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Spinel formation in thermal barrier systems with a Pt-enriched γ–Ni+γ'–Ni_3Al bond coat

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Abstract

The oxidation of electron beam physical vapour deposited thermal barrier coatings with a Pt-enriched γ–Ni+γ'–Ni_3Al bond coat was investigated. Due to the growth of the thermally grown oxide (TGO), γ–Ni formed underneath the TGO as a result of Al depletion. Phase characterisation by X-ray diffraction, as well as microstructural observations, indicated that a $NiAl_2O_4$ spinel phase formed at the TGO/bond coat interface after prolonged oxidation. It is proposed that the formation of spinel occurs when local cracks present at the interface and the underlying bond coat is Al-depleted. The cracks provide a direct path for oxygen and nickel oxide forms at the bond coat surface. With further oxidation, the spinel forms at the interface through solid state reaction between the TGO and nickel oxide.

Keywords: Thermal barrier coatings (TBCs); Bond coat; Oxidation; Spinel

1. Introduction

Thermal barrier coatings (TBCs) produced by electron beam physical vapour deposition (EBPVD) are usually applied on a bond coat, which consists of either a single phase Pt-modified nickel aluminide, β–(Ni,Pt)Al, or a multiphase (β, $\gamma+\gamma'$) NiCoCrAlY alloy [1,2]. The major change in the microstructure of these types of bond coat during exposure to high temperature is the formation of the γ'–Ni_3Al phase, which is attributed to aluminium depletion caused by the formation of Al_2O_3 on the bond coat surface and by inward diffusion of aluminium into the superalloy [3]. Localised volume reduction associated with this phase transformation usually results in rumpling of the TGO [3]. In addition, the thermal misfit stresses and growth stresses in the TGO during cycling might be large enough to exceed the yield strength of the bond coat, which also contributes to the TGO rumpling [4–7]. When undulations exist in the TGO, the stresses will redistribute around these sites and local tensions develop perpendicular to the interface at the convex portions of the TGO. Consequently, cracks nucleate and grow in this vicinity, as the system experiences thermal cycling, these cracks coalesce and lead to the spallation of the TBC, which is a primary failure mechanism for EBPVD TBCs [1].

Recently, a Pt-enriched $\gamma+\gamma'$ bond coat has attracted much interests due to its potential advantages over the conventional β–NiAl based bond coat, such as higher creep and yield strength [8–10]. As a result, the failure induced by TGO rumpling is largely suppressed. However, the Al content in the γ' phase Ni–Al alloys (~20 at.%) is much lower compared with those based on β–NiAl (~50 at.%). Due to growth of the TGO, the Al activity at the TGO/bond coat interface decreases. Under unfavourable conditions, the Al depletion might result in the formation of spinel ($NiAl_2O_4$) [11]. It is well known that the failure of TBCs is motivated by the strain energy density in the TBC and TGO, and resisted by the interfacial toughness. When spinel formation occurs, the interface toughness is significantly compromised due to its brittleness [12]. In addition, the volume increase associated with spinel formation leads to a large tensile stress [13], which might be responsible for the crack initiation and even the failure of the TBCs.

Previous studies on the oxidation of Ni–Al alloys found that the spinel formation during oxidation normally occurs at the outer layer of the TGO, through a solid state reaction between

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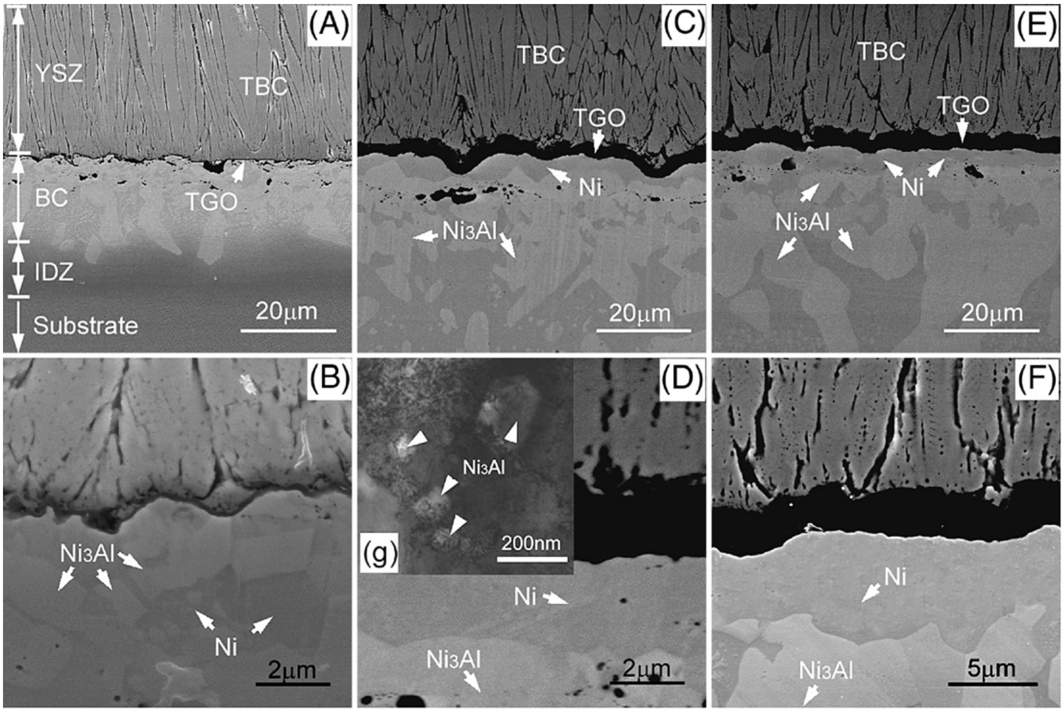

Fig. 1. Cross-sectional images of EBPVD TBCs with a Pt-enriched $\gamma+\gamma'$ bond coat after oxidation, from the top to the bottom are YSZ coating (TBC), bond coat (BC), interdiffusion zone (IDZ) and the substrate. (A and B) as-deposited; (C and D) 1100 °C for 90 h; (E and F) 1100 °C for 210 h; showing the evolution of the γ–Ni phase at interfacial areas; and (g) TEM image showing the fine γ'–N_3Al precipitates in γ–Ni.

NiO and Al_2O_3 [14–17]. However, in this study, it will be shown that the spinel can form at the TGO/BC interface of EBPVD TBCs with a Pt-enriched $\gamma+\gamma'$ bond coat, although it is not a prevalent phenomenon. Therefore, it is the purpose of this work to investigate why the spinel forms at the TGO/BC interface as well as to present some additional insight into the failure phenomenon of EBPVD TBCs.

2. Experiment details

2.1. Sample preparation and oxidation test

The TBCs samples consist of a 7–8 wt.% yttria-stabilised zirconia (YSZ) layer with a thickness of about 130 μm, and a Pt-enriched $\gamma+\gamma'$ bond coat (BC, 20–30 μm) on a CMSX-4 substrate. The Pt-diffusion bond coat was applied by electroplating a 5–10 μm layer of Pt onto the superalloy, followed by a diffusion treatment [18]. This forms a surface layer rich in Pt with the mixed $\gamma+\gamma'$ structure. The bond coat was lightly grit blasted prior to the deposition of the YSZ by EBPVD technique. All the samples were cut into 5 × 5 mm plates with a substrate thickness of about 1 mm.

The oxidation tests were carried out isothermally at 1100 °C and 1150 °C in laboratory air. After the required exposure time, the samples were withdrawn and cooled at the room temperature until the TBC failed. In order to examine the underside of the TGO (attached to the bond coat side) and the surface of bond coats, the samples were compressed along the lateral direction to make the TBC detach from the bond coat. Normally, the TGO was attached to the TBC side after spallation. Both the TGO underside and the bond coat surface were used for further examination.

2.2. Microstructural characterisation and chemical analysis

The crystallographic forms of the TGO formed on the Pt-enriched $\gamma+\gamma'$ bond coat were characterised by a photo-stimulated luminescence spectroscopy (PSLS) at room temperature, using a Renishaw Ramanscope 2000 (Renishaw™, UK). During the measurements, a laser beam (Argon, 514 nm) was focused on the top surface of the EBPVD TBC and the laser spot size was set to be about 3–5 μm. The phases in the bond coat surface after oxidation were also identified by X-ray diffraction (XRD, Philips X'pert).

The microstructure of the EBPVD TBCs was examined by scanning electron microscopy (SEM, Philips XL30). Line-scans of concentration measurements across the bond coat were acquired with a 1 μm step size, using energy dispersive X-ray spectroscopy (EDS, Rontec). The TGO thickness was measured

Table 1
Chemical composition of light and dark areas in the bond coat shown in Figs. 1A and 3B

Samples	Areas	Phase	Main elements (at.%)					
			Ni	Al	Pt	Cr	Co	W
As received	Lighter	γ'	50.3	22.5	23.5	0.9	2.6	
(Fig. 2A)	Dark	Mainly γ	61.8	8.2	11.8	9.3	7.4	1.0
	γ–Ni	γ	68.6	0.8*	8.9	12.1	9.6	
1150 °C 20 h	Lighter	γ'	51.3	20.7	22.2	2.2	3.6	
(Fig. 4B)	Dark	Mainly γ	52.7	5.8	9.2	16.3	12.1	3.9
	γ–Ni	γ	55.1	0.01*	7.4	17.1	20.3	

*These have exceeded the detection-limit of the EDS (~0.3 at.%), the value was determined by manually fitting the spectra.

The γ–Ni was measured by STEM/EDS while others were measured by SEM/EDS.