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Stress evolution in a Pt-diffused γ/γ′ bond coat after oxidation

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ABSTRACT

The residual stresses in a Pt-diffused γ/γ′ bond coat after oxidation were investigated using the curvature and X-ray $\sin^2\psi$ techniques. Contrary to the β-(Ni,Pt)Al, the Pt-diffused γ/ γ′ bond coat was in compression at room temperature due to a lower coefficient of thermal expansion. The stresses measured by the curvature method mainly came from the thermal misfit between the bond coat and the substrate, which decreased as the oxidation time increased. However, the stresses measured by the X-ray $\sin^2\psi$ method exhibited an opposite trend. This discrepancy can be attributed to the different origins of the stress evaluated by different techniques. It demonstrated that the lattice misfit between the γ and γ′ phases exerted a significant influence on the micro-stress in the bond coat, and thus restricted the use of X-ray to measure the stress in the Pt-diffused γ/γ′ bond coat. In addition, the effect of stresses on the texture and rumpling behavior of the bond coat was also discussed.

1. Introduction

Electron-beam physical vapor deposited thermal barrier coatings (TBCs) used for aero-engines are subjected to failure induced by the undulation growth, or rumpling of the thermally grown oxide (TGO) [1,2]. According to generally accepted theory, the rumpling is induced by the compressive stress in the TGO, either from the thermal misfit or from the TGO growth [1,3–5]. During thermal cycling, the TGO stress redistributed at the undulation sites might be large enough to exceed the yielding strength of the bond coat and, thereafter to induce cyclic yielding, or ratcheting [5,6]. However, subsequent studies demonstrated that the rumpling does not require the presence of the TGO. For example, it still occurs during thermal cycling in vacuum [7,8]. This clearly suggests that the TGO stress does not play a dominant role. Our works revealed that, the stress in the bond coat, induced either by the selective oxidation of aluminum or by the inter-diffusion between the bond coat and the substrate, is the major driving force for the rumpling [8]. In spite of its importance, few attempts have been made to investigate the stress in the bond coat.

The Pt-diffused γ/γ′ bond coat is now an industrial standard for TBCs used in aero-engines. It is fabricated by first depositing a Pt layer onto the superalloy substrate, followed by a diffusion treatment [9–11]. During diffusion, Pt destroys the initial crystal structure of the superalloy. The structure then precipitates into the γ and γ′ phases, with Pt in the solid solution. There are two sources of stresses in the bond coat. One is from the swelling of the lattice by Pt. During diffusion, Pt substitutes for the Ni atoms in Ni_3Al or Ni, resulting in expansion of the unit cell due to a larger atomic radius [12]. As a result, a compressive stress develops in the bond coat; in addition, there is a thermal misfit stress between the bond coat and the superalloy substrate. This is because Pt has a smaller coefficient of thermal expansion (CTE), when alloying with the superalloy, the overall CTE will be reduced. Therefore, a compressive thermal-misfit stress generates in the bond coat upon cooling. Those stresses not only affect the stability of the interface, but also affect the crystallographic orientation of the bond coat, and thereby influence the failure of TBCs. In addition, it also alters the creep rate of the underlying substrate at high temperature [13]. This is particularly true for the turbine blades, where the thickness of the substrate can be less than 1 mm. Unfortunately, both the stress induced by the diffusion and the thermal misfit are not known to date.

Therefore, the objective of this study is to measure the stress in the Pt-diffused γ/γ′ bond coat, as well as its evolution after the oxidation. Both the wafer curvature and X-ray $\sin^2\psi$ techniques were used to evaluate the stress in the bond coat. In addition, high resolution synchrotron beam diffraction was employed to determine the lattice parameters of γ or γ′ phase at different temperatures, so as to derive the CTE of the bond coat. The estimated thermal misfit stresses were also compared with those obtained by the wafer curvature and conventional $\sin^2\psi$ techniques. Finally, the effect of stresses on the texture and rumpling behavior of the bond coat was also discussed.

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2. Experiments

2.1. Materials

The specimens used in this work are cylindrical with a diameter of 12.7 mm and a thickness of 5 mm, which consist of a diffusional bond coat (25–30 μm) on a CMSX-4 substrate. The bond coat was prepared by first electroplating a 7–8 μm Pt onto the CMSX-4 single crystal superalloy, then followed by a diffusion treatment at 1150 °C for 1 h in vacuum [9]. This process results in a mixed γ/γ' microstructure near the surface region, with both phases rich in Pt. The bond coat specimens were then oxidized at 1150 °C for different times for the stress measurement.

2.2. Stress measurement in the bond coat

The stress in the bond coat was evaluated using the wafer curvature and the X-ray $\sin^2\psi$ methods, respectively [14]. The $\sin^2\psi$ method was carried out using a Proto iXRD system with a manganese K_α radiation ($\lambda = 2.1031$ Å). The diffraction peak from (311) plane of γ' phase at a two-theta angle around 140° was selected for all measurements. This is because the (311) reflection shifts linearly with the strain of the γ/γ' composite [15]. The peak position and width were obtained by fitting the profile with Gaussian function. To remove the instrument background, a gain measurement was always made on a non-diffracting ferrite material before the measurements. A linear background was then fitted in the angular range around the measured peak and subtracted from the measured intensity. The sample was illuminated by the X-ray beam at the center of the bond coat surface. Two orthogonal rotations normal to the surface were performed at each measurement position. At least three random positions were performed on each sample.

For the curvature measurement, rectangular plates ($10.0 \times 1.0 \times 1.0$ mm) were cut from the samples. Because a thin aluminum oxide forms on the surface of the bond coat after oxidation, to avoid this effect, the aluminum oxide was carefully polished away. Furthermore, to minimize the stress which might be introduced by polish, the bond coat surface was slightly electro-polished. The substrates were then mechanically thinned using the standard metallographic approach. The procedure was detailed elsewhere [16].

2.3. Determination of the CTE

The CTE of the bond coat was evaluated from the lattice parameters as a function of temperature, using synchrotron radiation (beamline I11 at Diamond Light Source, UK) [17]. The energy of the beamline was set at 15 keV ($\lambda = 0.825558$ Å) for all measurements. This gave a good balance between sample penetration depth and scattering angle convenience [17]. The X-ray was illuminated to the surface of the bond coat at an angle of 7°. In this case, the beam size on the surface is about ~0.8 mm in vertical direction and ~2.5 mm in horizontal direction, respectively. A multi-analyzing crystal detection system with 45 detectors was used to collect data simultaneously over a 140° 2θ range, with a nominal resolution of 0.8 mdeg, but then normalized and re-binned into constant 1 mdeg steps. The sample was heated in a flat plate furnace and the temperature was controlled with an accuracy of ±3 °C. Diffraction patterns were collected at temperatures between the room temperature and 1000 °C, with an interval of 200 °C. To minimize the oxidation of samples, the vacuum was controlled below 2.0×10^{-5} mbar. Each pattern was collected for 30 min. The final pattern was analyzed by the Rietveld refinement method using TOPAS software (Bruker, 2005).

2.4. Microstructure and phase characterization

The microstructure of the bond coat was examined by scanning electron microscopy (SEM, Philips XL30). The specimens were embedded in epoxy and the cross-section of the bond coat was polished into 1 μm, followed by a final step using active oxide polishing. The phase composition of the bond coat was identified using powder X-ray diffraction (XRD, Philips X'pert). The measurement was performed on the bond coat surface using a Cu K_α radiation ($\lambda = 1.5418$ Å) .

2.5. Elastic modulus measurement

The elastic modulus of the bond coat was measured using a nano-indenter (MTS, USA), with a Berkovich tip. The measurement was performed at the polished surface of an as-processed bond coat, which mainly consists of γ' phase. The penetration depth of indentation was 2 μm and the strain rate was 0.05 s^{-1}. The sampling volume can be approximated as a hemisphere with a radius of 10 μm (~5 times of depth), which is much larger than the size of γ' phase (sub- or micrometers), so that the average modulus of γ' phase can be measured without large error. At least 25 indents were made, with the adjacent indents separated by at least 100 μm. The Poisson's ratio of the bond coat is 0.3. The Young's modulus was obtained based on the unloading curve using the Oliver–Pharr method.

3. Results

3.1. Microstructure evolution of the bond coat

Fig. 1 shows the cross-sectional images of the bond coat. It consists of two phases: γ phase and γ' phase (shown by the bright contrast). Previous works demonstrated that the γ' phase has an ordered face-centered cubic (f.c.c.) crystal structure ($L1_2$ superlattice), and the γ phase is a disordered f.c.c. solid solution [18]. Both phases are rich in Pt and contain alloy elements partitioning into them. In as-processed condition, the bond coat surface mainly consists of γ' phase (Fig. 1a). After oxidation, a thin, continuous γ strip forms below the oxide, and fine γ' precipitates were dispersed in the γ matrix (Fig. 1d). Close to the substrate side, the γ' grains exhibit an elongated shape. With an increase of oxidation time, the bond coat thickness increases due to the inward diffusion of Pt, and the volume fraction of γ' phase in the bond coat decreases. Since the γ' phase exhibits a brighter contrast as shown in Fig. 1, it can be separated from γ phase using image processing software. Fig. 2 shows an example for the contours of the γ' phase (black region) extracted from Fig. 1b. The volume fraction of γ' phase can be estimated from the area ratio between the γ' phases and the whole bond coat. Based on image analysis, the volume fractions for as-processed bond coat, after 20 h and 40 h of oxidation are about 0.85, 0.35 and 0.30, respectively.

For the as-processed bond coat, the γ' phase is in sub- or micrometer range. In contrast, after oxidation (e.g., 20 h), the size of fine γ' precipitates in the γ strip (near the surface region) is in tens of nanometers. With an increase of oxidation time, the volume fraction of fine γ' precipitates near the surface gradually decreases due to the formation of surface oxide, which is similar to the bond coat in TBCs [19]. The change of grain size and volume fraction of γ' phase will affect the stress measurement, as will be shown later.

3.2. Determination of CTE of the bond coat

Since the γ and γ' phases have a very close lattice parameter, the resolution of laboratory X-ray is not enough to separate them. Thus, synchrotron radiation was employed to determine the lattice parameter. Due to high beam energy, the synchrotron X-ray can penetrate through the whole bond coat layer to obtain a well averaged and representative result. Fig. 3 shows the typical diffraction pattern measured from the surface of the bond coat. The incident angle of X-ray was 7° and the estimated penetration depth is around 30 μm. Two peaks between 22° and 23° can be attributed to the (100) diffraction of the γ' and γ phases. Since the γ' phase has a larger lattice parameter than the γ phase, the