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On the oxidation behavior of titanium within coated nickel-based superalloys

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Abstract—Rutile precipitation within alumina scales grown on coated nickel-based superalloy CMSX-4 has been found to occur preferentially at grain boundaries within the scale. Misorientation analysis using Rodrigues–Frank space has revealed clustering of the misorientation between neighboring grains of corundum and rutile about the established $\langle 0001\rangle_c\{11\bar{2}0\}_c//\langle 010\rangle_r\{101\}_r$ orientation relationship observed in Ti-containing sapphire crystals. The fraction of interfaces found to exist in this configuration is sufficient to explain the nucleation of rutile from a single corundum grain abutting the rutile grain. The diffusive behavior of Ti has been observed to vary considerably within three commercially used coatings, a plain aluminide coating, a plat-aluminide coating and a diffused platinum coating. Titanium diffusion is enhanced by the presence of Pt. However this did not lead to the precipitation of more rutile, which although observed in all three coatings, was present in sufficient quantity to be detected using XRD only within the plain aluminide coated samples.

Keywords: Nickel-based superalloy; Coating; Oxidation; Thermal barrier coatings (TBC); EBSD

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1. Introduction

In recent years, the increased temperature capability of nickel-based superalloys used in gas turbine applications has been largely due to the application and improvement of thermal barrier coatings (TBCs) and associated gas cooling. Current combustion temperatures in commercial gas turbines make thermal barrier coatings a necessity for both turbine blades and static vanes operating in the first stage of the turbine. Thus increasing the longevity of these coatings, limited by TBC spallation, is of the upmost importance to the industry. One such major improvement has been the electro-deposition of a thin Pt layer to the substrate as a stand-alone bond layer under the YSZ [1,2]. Spallation tests for superalloys coated with this diffused Pt coating (also termed Pt-modified or duplex γ/γ' coating), consistently display very good TBC spallation life compared with Pt-aluminide, plain aluminide and MCrAlY bond coats, with results consistent over a number of substrates [3–5].

In the last 5 years however, there has been increasing evidence that the use of Pt within coatings alters the activity of Ti [5,6], a low density alloying element, used for stabilizing and strengthening γ'. It is well established that Pt decreases the activity of Al, which then results in the uphill diffusion of Al from the substrate, maintaining a high concentration close to the surface facilitating alumina scale growth and re-formation. Pint et al. [5] have obtained micro-probe measurements showing raised Ti concentrations close to the surface of Diffused-Pt coated CMSX-4 after prolonged thermal cycling. Tawancy et al. [6] observed uphill Ti diffusion for the same system, with Ti and Pt both segregating to the γ' phase. Ab-initio calculations using density functional theory have shown that Pt stabilizes defect formation in β-NiAl, enhancing anti-site assisted and solute vacancy diffusion mechanisms [7,8].

Titanium (IV) oxide, exists as a multitude of polymorphs, three of which are stable at atmospheric pressure; anatase, brookite and rutile. Of these, brookite is difficult to synthesize and literature on its formation is sparse. The phase transformations between anatase and rutile have been extensively reviewed by Hanaor et al. [9]: anatase transforms to the stable rutile structure in air, at temperatures far below those experienced in gas turbines, although reported transformation temperatures do vary considerably [10,11]. Upon the application of pressure, the tetragonal rutile structure has been found to undergo a transformation to an orthorhombic polymorph with a α-PbO_2 structure, known as α-TiO_2 [12]. At temperatures below 500 °C, this

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critical pressure falls within the realm of TGO stresses measured during thermal cycling [13]. The α-TiO_2 phase has been observed to transform into rutile following stress relaxation within Ti doped sapphire [14].

The solubility of Ti within alumina scales is thought to occur via the formation of Ti_{Al} substitutional defects for Ti^{3+} ions and vacancy clusters consisting of $3Ti^{\bullet}_{Al}$ and V'''_{Al} for Ti^{4+}, preserving charge neutrality within the scale in accordance with the Schottky formalism [15] [16]. If a divalent cation M is available, $Ti^{\bullet}_{Al}M'_{Al}$ pairs may form, a theory supported by defect calculations performed by Grimes [17], although this has only been verified for Mg. Measurements of lattice parameter changes within Ti-doped sapphire by Mckee and Aleshin [18] and Roy and Coble [19] have indicated lower solubility of Ti^{4+} than Ti^{3+} within α-Al_2O_3 for annealing temperatures in excess of 1250 °C in air and 1400 °C in N_2 (firing in nitrogen reduces the Ti^{4+} ions to Ti^{3+} above this temperature). Above the solubility limit, rutile TiO_2 forms 'needle' and 'heart-shaped' precipitates, which are usually twinned [20,21]. At 1200–1300 °C, He et al. [21] observed α-TiO_2 precipitates which form initially, subsequently undergo twinning to minimize coherency strain energy with the sapphire matrix, then transform to the rutile structure. The long axis of the rutile needles, $[01\bar{1}]$, lies parallel to the $\langle 10\bar{1}0\rangle$ directions in α-Al_2O_3. This preferred orientation relationship (OR) between the two phases, leads to the 'asterism' seen in star sapphires. This OR has also been observed more recently Daneu et al. [22], the registry is typically defined as $[0001]_c(11\bar{2}0)_c//[010]_r(101)_r$. Langensiepen et al. [23] observed the precipitation of Al_2TiO_5 above 0.6 cation % titanium at triple junctions within polycrystalline sapphire. However, within the Al_2O_3–TiO_2 binary system Slepetys et al. [24] have found the Al_2TiO_5 to be unstable below about 1240 °C during heat treatment in oxygen.

Tawancy et al. [6] concluded that the formation of TiO_2 within scales formed on diffused Pt coated nickel superalloys, leads to increased oxide spallation. This is thought to occur via de-lamination of the alumina scale, assisted by void formation at TiO_2 particles forming at the oxide/metal interface. Other recent investigations of the resistance of these coatings to high temperature thermal exposure [25,26] have consistently observed rutile growth on plain aluminide coatings. Shirvani et al. [26] observed TiO_2 rutile formation upon plain aluminide coated CMSX-4 but not upon Pt-aluminide coated samples after cyclic oxidation.

The progressive removal of titanium from alloys designed for optimum environmental resistance has been a strong trend for a number of years, but our current understanding of the role Ti plays in such degradation of thermal barrier coatings is limited. As yet there has been no comparative study between the effects of different coating composition on the diffusional and oxidative behavior of Ti. The orientation relationship between rutile and corundum is well characterized in Ti-doped sapphire, but as yet there is no evidence for any orientation relationships occurring within thermally grown alumina scales. The main purpose of this investigation is therefore to observe and characterize the behavior of Ti and associated rutile formation within several bond coat systems during high temperature oxidation. Knowledge of the precipitation mechanism will assist in our understanding of the stress distributions associated with rutile formation in oxide scales.

2. Experimental

For this investigation, three commercially used diffusion coatings were applied to single crystal CMSX-4®.[1] Cylindrical test bars were cast by Rolls-Royce plc as single crystals with the $\langle 001\rangle$ orientation aligned with the cylinders' long axis. Bars were then subjected to hot isostatic pressing to reduce porosity and solutioning and aging heat treatments, forming cuboidal γ'-Ni_3Al precipitates approximately 0.5 μm in dimension to replicate the microstructure of components in service.

Samples were coated at Turbine Surface Technologies Limited (TSTL) in Annesley, Nottinghamshire, UK. Following normal commercial protocols, Pt was electro-deposited to a thickness of 7 μm in the Pt-aluminide samples and 10 μm to form the diffused Pt coating. In each case the samples were then annealed for 1 h at 1100 °C and 1150 °C for each coating respectively. Vapor phase aluminizing was used to produce high temperature low activity (HTLA) aluminide and Pt-aluminide coating microstructures. The resulting microstructures within each coating in the as received condition are shown in Fig. 1. The presence of both (Ni, Pt)Al and $PtAl_2$ phases within the Pt-aluminide coating is similar to that of an intermediate stage between outwardly and inwardly grown coating microstructures [27]. This is partly due to the slightly lowered temperature used during aluminizing and thicker Pt layer, reducing outward nickel diffusion. As the aluminum chips are pre-alloyed the designation 'Low-Activity' is still used.

Samples of coated CMSX-4 were oxidized both isothermally and cyclically in air at 1100 °C. The cycle consisted of a 5-minute ramping period, followed by a 55-minute hold at temperature, before a 20-minute cooling period. After 1, 25 and 100 cycles, oxide and coating phases were analyzed using XRD. Samples were oxidized isothermally for 25, 100 and 500 h. A JOEL 5800 scanning electron microscope was used to obtain micrographs. The diffusion of alloying elements within each coating has been mapped and quantified using wavelength dispersive X-ray spectroscopy (WDS) on a Cameca SX100 electron microprobe. Glow Discharge Optical Emission Spectroscopy (GD-OES) measurements were obtained using a Horiba GD-profiler 2 spectrometer, while XRD data were obtained using a Rint-2500 X-ray diffractometer. Transmission electron microscopy EDS data were collected using a JOEL JEM ARM-200F transmission electron microscope at 200 kV. The diffraction patterns, used for phase identification and orientation mapping, were recorded at 300 kV on a CM300 FEG-TEM that was retro-fitted with a Nanomegas ASTAR unit. This allows fast scanning of the electron beam across the sample with a high-rate digital camera used to record a diffraction pattern at each point of the scan [28]. The digitized pattern is compared to templates determined from the expected crystal structure(s) of the sample. Pattern matching is performed using a cross-correlation calculation (or correlation index) between the experimental pattern and the template patterns. The reliability of the pattern match is done by comparing the correlation index for the best pattern match with the index score for the second best match in the library. Large reliability therefore indicates an unambiguous orientation

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