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Proto-TGO formation in TBC systems fabricated by spark plasma sintering

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ABSTRACT

Thermal barrier coatings (TBC) are commonly used in modern gas turbines for aeronautic and energy production applications. The conventional methods to fabricate such TBCs are EB-PVD or plasma spray deposition. Recently, the spark plasma sintering (SPS) technique was used to prepare new multilayered coatings. In this study, complete thermal barrier systems were fabricated on single crystal Ni-based superalloy (AM1®) substrate in a one-step SPS process. The lifetime of TBC systems is highly dependent on its ability to form during service a dense, continuous, slow-growing alumina layer (TGO) between an underlying bond coating and a ceramic top coat. In the present paper, we show that such kind of layer (called proto-TGO in the following) can be in situ formed during the SPS fabrication of TBC systems. This proto-TGO is continuous, dense and its nature has been determined using TEM-EDS-SAD and Raman spectroscopy. This amorphous oxide layer in the as-fabricated samples transforms to α-Al_2O_3 during thermal treatment under laboratory air at 1100 °C. Oxidation kinetics during annealing are in good agreement with the formation of a protective α-Al_2O_3 layer.

1. Introduction

The need to increase gas turbine efficiency has led to the development of thermal barrier systems during the past decades. The role of these multilayered systems is to decrease the surface temperature and thus the oxidation and corrosion rates of the superalloys constituting turbine blades and vanes. High-temperature oxidation and corrosion protection is achieved by the growth of a protective, continuous and dense oxide layer (generally alumina) on a MCrAl-RE (M = Ni and/or Co, RE = reactive element) overlay coating or on an aluminide diffusion coating [1,2]. Thermal protection relies on a ceramic insulating layer about 150 µm thick, typically yttria-stabilized zirconia (YSZ), deposited by air plasma spraying (APS) or electron beam physical vapor deposition (EBPVD) [2]. The fabrication process of a thermal barrier system with a diffusion aluminide bond coating is composed of a large number of steps including: several surface preparations, electrolytic Pt plating, high-temperature heat treatments under secondary vacuum, high-temperature vapor phase aluminization, heat treatment, pre-oxidation under low PO_2 atmosphere and deposition of the insulating ceramic (EB-PVD or APS). The number of parameters to control for the fabrication of these systems often limits the production of good quality laboratory samples.

The SPS technique has led to an important number of studies on the development of new materials (fully dense materials [3,4], functionally graded materials [5,6], difficult to sinter materials, nanosized grain ceramics [7–9] and composites…). However, only few authors have reported the possibility to coat parts with the SPS technique [10–12]. In recent papers [13–15], co-workers have demonstrated the ability of the SPS technique to fabricate MCrAlY, Pt-Al–modified MCrAlY overlay coatings, NiPtAl diffusion coatings and complete thermal barrier systems on nickel-based superalloy substrates. The purpose of this paper is to contribute to the understanding of the formation of an alumina layer during SPS fabrication of a complete thermal barrier system.

2. Experimental procedure

2.1. Materials

The standard stack-up of materials used for SPS complete TBC systems fabrication is composed of the following materials and is described in Fig. 1

1/ a 24 mm diameter Ni-based superalloy substrate (AM1®), the composition and description of which is reported elsewhere [16]. Samples were ground with European grade 600 SiC paper before being oxidized in air for 1 h at 1100 °C. After air-quenching, the top face of the coupons was ground again with 600 SiC paper to remove the oxide layer. This procedure leaves a 1 µm oxide on all the parts of the substrates except the one to coat. This oxide acts as a carbon diffusion barrier during processing [15];

2/ a Pt-modified nickel aluminide bond coating prepared from Pt (2 or 5 µm thick) and Al foils (2 µm thick) (Goodfellow Corp.). In ref. [15], the possibility to dope the bond coating with reactive elements (Hf, Y) and Si is also reported.

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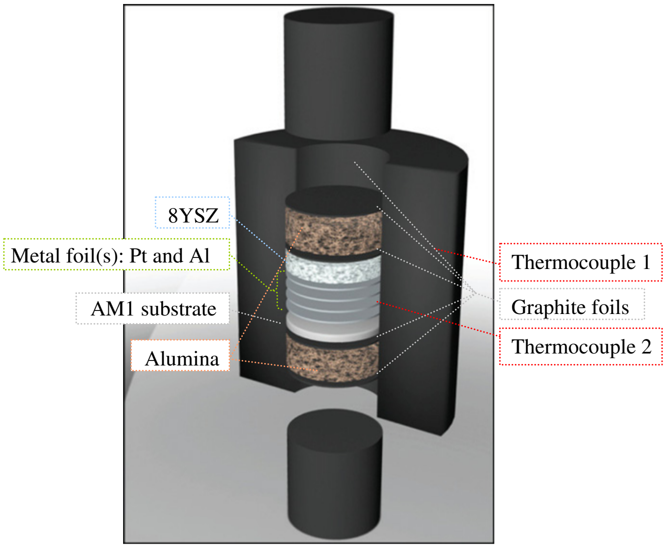

Fig. 1. Standard stack and thermocouples location for temperature monitoring during the spark plasma sintering process.

3/ a partially yttria-stabilized zirconia (YSZ) ceramic top coat composed of commercial fine grain (50–200 nm, 6 ± 2 m^2/g) 8 or 10 mol% YSZ (Tosoh Corp.).

2.2. Spark plasma sintering

A Dr Sinter 2080 (SPS Syntex Inc., Japan) SPS apparatus was used for fabrication of the thermal barrier systems. A standard 12/2 on/off 3.3 ms pulse pattern was used. Graphite punches and die were used. The temperature was monitored by a K-type thermocouple placed in a 3-mm-deep hole at the surface of the die (thermocouple 1) and the actual temperature of the sample was measured at the contact point with a second thermocouple (2) as shown in Fig. 1.

Depending on the temperature set point, a difference up to 150 °C was measured between the two thermocouples (the latter being hotter than the former). To enhance reproducibility, two electric barriers of alumina powders were placed in the graphite die on each part of the sample. These alumina barriers deflect the lines of electric current in the conducting graphite die (rather than passing through the sample) and then prevent the system from local overheating during processing as it is now heated by the die.

The thermal cycle during SPS consisted of heating the sample from room temperature to 1100 °C at 100 °C/min, and it was maintained at this temperature for 1 to 30 min. An additional dwell at 700 °C is added, before the 1100 °C dwell, when aluminum foil is used. The cooling is either unmonitored or at 20 °C/min. The pressure pattern begins with an initial dwell of 2 min at 0.2 MPa followed by an increase in 1 min to the desired pressure (16, 25 or 50 MPa). Then the pressure is held until the end of the thermal cycle and then relaxed in 1 min. A following heat treatment has been performed in air at 1100 °C for 5 or 10 h on sample D (Table 1).

Table 1 gives all needed details on the assemblies, SPS and heat treatments of the different samples.

Table 1
References of the fabricated samples. BC*: 5 μm Pt foil + 2 μm Al foil. [1]: secondary air vacuum in the SPS chamber.

Sample Name	Assembly	SPS			Heat treatment	
		t (min)	*T* (°C)	*P* (MPa)	*t* (h)	*T* (°C)
A[1]	AM1/Pt 2 μm/TZ10Y	10	1100	16		
B[1]	AM1/BC*/TZ8Y	10	700	16		
		10	1100			
C[1]	AM1/BC*/TZ8Y	10	700	25		
		10	1100			
D[1]	AM1/BC*/TZ8Y	10	700	50		
		10	1100			
D1[1]	AM1/BC*/TZ8Y	10	700	50	5	1100
		10	1100			
D2[1]	AM1/BC*/TZ8Y	10	700	50	10	1100
		10	1100			
D3[1]	AM1/BC*/TZ8Y	10	700	50	15	1100
		10	1100			

2.3. Characterization

Microstructural investigations were performed with a LEO 435 VP SEM equipped with a PGT EDX analyzer and with a JEOL Jem 2010 TEM. The samples were previously cross-sectioned, mounted in a resin and ground with SiC paper from grade 600 to 2400, and then polished up to 1 μm diamond paste. For composition profiles, analysis zones were 1*200 μm boxes parallel to the surface of the samples. The composition given is a quantitative mean value for each box. The calculations were made using real standards.

Cr^{3+} fluorescence spectra were recorded with a Raman spectrophotometer Jobin Yvon-Spex Horiba T64000 with a Raman laser wavelength of 514.532 nm.

3. Observations

SPS fabricated TBCs exhibit a dense, homogeneous and default-free bond coating (BC; Fig. 2a). Fig. 2b shows that the bond coating is dense and adherent after SPS. It contains no Kirkendall voids and former interfaces between the foils and with the superalloy substrate are invisible. The ceramic top coat is adherent, fracture-free and its volume porosity has been measured by image analysis. The value of 18 ± 3% is achieved by selecting the appropriate SPS parameters depending on the YSZ grain size. A thin oxide layer, continuous and adherent, has grown during the SPS fabrication process. The TEM micrograph reported in Fig. 2c confirms that this layer is homogeneous, amorphous and between 200 and 300 nm in thickness. We can also note that some YSZ grains are trapped in this layer.

On the composition profiles given in Fig. 2d we can see clearly the uphill diffusion of aluminum in the bond coating. Indeed, this sample (A) did not contain an Al foil, i.e. Al is diffusing from the substrate to the surface because of its activity gradient due to the Pt effect [20]. Reporting the composition of the different layers on a NiPtAl ternary phase diagram shows that the bond coating is composed of the α-NiPt$_2$Al [17,18] and γ′- Ni$_3$Al phases Fig. 2b.

In order to transform both the α-NiPt$_2$Al phase into γ′-Ni$_3$Al and the proto-TGO into α-Al$_2$O$_3$, we have performed a thermal treatment at 1100 °C under air for several durations (Fig. 3). Due to diffusion phenomena, the proto-TGO as well as bond coating have grown in thickness and phase transformations have occurred. After 5 h, there are still few grains of α-NiPt$_2$Al (Fig. 3a) near the TGO region whereas α has completely transformed into γ′ after 10 h of annealing (Fig. 3b). After thermal treatment, the TGO has been identified by fluorescence spectroscopy as α-Al$_2$O$_3$ (Cr^{3+} fluorescence peaks in α-Al$_2$O$_3$ at 14360 cm^{-1} and 14396 cm^{-1}).

4. Discussion

4.1. Formation of the proto-TGO

The formation of an alumina TGO layer in a conventional EB-PVD thermal barrier system is achieved by a pre-oxidation treatment before EB-PVD top coat deposition and by growth during the EB-PVD process. In the case of a SPS fabricated thermal barrier system, there is no pre-oxidation treatment before top coat deposition, as it is a one-