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Corrosion mechanisms of $\text{ZrO}_2\text{-Y}_2\text{O}_3$ thermal barrier coatings in the presence of molten middle-east sand

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Abstract. — The deposition of mineral debris in the turbine sections of various jet engines occurred after operation on Middle-East routes. Plasma sprayed $\text{ZrO}_2\text{-Y}_2\text{O}_3$ thermal barrier coatings were aged with sand samples from several Middle-East locations at temperatures of 1200 to 1500 °C. At temperatures above 1400 °C, the molten sand formed glassy silicate debris that penetrated the ceramic coating completely, resulting in the absorption of ZrO_2 and Y_2O_3 into the silicate. Two corrosion mechanisms were identified, determined by the amount of calcium-based minerals in the sand.

1. Introduction.

Deposition of abnormal contaminants in the turbine sections of jet engines was experienced during operation on Middle-East routes [1]. Examination of the aerofoil pressure surface of high pressure turbine blades (Fig. 1) revealed the presence of two types of deposits. The first consisted of a thin, smooth, pink-brown deposit present to varying degrees over most of the turbine blade surfaces, and was an anhydride, calcium sulphate (CaSO_4), originating from the ingestion of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as a mineral dust. The second consisted of a much thicker light-brown deposit with a rough surface, and was a complex calcium-magnesium silicate, with a structure relating closely to the mineral, diopside ($\text{CaMg}(\text{SiO}_3)_2$). This compound was believed to form during fusion above 1250 °C in the combustion chamber as the reaction product of several minerals unique to this area.

Adhesion of the silicate to the blade was influenced by several factors, and occurred most probably only whilst the silicate was in the molten or semi-molten state, controlled by the melting point of the silicate and the gas temperature. A strong correlation was apparent between areas of deposition and the surface temperature of the blade. Comparison of the deposited HP turbine blades of affected engines with their thermal paint diagrams suggested that adhesion of the silicate may in general, only occur in areas on the blade above a fixed temperature. It is not known how such deposited contaminants will affect the service lives of thermal barrier coated components.

2. Experimental procedure.

Sand samples were obtained from several Middle-East locations, namely Doha, Dubai, Abu

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Fig. 1. — Silicate deposition on the aerofoil pressure surface of a civil HP turbine blade after Middle-East operation.

Dhabi and Bahrain airports in the Persian Gulf region as well as Sinaiyah in western Saudi Arabia. The samples were characterized by means of X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), and differential thermal analysis (DTA).

Free standing plasma sprayed ZrO_2 -8 wt% Y_2O_3 thermal barrier coated specimens, with thicknesses of 200-300 μm , were prepared by dissolving the nickel-based substrate. The thin ceramic specimens were aged with small amounts of each of the sand samples at temperatures of 1200 to 1500 $^\circ\text{C}$ for durations varying between 1 and 120 h. The aged specimens were air quenched to retain the high temperature phases.

A series of simple silicate debris with CaO contents increasing from zero to approximately 60 wt% (Tab. I) was produced in a laboratory furnace. Hot-pressed, monolithic ZrO_2 -14 wt% Y_2O_3 discs were aged with the silicate glasses/debris for 1 h, 71 h and 120 h at 1500 $^\circ\text{C}$.

Table I. — *Composition of silicate glasses/debris.*

Oxide	Composition of Selected Glass/Debris (wt%)					
	4	7	8	9	9A	9B
CaO	10.4	20.2	27.1	35.1	49.3	59.3
SiO_2	82.9	71.1	62.5	53.9	41.5	32.1
Na_2O	6.7	8.8	10.4	10.9	9.3	8.7

3. Results and discussion.

3.1 ANALYSES OF MIDDLE-EAST SAND. — Visual examination of the sand samples showed that each consisted of non-homogeneous mixtures of various phases, with variations in particle size, texture and colour. XRD, EDX and DTA analyses showed that the minerals common

to all the samples were quartz ($\alpha\text{-SiO}_2$), calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and the feldspar silicates albite ($\text{NaAlSi}_3\text{O}_8$) and microcline (KAlSi_3O_8), with the Doha sample exhibiting a dominant presence of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Tab. II). The samples can be classified into three categories:

a) Sinaiyah sand, consisting mainly of quartz and feldspar silicates; b) Bahrain, Dubai and Abu Dhabi sand, with a strong presence of quartz, calcite and dolomite; and c) Doha sand, consisting mainly of gypsum, with a very low presence of quartz.

Table II. — *X-ray diffraction analyses of Middle-East sand samples; vs = very strong, s = strong, m = medium, vw = very weak.*

Mineral	Sinaiyah	Bahrain	Dubai	Abu Dhabi	Doha
Quartz $\alpha\text{-SiO}_2$	vs	vs	s	vs	w
Calcite CaCO_3	w	w/m	vs	s	w
Aragonite CaCO_3	-	m	-	-	-
Dolomite $\text{CaMg}(\text{CO}_3)_2$	w	w/m	w	w	m
Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-	-	-	-	vs
Albite $\text{NaAlSi}_3\text{O}_8$	m	w	w	m/s	-
Microcline KAlSi_3O_8	m	w	w	w	-
Diopside $\text{CaMg}(\text{SiO}_3)_2$	-	w/m	-	-	-

Chemical interactions between the ingested sand and the thermal barrier coatings are believed to occur only when the sand adheres to the hot blade surface, and, therefore, only when the sand is in the molten or semi-molten state. During ageing of sand samples at 1200°C , melting of the Sinaiyah sand initiated, while the other samples were still unmolten. XRD analyses indicated that the Sinaiyah sand glassified, while the unmolten sand samples consisted mainly of calcium oxide, magnesium oxide, quartz, cristobalite and various calcium silicates. The CaO and MgO were formed as a result of the dissociation of calcite, dolomite and gypsum, but the presence of calcium silicates indicated that fusion occurred between the minerals [2].

3.2 CORROSION OF THERMAL BARRIER COATINGS BY MOLTEN MIDDLE-EAST SAND. — Microstructural damage was observed after ageing of plasma sprayed coatings with Sinaiyah sand at 1400°C and 1500°C (Fig. 2a). Chemical interactions between the ceramic and silicate occurred, and approximately 5 wt% Y_2O_3 and 13 wt% ZrO_2 were absorbed into the silicate.

The molten silicate penetrated through the entire thickness of the coating, causing its break up. The ceramic parts adjacent to the silicate exhibited a much finer grain structure. EDX

a)

b)

c)

Fig. 2. — Plasma sprayed ZrO_2 -8 wt% Y_2O_3 ceramic coating aged with: a) Sinaiyah sand at 1500 °C for 20 h; b) Bahrain sand at 1400 °C for 20 h; c) Doha sand at 1400 °C for 20 h.

analyses indicated that the fine ceramic grains were depleted in the yttria stabiliser, with only 2 to 3 wt% Y_2O_3 in the ZrO_2 matrix, while the larger grains remained unaffected, with the

original 8 wt% Y_2O_3 content. The leaching of the stabiliser initiated the disruptive tetragonal to monoclinic phase transformation during cooling, as confirmed by XRD.

Plasma sprayed coatings aged with sand from Bahrain, Dubai and Abu Dhabi exhibited similar corrosion mechanisms and microstructures (Fig. 2b). Two ceramic phases could be distinguished. As with the Sinaiyah sand, the upper part of the ceramic exhibited a fine grain structure, depleted in yttria. However, the strong presence of calcite and dolomite in the sand (Tab. II) caused severe grain boundary attack through the entire thickness of the coating, resulting in large, rounded ceramic grains with glassy silicate slag between them. The slag was mainly silica (33 wt% SiO_2) and calcia (36 wt% CaO), although yttria (7 wt% Y_2O_3) and zirconia (21 wt% ZrO_2) were absorbed during grain boundary attack.

Ageing of plasma sprayed coatings with Doha sand, consisting mainly of gypsum (Tab. II), caused diffusion of calcium from the calcium-rich silicate into the ceramic grains. The diffusion resulted in 4.2 wt% CaO in the ceramic after 20 h at 1400 °C, and 7.4 wt% CaO after 120 h at 1500 °C. Examination of the ceramic after 20 h at 1400 °C (Fig. 2c) revealed grain boundary attack that caused large rounded grains with silicate between them. Yttria (4 wt% Y_2O_3) and zirconia (14 wt% ZrO_2) were again absorbed into the silicate slag, but higher calcia (41 wt% CaO) and lower silica (30 wt% SiO_2) contents were measured relative to the silicate formed during ageing with Bahrain sand.

Comparison of figures 2a, b and c showed that the corrosion mechanisms are affected significantly by the presence of calcium-based minerals in the sand and, therefore, of calcium oxide in the silicate slag. The effect of CaO on the corrosion mechanisms was examined during ageing of monolithic ZrO_2 -14 wt% Y_2O_3 discs with silicate glasses/debris (Tab. I) having various calcium oxide contents.

3.3 EFFECT OF CALCIUM OXIDE ON THE CORROSION MECHANISMS. — The microstructures of the ceramic-silicate interfaces after ageing of the monolithic ZrO_2 -14 wt% Y_2O_3 discs at 1500 °C for 71 h with the silicate debris (Tab. I), are shown in figures 3a to e. After ageing with glass 4 (10.4 wt% CaO), a finely structured ceramic layer occurred at the ceramic-silicate interface (Fig. 3a). This layer was depleted in yttria, with only 6 wt% Y_2O_3 . After ageing with glass 7 (20.3 wt% CaO), a similar, but thinner, depleted layer was formed, while the depth of grain boundary attack increased (Fig. 3b). Round, ceramic protrusions on top of the depleted layer contained approximately 14 wt% Y_2O_3 , similar to the bulk composition.

The molten silicates attacked the ceramic along the grain boundaries and both yttria and zirconia went into solution [3], as indicated by EDX analyses of the silicate after ageing for 71 h (Tab. III). With only 15 wt% yttria in the ceramic matrix, the solubility limit of zirconia was reached before that of yttria, resulting in the redeposition of a ceramic layer, depleted in yttria, after only 1 h of ageing (Fig. 4a). An equilibrium between absorption and redeposition of zirconia was maintained, while silicate attack along grain boundaries, and consequently, yttria absorption, continued. After 71 h of ageing with glass 7, the solubility limit of yttria was also reached, and large protrusions of a ceramic phase with the same composition as the bulk, were deposited onto the depleted layer (Fig. 4b).

During ageing with glass 8 (27.1 wt% CaO), redeposition of a depleted layer did not occur, and it appeared as if the silicate penetrated the ceramic and “lifted” the surface layers (Fig. 3c). Little grain-boundary attack occurred after 1 h at 1500 °C, (Fig. 4b), although the silicate absorbed 22 wt% ZrO_2 and 10 wt% Y_2O_3 from the ceramic during the short ageing cycle.

The depth of grain boundary attack increased marginally after ageing with glass 9 (35.1 wt% CaO) (Fig. 3d). Ageing with silicate debris having higher calcia contents (glass 9A - 49.3 wt% CaO) resulted in a significant increase in the depth of attack (Fig. 3e), while silicate from glass 9B (59.3 wt% CaO) penetrated the ceramic thickness of 1 mm. Simultaneously, the

a)

b)

c)

d)

e)

Fig. 3. — Dense, monolithic ZrO_2 -14 wt% Y_2O_3 ceramic discs aged at 1500 °C for 71 h with silicate debris containing: a) glass 4; b) glass 7; c) glass 8; d) glass 9; e) glass 9A.

Table III. — Silicate composition after ageing of dense, monolithic ZrO_2 -14 wt% Y_2O_3 discs with soda-lime glasses/debris at 1500 °C for 71 h.

Oxide	Silicate composition (wt%)					
	Glass 4	Glass 7	Glass 8	Glass 9	Glass 9A	Glass 9B
CaO	6	12	15	17	26	32
SiO_2	62	53	49	48	42	39
Na_2O	2	2	1	2	—	—
Y_2O_3	11	13	14	15	16	12
ZrO_2	20	20	21	18	28	17

a)

b)

c)

Fig. 4. — Dense, monolithic ZrO_2 -14 wt% Y_2O_3 ceramic disc aged at 1500 °C for 1 h with silicate debris containing: a) glass 7; b) glass 8; c) glass 9A.

rate of grain-boundary attack increased with increased calcium oxide content to such an extent that, during ageing with glass 9B, the molten silicate penetrated the ceramic matrix without spreading over the entire surface, resulting in severe attack in the middle of the specimen, with the edges unaffected. The initial stages of this silicate attack exhibited rapid grain-boundary penetration and grain fragmentation (Fig. 4c). After the chemical reaction reached an equilibrium, grain growth occurred and, concurrently, diffusion of calcium into the ceramic (3 wt% CaO after 120 h).

The corrosion rate depends on the rate of transport of zirconia and yttria in the silicate, which is determined by their positions in the short-range order of the silicate glass. ZrO_2 can act as either a glass-former, with a cation coordination number of 6, or as an intermediate oxide, with a coordination number of 8, while Y_2O_3 will enter the glass structure in the same way as CaO, a modifier [4]. Modifying atoms move in interstitial regions and channels in the glass structure, and the rate of diffusion increases when the modifying content of a glass is increased, due to the break-up of the network structure on the addition of such atoms [5].

The rate of diffusional transport varied according to the composition of the original silicate/debris during ageing. In acidic silicates with a low modifier content (glasses 4 and 7), the absorbed ZrO_2 entered the random network structure as an intermediate oxide. However, similar to the dual coordination of TiO_2 in the $\text{Na}_2\text{O-SiO}_2\text{-TiO}_2$ system [6], basic silicates with a high modifier content (glasses 9, 9A and 9B) absorbed ZrO_2 as a network-forming oxide in the random network structure.

4. Conclusions.

- 1) Molten Sinaiyah sand, with a low calcium-based mineral content, exhibited the same corrosion mechanism as acidic silicates. Yttria and zirconia were absorbed during grain-boundary attack, but zirconia in excess of the solubility limit of the silicate, was redeposited as a monoclinic, fine grain structure depleted in yttria.
- 2) Molten Doha sand exhibited the same corrosion mechanism as basic silicates. This involved rapid grain boundary attack coupled with grain fragmentation during the initial stages; however, after equilibrium was reached, grain growth and calcium diffusion into the ceramic matrix occurred.
- 3) Molten sand from Bahrain, Dubai and Abu Dhabi exhibited a combination of the two corrosion mechanisms, with the presence of redeposited zirconia depleted in yttria generally in the upper half of the ceramic, where the silicate was originally deposited, while grain growth and calcium diffusion into the large, rounded ceramic grains occurred in the rest of the ceramic matrix. Similar microstructures were obtained after ageing of plasma sprayed $\text{ZrO}_2\text{-Y}_2\text{O}_3$ coatings with intermediate silicate debris.

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