ELEVATED TEMPERATURE COATINGS:

Science and Technology III

Edited by

Janet M. Hampikian

Narendra B. Dahotre

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PREFACE

Elevated Temperature Coatings: Science and Technology III is the third volume in a series of invited and contributed papers presented in the symposium: "High Temperature Coatings III". This symposium was organized by Janet M. Hampikian and Narendra B. Dahotre, and held in San Diego, California, during the TMS annual meeting, February 28-March 4, 1999. This volume consists of invited and contributed papers from national and international researchers representing universities, federal laboratories and industries. Thus, it provides a rich diversity of material in the research area of High Temperature Coatings. The sponsorship of the TMS Surface Modification and Coatings Technlogy Committee, Materials Processing and Manufacturing Division, and the Joint TMS/ASM Corrosion and Environmental Effects Committee, Structural Materials Division, is gratefully acknowledged.

The motivation for holding a series of symposia on the topic of High Temperature Coatings is evident considering the current aim of achieving better surface characteristics (e.g. hardness, corrosiveness) from a wide range of materials without compromising bulk characteristics such as, for example, mechanical performance. An example of this is the current thrust toward achieving higher operating temperature in industrial gas turbine engine components through use of thermal barrier coatings in high temperature gradient areas such as experienced by turbine nozzles and blades. It should be noted that the platform provided by this symposium emphasizes the coating materials rather than the processes used to form them. Accordingly, specific materials topics covered include: Thermal Barrier Coatings, Overlay Coatings for Engine Applications, Coatings for Steels, Ceramic Coatings, and Intermetallic Coatings. This is an edited proceeding, and we thank the reviewers for their time, diligence and promptness in responding to our many requests. In particular, J.M.H. would like to thank A. Alexiou, T. Chen, J. Griffin and G. Grandinetti for their assistance.

We are grateful for the institutional support provided by the School of Materials Science and Engineering at the Georgia Institute of Technology, and the institutional support of the University of Tennessee Space Institute. We thank in particular Mrs. Teresa Bailey for her secretarial support. Finally, we appreciate the continuing assistance from TMS for this Symposium on High Temperature Coatings.

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THE EFFECT OF SEGREGANTS ON THE OXIDATION OF THE BOND LAYER FeCrAl

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Abstract

The performance of thermal barrier coatings is determined predominantly by the behavior of the 1 µm thick oxide scale, formed beneath the zirconia layer. Several factors may affect the cracking behavior of that interface. These factors include the composition of the alloy substrate and the coatings as well as thermal stresses. Studies by advanced transmission electron microscopy (TEM) techniques reveal the microstructure, composition and bonding at the interfaces and regions close to interfaces in that area. The results will be reported and discussed using different models which are required for an explanation of the failure behavior. Segregation to the interface between the bond coat and the oxide scale and formation of stresses in the scale are expected to play a major role.

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Introduction

Recent workshops on thermal barrier coatings (TBCs) suggest that TBCs comprise a system involving the substrate alloy, the bond coat, the TBC itself, and the thermally grown oxide (TGO) between the TBC and bond coat, as well as the environment. A systematic approach is needed to both control and enhance the performance. The spall life is generally dictated by a TGO growth. The failure mechanisms involve the TGO and the TGO/bond coat interface. All motivated by the residual compression in the thermally grown oxide. For that reason, the interfaces between the thermally grown oxide and the bond layer FeCrAl are studied in detail.

The lifetime of high-temperature materials in corrosive environments depends strongly on their resistance against high-temperature oxidation. Therefore, the technical applicaton of these materials requires the formation of a protective, slow growing oxide scale. Fe20Cr5Al based alloys form thermodynamically stable α-Al_2O_3 scales with slow growth rates at temperatures above 1000 °C. A serious problem, particularly under cyclic temperature conditions, is the spallation of the oxide scale. The repeated exposure of the metal to the gas atmosphere leads to Al depletion in the alloy and, finally, to breakaway oxidation and failure of the material.

It is well known that doping the alloys with small additions (< 0.1 wt.%) of so-called reactive elements (RE) such as Y or Zr improve the spallation resistance dramatically (reactive element effect). It is known that in the absence of RE, a few ppm of S, which exists as a natural impurity in these materials, has a detrimental effect on the scale adhesion [1]. Regarding this effect, the RE are assumed to tie up the S by forming thermodynamically stable sulfides, thus preventing S from segregating to the metal/oxide interface of interfacial voids. Indeed, it could be shown that oxide scales grown on hydrogen annealed, RE-free FeCrAl-alloys with extremely low S content (less than 1 ppm) do not spall and have the same good oxidation resistance as Y-doped alloys up to oxidation times of 1800 h [2]. However, the question arises, as to whether the sulfur effect is the only possible mechanism by which Y improves the spallation resistance or whether other beneficial Y effects have to be taken into account. Therefore, we compared Y-doped and undoped FeCrAl with regard to scale morphology, microstructure and stresses in the oxide. To exclude effects of other dopants or impurities, model alloys with high purity have been investigated. In this study the characterization of alumina scales with TEM has been combined with stress measurements using optical fluorescence spectroscopy.

Experimental

The composition of the investigated FeCrAl model alloys is shown in Table I. The high purity of the alloys was ensured by the control of more than 70 elements, all of which have concentrations of less than 3 ppm [3]. Metal pieces of 1 mm thickness were polished down to a ¼ µm diamond finish and utrasonically cleaned in acetone before oxidation. The specimens were oxidized at 1200 °C for 5 h in air.

Scanning electron microscopy (SEM) was applied in order to investigate the scale morphology. Cross-sectional specimens were prepared for TEM. the detailed procedure of sample preparation has been described elsewhere [4]. Conventional TEM studies were performed in a JEOL 2000 FX (200 kV). For the analytical studies a VG HB 501 STEM (100 kV) equipped with a field-emission gun and an EDS Ge detector was used.

Table I Composition of high purity model alloys

Alloy	Fe	Cr (wt.%)	Al (wt.%)	Y (wt.%)	S (ppm)
A	bal	20.2	5.0	-	2
B	bal	19.9	5.0	-	45
C	bal	19.7	5.0	0.093	3
D	bal	20.0	4.9	0.080	15

The stress measurements were performed on alloys A (low S, no Y) and C (low S, with Y). They were oxidized at temperatures between 1100 °C and 1400 °C. The oxidation time was chosen so that, for all temperatures, a scale thickness of approximately 2 μm was achieved (Table II). After oxidation, the specimens were removed from the hot furnace and cooled to room temperature in a few minutes. For the temperature range above 800 °C cooling rates of about 30 K/s were estimated. For a given temperature, alloy A and C were always oxidized in the same exposure, so that both specimens have exactly the same cooling rate.

Stress measurements in the oxide scale were carried out using optical fluorescence of Cr-doped α-Al_2O_3. In the α-Al_2O_3 lattice trace impurities of Cr^{+3} substitute for Al^{+3}. The electron relaxation processes, following excitation with a laser, give rise to two radiative electron transitions in the red optical spectrum, the so-called R1 and R2 ruby fluorescence lines. Deformation of the alumina lattice due to stress causes an energy shift relative to the unstressed crystal. The dependence of the fequency shift $\Delta\nu$ from the stress tensor σ can be approximated by a linear relationship [5,6]. For a randomly oriented, polycrystalline material with small grain size compared to the excited volume, Ma and Clarke [5] have calculated the average value of $\Delta\nu$:

$$\overline{\Delta\nu} = \frac{1}{3}\left(\Pi_{xx} + \Pi_{yy} + \Pi_{zz}\right)\left(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}\right) \qquad (1)$$

where Π_{ii} are the diagonal elements of the piezospectroscopic tensor. The tensor trace $\Pi_{xx} + \Pi_{yy} + \Pi_{zz}$ was experimentally determined by He and Clarke [6] to be 7.61 cm-1/GPa for the R2 line. Assuming a two-dimensional stress state in the oxide plane with the z-axis normal to the metal/oxide interface with $\sigma_{xx} = \sigma_{yy} = \sigma, \sigma_{zz} = 0$ leads to

$$\sigma = \frac{3}{2} \cdot \frac{\overline{\Delta\nu}}{\Pi_{xx} + \Pi_{yy} + \Pi_{zz}} \qquad (2)$$

Through this equation the stress in the oxide scale can be calculated when $\Delta\nu$ has been determined. Fluorescence spectra of the alumina scales were obtained by exciting the specimen with the 543 nm line of a 1.5 mW He-Ne laser which was focussed to a 10 μm spot on the oxide surface. The fluorescence signal was collected by a 0.85 meter double monochromator and a GaAs-photomultiplier. The peak frequency was determined by fitting a double Lorentzian function to the experimental spectra.

Table II Oxidation times and temperatures of alloys A and Ca which were used for stress measurements

Temperature	1100 °C	1200 °C	1300 °C	1400 °C
Oxidation time	11.1 h	2.5 h	35 min	14 min

Results

Characterization of the Microstructure

Figure 1 shows SEM cross-sections for the alloys oxidized at 1200 °C for 5 h. The alumina scale thickness was for all specimens about 2.7 μm. The oxidation behavior of the samples without Y depended strongly on the S content. The low S alloy A (2 ppm S) showed a flat, adherent oxide scale whereas the high sulfur alloy B (45 ppm S) revealed a heavily convoluted scale. More than 30 % of the oxide on the high S specimen spalled during cooling. The uncovered metal surface showed many large voids with a smooth surface where the oxide has lost contact with the metal at temperature, whereas areas with oxide grain imprints indicate contact of the oxide to the substrate at temperature. Both Y-containing alloys C and D showed a flat, well adherent oxide scale. No spallation of the scale and no voids at the metal/oxide interface could be observed.

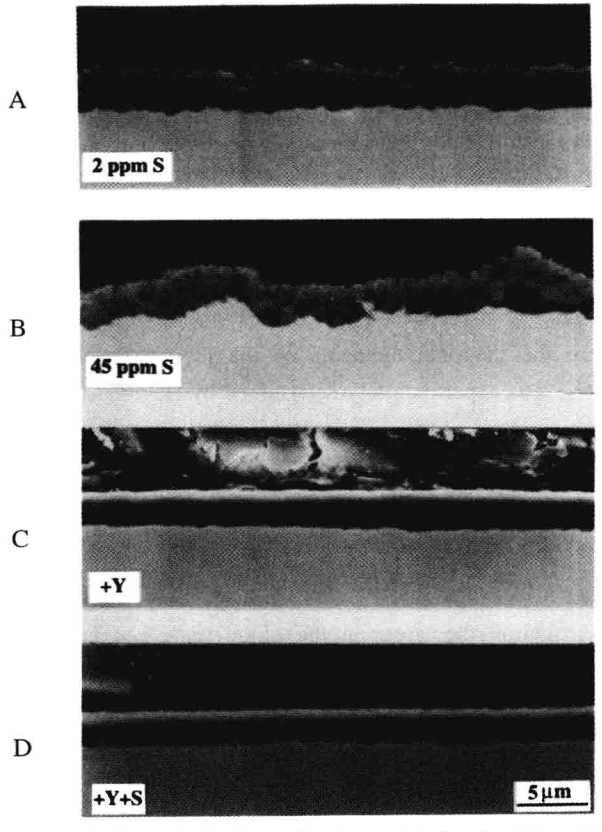

Figure 1 - SEM cross-sections of alloys A, B, C and D after oxidation for 5 h at 1200 °C

The grain structure of the oxide was studied with TEM. Figure 2 shows TEM cross-sections of the oxidized low sulfur specimens with and without Y (alloy C and A). The sample A showed large equiaxed α-Al_2O_3 grains with a diameter of approximately ½ - 1 μm. At the metal/oxide interface small voids were present at relative distances of a few microns, where an oxide grain boundary leads to the metal surface. Generally, the oxide grains were well in contact with the metal substrate. The Y-containing material had a columnar grain structure beneath a thin scale

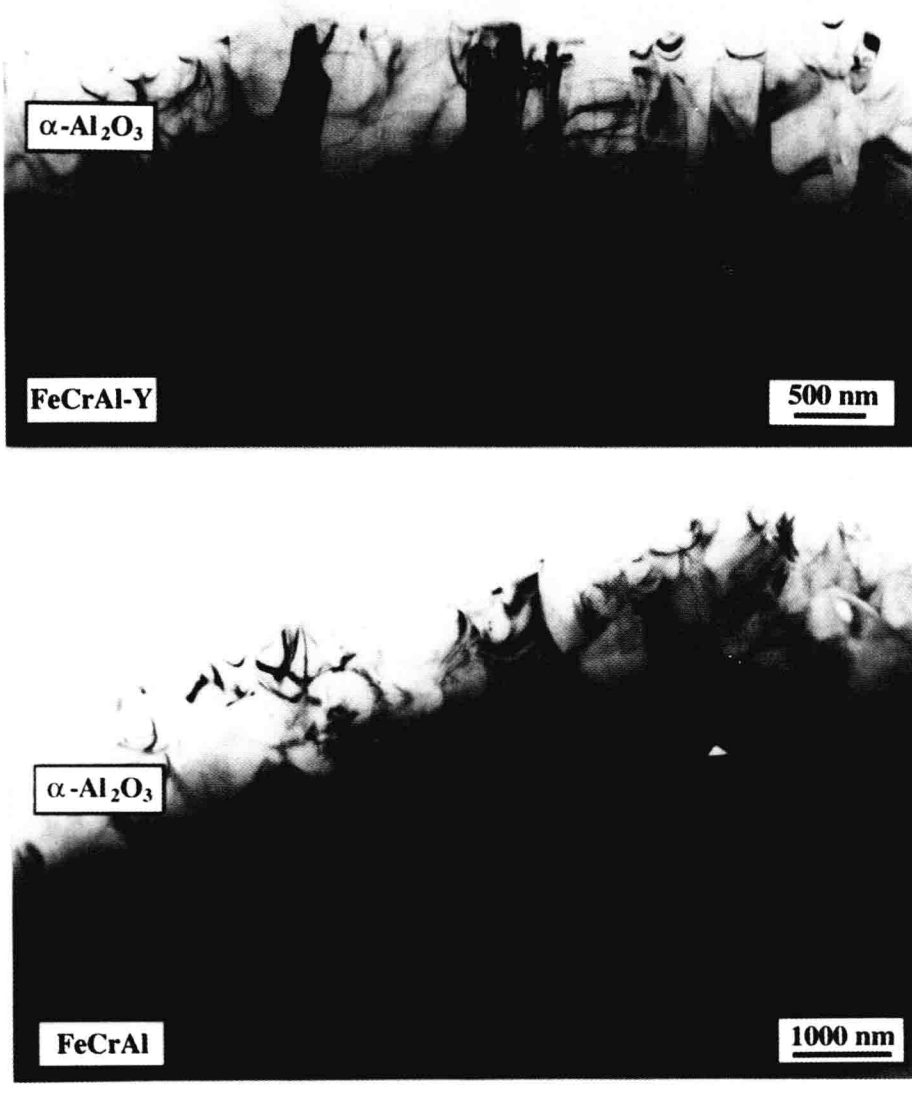

Figure 2 - TEM cross-sections of alloy C and A after oxidation at 1200 °C for 5 h

of small equiaxed grains at the gas/oxide interface. The formation of α-Al_2O_3 was demonstrated by electron diffraction. The dimensions of the columnar grains were at least 1-2 μm in length and about 0.3-0.4 μm in width. Figure 3 shows a TEM micrograph of the columnar part of the oxide scale. At the oxide/metal interface no microvoids or precipitates were detectable. The small particles near the interface in the metal revealed a large Y content and are probably internal oxides.

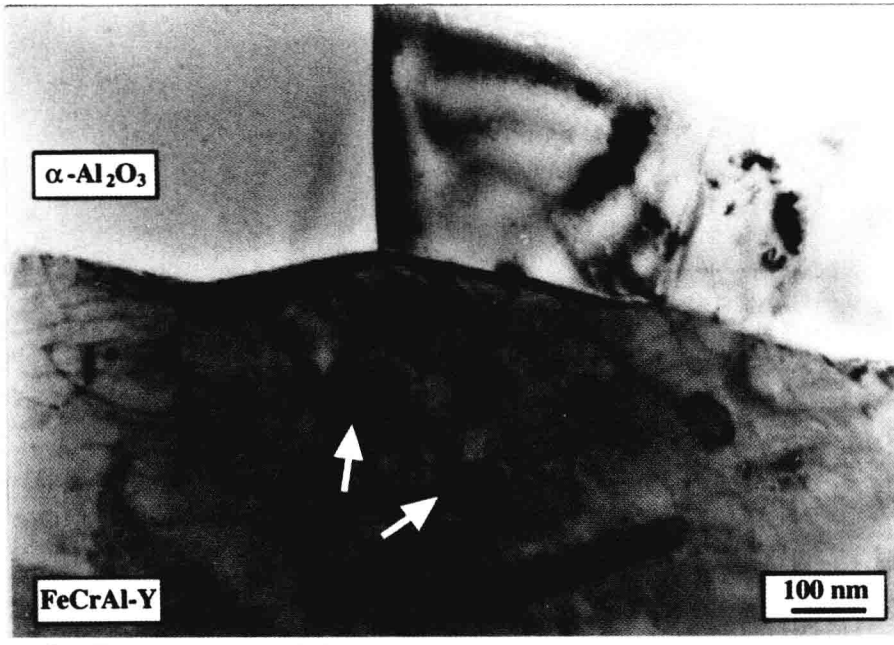

Figure 3 - TEM cross-section of alloy C after oxidation at 1200 °C for 5 h

More than 20 grain boundaries of each sample were investigated with STEM-EDS. A clear Y signal was detected at all examined grain boundaries for both specimens C and D. Figure 4a

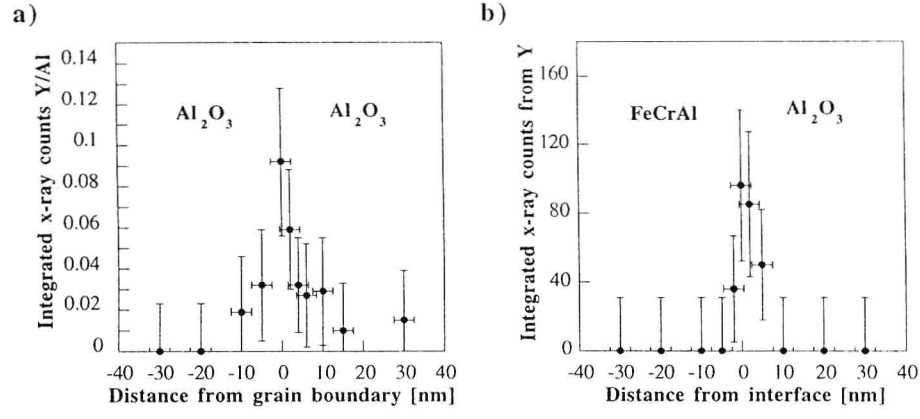

Figure 4 - STEM/EDS spot measurements at a) oxide grain boundary on alloy C and b) at the metal/oxide interface of alloy D after oxidation for 5 h at 1200°C

shows a set of spot measurements performed in a line perpendicular to the "edge-on" oriented grain boundary at varying distances. Y segregation was found at all grain boundaries. EDS measurements at the metal/oxide interface showed also Y segregation (Fig. 4b). No S signal above the detection limit of 0.1 monolayers could be detected.

Stress Measurements

Figure 5 shows typical measured fluorescence signals which were used for stress determination of the alumina scale. The R2 frequency of the spectrum of an unstressed piece of oxide which spalled off during cooling was used as reference (14432.7 cm-1). The shifted spectrum of an adherent piece of oxide indicates compressive stresses of 4.9 GPa. The absolute stresses in the oxide on alloys A (no Y) and C (with Y) are given in Fig. 6 versus the oxidation temperature. The dotted line represents the calculated stress due to cooling as discussed in the next chapter. The Y containing scales withstood stresses more than 6 GPa without spallation. The scales without Y spalled in only a few small areas.

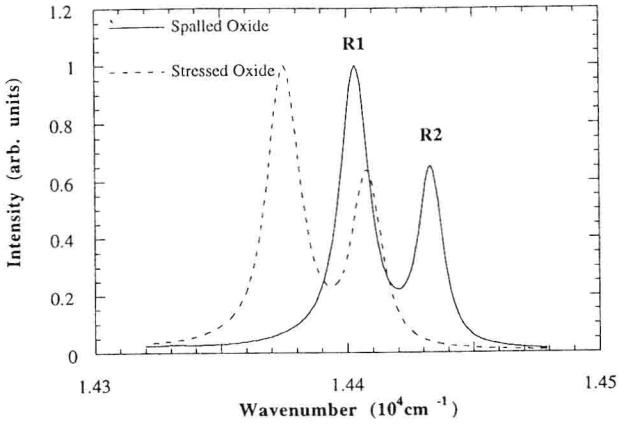

Figure 5 - R1/R2 fluorescence lines of polycrystalline α-Al_2O_3 scales from a spalled piece of oxide on alloy B and from a stressed adherent oxide on alloy A with 4.9 GPa compressive stress

It was shown that this leads to a local stress release. Fluorescence measurements were therefore always made at least 200 µm from a spalled region. The standard deviation of stress measurements at different places on the same sample was always less than 3 % indicating a homogeneously lateral stress distribution. For the oxidation temperatures of 1100 °C and 1200 °C compressive stresses of the same magnitude occurred for both specimens, whereas for higher temperatures the Y-doped scales exhibited significantly higher stresses than in the undoped oxide.

Discussion

The spallation of the oxide on undoped FeCrAl, containing S levels higher than a few ppm, is generally explained by the segregation of S to the metal/oxide interface or to interfacial voids. There is still some discussion as to whether S segregates to the intact metal/oxide interface [7] weakening the bond between oxide and metal, or whether S can only segregate to the metal/gas