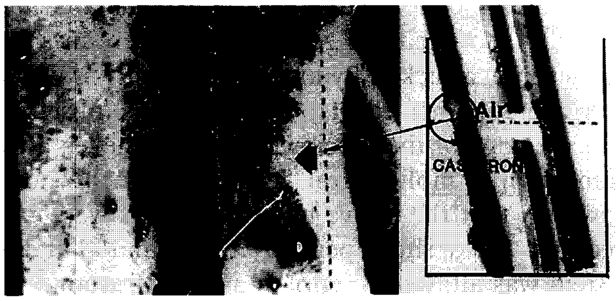

Fig. 7. Photographs showing attack of molten cast iron on an uncoated sialon sample. A strong pitting corrosion is evident at the air–metal interface of the uncoated sample.

Fig. 8. Backscattered SEM micrographs showing the excellent protection of the coatings against attack by molten cast iron. (a) Sample coated with $ZrSiO_4$ and (b) sample coated with Al_2TiO_5.

In the case of the Al_2TiO_5 coating, a very thin reaction zone limited to a few micrometres was just detected by determining the iron concentration using EDAX analysis. However, the backscattering contrast was poor due to a relatively small difference of the atomic numbers of Ti and Fe.

There is limited information available regarding the resistance of sialon to molten metal attack. Results from the tests carried out by Lumby *et al.*[21] indicate that sialon has a very high resistance to molten metal attack. Tests by Yeomans and Page,[20,22] show that, in general, sialon ceramics are not severely attacked by any of the metals in which they were immersed. However, it was observed that the edge of the specimens looked uneven after immersion in molten iron. It is important to note, however, that the above immersion tests were carried out for a short period (150 s) and that the system was allowed to cool in a flow of argon.

The pitting corrosion of uncoated samples was mainly observed in the air–molten cast iron interface region. There was very little corrosive reaction observed in the part of the sample which was well inside the molten cast iron (Fig. 7). This suggests that the presence of oxygen enhances the corrosive reaction. The formation of a low liquidus (~1200°C) metal silicate in the presence of oxygen in the interface region, which could allow more molten metal to react with the ceramic, is a possible explanation for this behaviour. On the other hand, the formation of a relatively high liquidus metal silicide film on the surface of the lower part of the sample could act as a protective layer for further reaction.

EDAX analysis showed no evidence of the presence of iron in the remaining part of the ceramic after the corrosive reaction. Similar observations have been reported earlier in immersion tests with molten iron[20] and in machining tests with cast iron.[23] However, SEM and EDAX analysis showed that the reaction products removed from the ceramic were distributed in the melt. The reaction products seem to be iron-rich metal silicates. In contrast, the section of the ceramic which was well inside the molten cast iron showed no multiphase appearance and analysis showed that mainly silicon and some iron were present. This supports the formation of a silicide protective layer during the reaction. However, the presence of oxygen in the pre-oxidized layer of the substrate ceramic made it difficult to conclude whether silicate or silicide was formed in the interface region.

5 Summary and Conclusions

(i) Plasma-sprayed coatings were found to be crystalline.

(ii) The coatings showed better cohesion with the pre-oxidized surface due to the reaction between SiO_2 and coating materials. The presence of the SiO_2 layer is necessary in ZrO_2 coatings to produce the low thermal expansion reaction product, zircon.

(iii) Thin layer coatings showed better cohesion than thicker layer coatings on thermal cycling.

(iv) There was no reaction between Al_2O_3 and TiO_2 during plasma-spraying. The formation of Al_2TiO_5 exhibited a volume expansion and this may be partly responsible for the spalling of the coatings.

(v) Oxidation and molten metal immersion experiments revealed that the coatings provide significant protection against oxidation and molten metal attack.

In conclusion, coating zircon and aluminium titanate on pressureless-sintered sialon surfaces using plasma-spraying provides a simple and effective method of increasing the high-temperature limit of these ceramics in oxidizing and corrosive conditions. Refinement of plasma powder compositions, prealloying and varied spraying conditions are required to optimize coating structure and to avoid the complexity of post-spraying heat treatment.

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