Migration of sulphur in thermal barrier coatings during heat treatment

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ABSTRACT

The sulphur effect in thermal barrier coatings (TBCs) mainly refers to a segregation of sulphur at the interface between thermally grown oxide (TGO) and the bond coat, which significantly deteriorates scale adhesion to alloys. Restricted by the extremely low concentrations of sulphur (0–10 ppm) in TBCs, previous investigations using conventional analytical techniques failed to provide a complete mechanism for the migration of sulphur. In this study, high resolution secondary ion mass spectrometry (NanoSIMS) was employed to detect trace sulphur distributions in commercial TBCs. After heat treatments, sulphur segregates at three typical areas in TBCs: (1) the yttria stabilized zirconia (YSZ) top coat; (2) the TGO/bond coat interface and (3) the grit blasted surface. This indicates that during heat treatment a significant outward diffusion of sulphur occurs from the superalloy to YSZ top coat through the TGO, and a possible mechanism for the migration of sulphur in TBCs is described. The undesired "sulphur effect" on scale adhesion was suggested to be caused by the formation of residual sulphides beneath the alumina scale with weaker ionic bonding to alloy cations. Possible solutions are suggested aiming to alleviate the sulphur effect in TBCs.

1. Introduction

The degradation of thermal barrier coatings (TBCs) mainly depends on the stability of the protective oxide scale produced by oxidation of the bond coat alloys [1]. The adhesion at the clean TGO/bond coat interface (e.g. Al_2O_3/Ni interface) is fundamentally strong, because it involves both covalent and ionic bonds [2]. However, it is significantly compromised by the presence of trace impurities (e.g. sulphur, carbon, etc.), which results in a greater tendency for scale spallation. Among these, sulphur is the most detrimental impurity, and has been widely studied for decades on both Al_2O_3 and Cr_2O_3 scale formers [3–6]. Although the normal bulk sulphur level in superalloys is only tens of parts per million (10 ppm), a significant improvement in scale retention can be achieved if the superalloys are desulfurized to an ultra-low level (<1 ppm) [7,8]. The segregation of sulphur at the TGO/bond coat interface at very low levels was suggested to decrease scale adhesion by up to 70% [9–11].

Nevertheless, the complete mechanism for the migration of sulphur during oxidation is still a subject of debate; while at the same time approaches are urgently needed to alleviate the deleterious effect of sulphur on scale adhesion. Earlier studies suggested that during oxidation

sulphur migrates from the inner alloy to the TGO/bond coat interface and weakens the interface in the same way as it embrittles alloy grain boundaries [3]. Grabke et al. [12] suggested that sulphur tends to absorb on free alloy surfaces within the voids at the TGO/bond coat interface, which promotes the growths of voids and defects, and therefore decreases the critical stress required for spallation. Recent developments of advanced analytical instruments have provided more accurate observations. Auger electron spectroscopy (AES) has revealed that sulphur does indeed segregate at the TGO/bond coat interfaces [13]. It was also suggested using analytical transmission electron microscopy (TEM) that the segregation of sulphur occurs not only in voids or cavities but also in regions of contact [14]. Gheno et al. [15,16] used secondary ion mass spectrometry (SIMS) depth profiling to observe the distribution of sulphur in Ni-based superalloys, as well as TBCs, and observed sulphur hotspots in low resolution images. We are, however, still uncertain about the form of segregated sulphur, i.e. either as sulphur ions or sulphur atoms. In this study, sulphur distributions with a greater area scope in commercial TBCs was analysed by using a Cameca NanoSIMS, which is an SIMS instrument specifically designed for high spatial resolution (down to 50 nm) imaging while still maintaining high mass resolution and high sensitivity. Subsequently, energy dispersive X-ray spectroscopy (EDX) under higher spatial resolution scanning transmission electron microscopy (STEM) was employed to examine the sulphur segregation in localized areas identified in the NanoSIMS.

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2. Experiments

2.1. Sample preparations

TBC samples were taken from high-pressure turbine blades provided by Rolls Royce plc, which consist of a 7–8 wt% YSZ top coat deposited by electron beam physical vapour deposition (EBPVD), a Pt-aluminide β-phase bond coat (32Pt 18.9Al 35.1Ni 5.1Co 2.2Cr 1.7 W 0.3Ta in wt.%) and a CMSX-4 single crystal superalloy (Ni 9.6Co 6.4Cr 6.4 W 6.6Ta 5.6Al 2.9Re 1.03Ti 0.1Hf in wt.%). As-received TBC samples were sectioned from turbine blades with an average width of 12 mm, pre-treated at 1150 °C for 1 h in laboratory air, and then subjected to an isothermal treatment at 1150 °C for 100 h in laboratory air and in vacuum ($1 \times 10^{-5} - 1 \times 10^{-6}$ mBar), which is later referred to as long-term oxidation and diffusion treatments respectively. After the required exposure time, TBC samples were rapidly cooled to room temperature by using an automatic lifting platform (CM™) and a powerful cooling fan. Both heating and cooling were completed in <10 min.

2.2. Characterization methods

Cross-sectional microstructures of the TBCs samples were examined by using a scanning electron microscope (SEM, FEI Quanta 650). Observation of trace sulphur distributions in TBCs was performed by high-resolution SIMS analysis using a CAMECA NanoSIMS50 (CAMECA, France) operating with a 16 keV primary Cs$^+$ beam. Quantitative mappings of Pt and S were drawn according to the counts per second (cps). Line scans and area mappings were carried out by STEM imaging combined with EDX analysis (Oxford Instruments X-MaxN 80 T SDD) on a TEM (FEI Tecnai F30) operating at 300 keV. The S/TEM samples were prepared by focused ion beam (FIB, FEI Quanta 3D) using the in-situ lift-out technique.

2.3. Thermodynamic calculations

The Gibbs energy of chemical reactions is calculated at 1150 °C by using the Thermo-Calc software (Version 4.1) with the TCS Ni-based Superalloys Database (TCNI6) and the SGTE Substances Database (SSUB5). The calculations are based on thermodynamic parameters, which are produced through critical assessment and systematic evaluation of experimental and theoretical data, following the well-established CALPHAD technique [17].

3. Results and discussion

3.1. Sulphur in TBCs

Fig. 1 shows NanoSIMS images of Pt and S distributions on the cross-sections of TBCs after different heat treatments: (A) as-received; (B) after treatment at 1150 °C in vacuum for 100 h; and (C) after treatment at 1150 °C in air for 100 h. The colour scale on the right side indicates the counts of 32S (0–15 cps) and 195Pt (0–40 cps). After oxidation, a significant increase of total S counts is observed in comparison with the as-received sample. According to the NanoSIMS maps, S mainly segregates in three typical areas: (1) YSZ top coat; (2) TGO/bond coat interface; and (3) grit blasted surface (i.e. the original superalloy surface prior to deposition of the Pt layer ~10 μm from the TGO/bond coat interface). These three typical areas for S segregation all involve ceramic oxides, i.e. the YSZ top coat, the Al_2O_3 scale and the embedded Al_2O_3 grits (marked by white arrows). On the other hand, the S shows no preferential segregation in the alloys matrix, i.e. no difference in S content is observed between the β-phase and γ'-phase (which forms due to the depletion of Al during oxidation), or between high and low-Pt regions identified in the NanoSIMS Pt maps. These NanoSIMS results indicate that S interacts more strongly with the ceramic oxides rather than
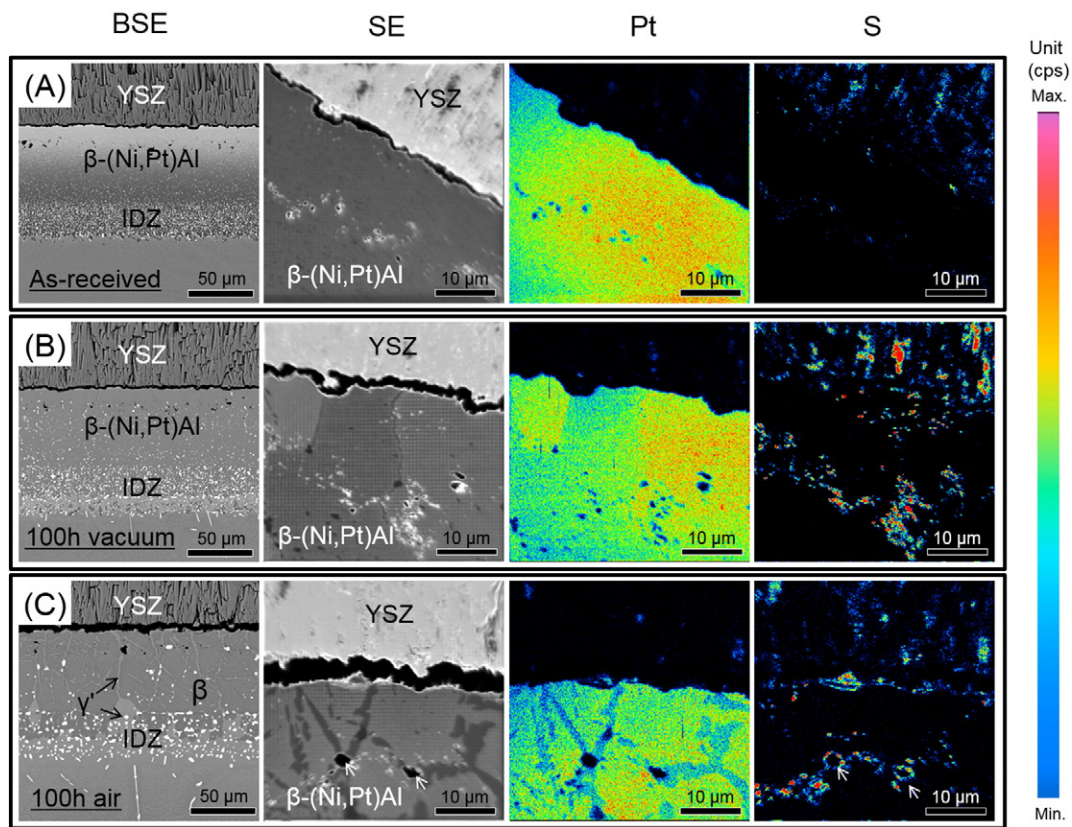

Fig. 1. BSE images, SE images and NanoSIMS mappings of Pt and S on the cross-sections of TBCs with an EBPVD YSZ top coat, a Pt-aluminide β-phase bond coat and a CMSX-4 single crystal superalloy: (A) as-received; (B) after 1150 °C 100 h in vacuum; and (C) after 1150 °C 100 h in air. The colour scale on the right side indicates the counts per second of 32S (0–15 cps) and 195Pt (0–40 cps).