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Modelling of the Interdiffusion and Oxidation of a Multilayered Chromia Forming Thermal Barrier Coating

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The stability of multilayered coatings is important in long term use and thus accurate predictions of the effects of exposure at temperature are extremely important. In this paper the prediction and validation of a multilayered Thermal Barrier Coating with a bond coating based on the MCrAlY system is presented. The coating was a three layered bond coat consisting of a NiCrAlY layer with an aluminised outer region onto which a NiCr with 2%Si had been deposited. Onto this an yttria partially stabilised zirconia topcoat was applied. The coating system was exposed to 800°C for times up to 3000 hours. The specimens were sectioned and Scanning Electron Micrographs obtained. Energy Dispersive Spectroscopy, EDS, was used to provide compositional data on each of the layers in the starting condition and also to produce elemental profiles through the sections with increasing time at temperature. The oxidation kinetics was determined from oxide growth measurements over time.

The model used is a finite difference code devised to produce elemental profiles at various stages in the oxidation process for simple alloy systems and termed Oxidation Diffusion and Interdiffusion (ODIN). The input parameters include the oxidation kinetics in either simple or polynomial algorithm form, starting compositions of each layer as either weight percentage or atomic percentages and diffusion coefficients for the dominant elements. The model can accommodate a single alloy oxidising from the outer surface or a multilayered coating system and has the capability of modelling interdiffusion between the layers in addition to elemental depletion due to oxidation from one surface. The output can be in the form of a simple 1-dimensional profile or as a map showing 2-dimensional features such as corners or ribs.

SEM images of sections through the TBC system at various time intervals will be presented along with EDS profiles which will be compared to that predicted by ODIN. A good agreement has been found between the prediction and the experimental results.

INTRODUCTION

A Thermal Barrier Coatings, TBC, consist of an outer ceramic layer of yttria stabilised zirconia (YSZ), which acts as a thermal insulator, above a thermally grown oxide (TGO) formed by the oxidation of an intermetallic bondcoat. Usually, the TGO is α -alumina formed on an aluminium-rich bond coat [1]. In this paper a chromia forming TBC is studied. The coating has been designed to protect the substrate alloy against type 1 and type 2 corrosive attack as well as high and intermediate temperature oxidation. Under these conditions, and where a gaseous species such as sulphur is present, a chromia TGO would provide the best protection [2]. The structure of the bond coat is based on a SmartCoat system containing alternate layers rich in aluminium and chromium. Previous studies on this TBC have been published presenting the concept and preliminary oxidation data [3, 4]. In this paper further development of the bond coat is presented with the inclusion of an aluminium-rich layer within the structure. The reasoning for this inclusion was to provide an additional reservoir of aluminium as security should spallation of the outer ceramic layer occur. If this did occur during operation the temperature at which the bond coat would be exposed would increase moving the conditions into one where an α -alumina TGO would be desirable.

Stability of such complex coating systems during operation is important. In this paper a combined experimental and modelling approach is taken to assess the effect of exposure of the TBC to realistic operating temperatures, i.e. 800°C. Details of the model used are given below.

The Model

The computational model, termed ODIN (Oxidation, Depletion and INterdiffusion), has been developed to predict subsurface solute depletion due to oxidation and also inter-diffusion between metallic layers [5]. At the oxidising surface the boundary condition defining solute (chromium) depletion due to oxidation is provided by the (measured) oxidation kinetics. The concentration profile reflects the mass balance at the oxide/metal interface between the rate of demand for the solute and the rate of supply, Figure 1. Single diffusion coefficients can be input or iterative finite-difference techniques are used to solve the ternary diffusion equations within the subscale region in two dimensions, although in the present application only one dimension is considered. The elemental concentration is held in an array of discrete nodes,

and assumed to vary linearly between neighbouring nodes. Concentration-dependent cross-term interdiffusivities were employed; due to the relative scarcity of such data, the concentration dependence parameters were taken from an extensive study of interdiffusion in similar NiCrAl systems by Nesbitt *et al* [6]. These parameters define a quadratic regression equation that yields the diffusion coefficients at any point across the diffusion profile based on the local composition. Only Al and Cr interactions are modelled – the matrix concentration is then taken as the balance. The substrate is assumed to be infinitely deep and the initial conditions assume a sharp compositional transition across interfaces: those between layers within the coating and at the coating / substrate interface.

The model has been validated against the existing analytical models for the parabolic oxidation of planar surfaces applying Fick's 2nd law [7,8] and has also been validated against experimentally determined data [8,9]. It should also be noted that the model assumes only single-phased, homogenous ternary alloys and does not consider phase transformations or precipitates. The application of this model to this system enables a comparison with idealised behaviour.

The purpose of the present study is to use of the ODIN finite-difference code to predict the compositional profiles of the multi-layered bond coat as a result of exposure to 800°C for increasing times in air. The additional feature in this coating, compared to previously reported work [4], is the incorporation of an aluminium rich layer within the layered bond coat.

EXPERIMENTAL

The multilayered bond coat was applied to the flat surface of 20 mm diameter by 5mm samples of the Ni-based superalloy CMSX-4, Table 1. The first layer consisted of between 160-200 µm of Amdry 962, Table 2, and was deposited using High Velocity Oxy-Fuel, HVOF. This was followed by annealing, under vacuum, for 4 hours at 1080°C. The surface was grit blasted prior to the enrichment by vapour aluminising. Another grit blast prepared the surface for the application of an 80-110 µm thick layer of 50:50 nickel chromium, Table 2, again by HVOF. There was a final grit blasting stage before the application of a 220-250 µm thick yttria stabilised zirconia layer using air-plasma spraying. A cross section of the

multilayered structure, after 10 hours at 800°C, is given in Figure 2. The coatings were manufactured by Praxair Surface Technologies.

Oxidation testing was performed in laboratory air at 800°C for times up to 3000 hours, in calibrated tube furnaces. Samples were removed from the furnaces after 10, 100, 500, 1000, 2000 and 3000 hours for cross-sectional examination. These samples were vacuum impregnated with low viscosity resin to maintain the integrity of the coating during sectioning. The cross-sections were prepared by grinding on progressively finer silicon carbide papers from 120 to 1200 grit and polishing using 9 μm , 3 μm and 1 μm diamond solutions and finished using silica sol. The samples were gold coated for scanning electron microscope examination using a Phillips XL30 with energy dispersive X-ray microanalysis (EDS) or a Jeol JSM-7000F also with EDS capability.

RESULTS

Experimental

SEM images of cross-sections through samples held at 800°C for 10, 1000 and 3000 hours are given in Figures 2 to 4, respectively. These show that the individual 962 and 50:50 layers within the bond coat, produced via HVOF, are multiphase, distinguished by the difference in contrast seen when using back-scattered SEM. This can be seen clearly in Figure 3. Within the NiCrAlY darker contrast phases of β (NiAl) form with a lighter contrast γ (Ni-rich) matrix. Whereas in the 50:50 NiCr the darker contrast phase is α -chrome also within a γ matrix. The aluminised layer is also distinguishable at the centre of the bond coat being of lighter contrast and composed of a single phase.

Interestingly, after a short time at temperature, a chromium-rich layer develops in the 50:50 NiCr layer adjacent to the aluminised region. There is some evidence of the beginnings of the formation of this continuous layer after 10 hours at 800°C, Figure 2, but at 1000 hours, Figure 3, it is a very obvious feature of the coating. Examination of the 50:50 NiCr layer adjacent to the outer oxidising surface shows a reduction in the relative amounts of α – chrome, signifying depletion of the chromium from this region to form an externally growing TGO.

The compositional profiles of the coatings at each of the test times were obtained by collecting EDS data over rectangular areas of approximately 15 by 80 μm with the long axis running parallel to the interface between the coating and the substrate. This approach and the dimensions of the rectangles ensured that representative average compositions were obtained for later comparison to the ODIN predictions.

The compositional profiles for aluminium and chromium, produced in this way are given Figure 5. There is always some degree of variability in coating thickness when using techniques such as HVOF. Thus, to enable a study of the effect of increasing time at temperature on the various layers, it was decided to align the coating compositions using the interface between the aluminised NiCrAlY and the Ni:Cr layers. This was a clearly identifiable interface in all the micrographs and, it can be seen from Figure 5, the definition of this boundary was maintained throughout the test period.

At 10 hours, solid lines on Figure 5, the profiles show the three distinct layers: the outer chromium-rich layer, the intermediate layer with aluminium and chromium content of 32 at% and 8 at% respectively, and the NiCrAlY layer of approximately 18 at% aluminium and 22 at% chromium. The width of the aluminium enrichment, due to the aluminising process, extends beyond the dense region seen in the micrographs, Figure 2. Closer examination of the adjacent region did show an increase relative amount of the darker contrast β (NiAl) phase locally. With increasing time at temperature the aluminium content of the layer decreases and a slight increase in the aluminium content in the NiCrAlY is detected along with clear diffusion into the Ni:Cr layer. The chromium profile shows the greatest change over time with the formation of the highly enriched layer adjacent to the aluminised layer described above. At 500 hours the chromium content of this layer reaches 75 at%. The width of this layer stays fairly uniform throughout the oxidation period examined, although some local variability in width can be seen on the micrographs, Figure 4. The profiles in Figure 5 do show a gradual reduction in chromium content with time.

The oxidation kinetics for this coating was determined from total oxide thickness measurements taken from representative sites across each sample, Figure 6, a minimum of 25 measurements were taken from each sample. Analysis of these data demonstrated that the growth kinetics followed a parabolic law with a parabolic rate constant, k_p , of $9.52 \times 10^{-19} \text{ m}^2 \cdot \text{s}^{-1}$, Figure 7. This value compared well to the literature values for chromia formation [10]

and to the kinetics determined from a more extensive study on the same bond coat on Hastolloy X for times up to 1000 hours [4].

Modelling

The ODIN model had been successfully used in earlier studies on a variant of this coating without the aluminising layer, using interdiffusion coefficients for the MCrAlY system [4 and 6]. It became clear in this variant that the ODIN model would not be able to successfully model the whole coating even as a series of layers due to the formation of the chromium-rich layer, thus a different approach was needed. The coating structure was divided into two sections as follows: the outer Ni:Cr layer - to examine the effect of oxidation and diffusion of chromium diffusion between the α -chrome layer and the Ni:Cr layer, and the aluminised / NiCrAlY / substrate.

Ni:Cr Layer

The input parameters to ODIN were: for the oxidation kinetics $9.52 \times 10^{-19} \text{ m}^2.\text{s}^{-1}$, and the diffusion coefficient for chromium in a nickel matrix $2.80 \times 10^{-18} \text{ m}^2.\text{s}^{-1}$ [11]. Using these parameters and the starting compositions of 50 at% and 75 at% chromium for the two layers, a prediction for the chromium profile was produced, Figure 8. Comparison of this profile to the EDS profile shown in Figure 5 shows a reasonable agreement between the depth of the chromium profile due to oxidation, e.g. approximately 20 μm after 3000 hours and the relative stability of the α -chrome layer. The EDS profiles show some variability between individual samples and in the thickness of the layers, as expected, but it can be appreciated that the ODIN model has successfully predicted the depletion profile for a solute by the process of selective oxidation, using actual oxidation kinetic data. It has also shown good agreement regarding the diffusion of chromium from an α -chrome layer to the Ni:Cr showing the endurance of the former with increasing time at temperature.

Aluminised / NiCrAlY / substrate

No oxidation depletion was permitted in the prediction of the remainder of the coating. This region was modelled using the concentration-dependent cross-term interdiffusion coefficients produced by ref 6 and reproduced here in Table 3. The aluminium and

chromium profiles are given in Figure 9. Comparison to Figure 5 shows a reasonable agreement. The model predicts the gradual reduction in the aluminium concentration within the aluminised region and also the interdiffusion with the substrate. Less good is the prediction of the chromium profile at the aluminised layer.

CONCLUSION

A TBC with a multilayer, chromia forming bond coating has been developed and tested at 800°C for times up to 3000 hours. In this variant, an additional aluminised layer has been incorporated to give additional protection should spallation of the outer top coat occur during operation. The coating performed as expected in these conditions in that a protective chromia was formed. Examination of cross-sections showed that the complex structure was maintained during the testing period and that an additional layer, of α -chrome, developed early on.

It was unfortunate that a single step approach to modelling this coating was not possible. This was achieved in the variant of this coating without the additional aluminised layer [4]. However, once a modified approach was taken whereby the coating was divided in to two and the α -chrome layer was incorporated into the modelled structure ODIN did provide reasonable predictions of compositional profiles. Further adaptations to the input parameters can be made to refine the predictions.

Challenging a model, e.g. by application to more complex structures, will show up any limitation and that has been achieved here. The limitations have been the inability for the model to predict the formation of a new phase. In defence, ODIN was never intended to perform this task, it was designed to accurately predict average compositional profiles developed due to oxidation depletion and diffusion using actual data and this it has done successfully

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Table 1. Composition of CMSX-4 in wt%

Ni	Cr	Co	Ta	W	Al	Re	Ti	Mo	Hf
60.7	6.5	9.6	6.5	6.4	5.6	3.0	1.0	0.6	0.1

Table 2. Composition of the coatings in wt%

wt%	Ni	Cr	Al	Y	Si
962	67.0	22.0	10.0	1.0	
50:50	49.0	49.0			2.0

Table 3 Ternary diffusion coefficients for Cr and Al in MCrAlY

Temp /°C	D_{CrCr}/m^2s^{-1}	D_{CrAl}/m^2s^{-1}	D_{AlCr}/m^2s^{-1}	D_{AlAl}/m^2s^{-1}
800	2.67×10^{-17}	8.56×10^{-18}	4.62×10^{-18}	1.36×10^{-17}

Figure 1. Schematic diagram showing the situation modelled in ODIN at the oxidising front.

Figure 2. SEM image of a cross section through the multilayered TBC after exposure to 800°C in air for 10 hours.

Figure 3. Back-scattered SEM image of a cross section through the multilayered TBC after exposure to 800°C in air for 1000 hours showing detail of the phases distribution within of the individual layers.

Figure 4. Back-scattered SEM image of a cross section through the multilayered TBC after exposure to 800°C in air for 3000 hours showing detail of the phases within of the individual layers.

Figure 5. Compositional profiles of (a) aluminium and (b) chromium through the layered bond coat at 10, 500, 1000 and 3000 hours exposure. The values relate to average compositions obtained from area scans.

FIGURE 6. Plot of oxide thickness against time, showing means and standard deviations. The best fit thicknesses were calculated assuming the parabolic oxide growth using the rate constant presented in Table 3.

Figure 7. Plot of square of the mean oxide thickness against time showing a linear relationship indicating parabolic kinetics are occurring.

Figure 8. Predicted compositional profile for chromium using ODIN for 500, 1000 and 3000 hours.

Figure 9. Concentration profiles for aluminium and chromium in the aluminised, NiCrAlY and substrate for exposures at 800°C for times of 500, 1000, 2000 and 3000 hours.