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Stress Determination in Thermally Grown Alumina Scales Using Ruby Luminescence[*]

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Stress Determination in Thermally Grown Alumina Scales Using Ruby Luminescence

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Abstract

By exploiting the strain dependence of the ruby luminescence line, we have measured the strain in alumina scales thermally grown on Fe-Cr-Al alloys. Results are compared, and found to be reasonably consistent with strains determined using x-rays. Oxidation studies were carried out on alloys with compositions Fe - 5 Cr - 28 Al and Fe - 18 Cr - 10 Al (at. %, bal. Fe). Significantly different levels of strain buildup were observed in scales on these alloys. Results on similar alloys containing a "reactive element" (Zr or Hf) in dilute quantity are also presented. Scales on alloys containing a reactive element (RE) can support significantly higher strains than scales on RE-free alloys. With the luminescence technique, strain relief associated with spallation thresholds is readily observed.

I. Introduction

For many systems which operate in high temperature oxidizing environments, thermally grown alumina scales play an essential role in providing protection against environmental attack. However, scale failure can occur because of stresses that develop in the scales. Stresses can occur as a result of growth processes and from thermal expansion mismatch between scale and substrate. For different alloy substrates, sustainable stresses in thermally grown scales might vary significantly. To develop an understanding of the failure mechanisms, it is important to obtain reliable methods for measuring stresses in the scales and for detecting the onset of scale failure [1,2].

We have discovered that stresses can be determined in thermally grown alumina scales by measuring shifts in the "ruby fluorescence", a spectral doublet that occurs near 14000 cm^{-1} in chromium doped aluminas [3]. This fluorescence doublet results from a crystal field excitation in the Cr 3d electrons when Cr atoms are substituted for Al atoms in α-Al_2O_3. We have also recently learned of similar studies by Clarke , et al [4].

In this paper, we monitor the evolution of the ruby luminescence line from oxide scales grown on Fe - 5 Cr - 28 Al and Fe -18 Cr - 5 Al alloys (at %, bal. Fe), and from scales grown on alloys with similar compositions but containing the reactive elements Zr and Hf, respectively. We find that the amount of strain appearing in scales grown on these alloys differs substantially. For both alloys, the addition of a reactive element dramatically increases the maximum observed strain prior to spallation.

II. Experimental

Oxidation studies were carried out on samples of Fe - 5 Cr - 28 Al [FA71] and Fe - 5 Cr - 28 Al - 0.1 Zr - 0.05 B [FAL]; and on samples of Fe - 18 Cr - 10 Al and Fe - 18 Cr - 10 Al - 0.5 Hf (at. %, bal. Fe). All samples were polished with 1 micron alumina polishing grit before oxidation treatments.

The samples were oxidized in air at systematically increasing temperatures (in 50 C or 100 C increments), beginning at 300 C, for durations of one hour. After each oxidation treatment, the ruby fluorescence and Raman spectra were measured at room temperature. Higher temperature anneals were then performed on the same sample; ie, oxide scale growth was cumulative with increasing temperature. Thus samples were thermally cycled between the reaction temperature and ambient as the scale accumulated.

Raman and fluorescence spectra were excited with 50 to 100 mW of 476 nm radiation from a Kr ion laser. The scattered light was analyzed with a triple Jobin-Yvon grating spectrometer and detected with a CCD detector from Princeton Instruments. The Raman spectra were acquired in 500 sec runs at room temperature after the oxidation treatments. A given oxide phase has a characteristic Raman spectrum that can be conveniently used as a "fingerprint" to identify the presence of that phase in the scale. Raman spectroscopy is typically very sensitive to oxides (including Fe_2O_3 and Cr_2O_3) while being completely insensitive to the underlying metal.

The fluorescence radiation from unstrained α-Al_2O_3, doped with Cr^{3+}, appears as a very sharp doublet, detectable at very low levels of Cr doping, with peaks at 14402 and 14432 cm^{-1}. The peak positions are strongly dependent on the state of strain in the sample. (This well known "ruby doublet" has long been used to calibrate pressure in diamond anvil cells.) The peak positions are very weakly dependent on Cr concentration and temperature [4,5]. We find that, for thermally grown scales, the fluorescence doublet is often visible, even when the substrate is nominally Cr - free. Consequently, the fluorescence feature provides a very sensitive and convenient probe of strain in thermally grown scales.

III. Fluorescence Spectroscopy - Strain Analysis

The shift in frequency of the fluorescence doublet is approximately given by

$$\Delta v = \pi_{ij} \sigma_{ij} \tag{1}$$

where π_{ij} are the known piezospectroscopic coefficients [4] and σ_{ij} is the stress. Small relative shifts of the two components of the doublet are not considered here. For a strained scale on a substrate, we have

$$\sigma_{11} = \sigma_{22} \text{ and } \sigma_{33} = 0 \tag{2}$$

where σ_{11} and σ_{22} represent the in-plane stress components and σ_{33} is the out-of-plane stress. Since the stress σ_{ij} and strain ε_{kl} are related through

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl}, \tag{3}$$

using the known coefficients C_{ijkl} for sapphire [6] and performing a polycrystalline average, we obtain the ratio of in-plane ($\varepsilon_{in} = \varepsilon_{11} = \varepsilon_{22}$) and out-of-plane ($\varepsilon_{33} = \varepsilon_{out}$) strains. It is interesting to note that the usual in-plane compression ($\varepsilon_{in} < 0$) leads to an out-of-plane expansion ($\varepsilon_{out} > 0$). Combining Eqs., we obtain

$$\varepsilon_{out} = \varepsilon_{33} = -0.48\,\varepsilon_{in} \qquad (4)$$

and

$$\Delta\nu = 2810\,\varepsilon_{in} \qquad (5)$$

where $\Delta\nu$ is expressed in cm^{-1}.

IV. Results and Discussion

Since it appears that transient phases of Fe_2O_3 and Cr_2O_3 might significantly influence the early formation of α-phase alumina scales, we have used Raman spectroscopy to study the early stage evolution of these sesquioxides [3]. For the alloys in this study, the Fe_2O_3 signal is first apparent after oxidation at 500 C. Oxidation at higher temperatures increases the Fe_2O_3 signal which reaches a maximum at ~ 750 C, and then decreases and completely disappears by ~ 1000 C. A transient Cr_2O_3 is also visible, between 600 - 800 C on the Fe -18 Cr - 5 Al alloy. When oxidized at temperatures above 1000 C, both the Fe_2O_3 and Cr_2O_3 Raman signals disappeared and were replaced by a Raman signal from α-Al_2O_3.

Fig. 1 shows ruby fluorescence signals from the systematically oxidized Fe - 5 Cr - 28 Al alloy [FA71]. The fluorescence signal is first detectable in the scales after treatment at ~ 750 C. The intensity of this signal grows very rapidly as the sample experiences additional oxidation treatments. The lower spectrum in Fig 1, taken from a fully strain relieved scale, is the same as that from a bulk ruby crystal. Note, however, that the other spectra in Fig 1 show red shifts, of varying amounts, indicative of compressive strain in the scales. There is also substantial broadening of the spectra. Taking the peak position as a measure of the strain induced spectral shift and applying Eq. 5, we obtain the in-plane compressive strain. We make no attempt to interpret the observed broadening because it has contributions from crystal anisotropy, strain inhomogeniety, and perhaps defects in the growing Al_2O_3 crystals.

Fig 2 shows the measured in-plane strain as determined from the fluorescence spectra plotted against the oxidation temperature. The solid circles show strain measurements for Fe - 5 Cr - 28 Al (FA71); the solid triangles are equivalent measurements for the alloy Fe - 5 Cr - 28 Al - 0.1 Zr - 0.05 B (FAL). To ~ 900 C, both alloys show scales that develop increasing strains as oxidation temperature is increased and scale thickness grows. At T ~ 900 C, the FA71 alloy begins to show strain relaxation indicating the onset of failure. With increasing reaction temperature, the scale exhibits catastrophic failure and apparently becomes completely debonded at T > 1000 C. Spalled flakes are visually observable. For the acumulating scale on FAL, however, increasing strain buildup is observed to temperatures of about 1100 C. This is a dramatic manifestation of the reactive element (RE) effect - samples containing a RE develop thermally grown scales that are capable of sustaining substantially larger strains than scales on the RE-free alloys.

The maximum compressive strains obtained from measurements of the FAL scale are surprisingly large, being approximately 2.5 %. The solid line in Fig 2 gives the compressive strain at room temperature from thermal mismatch

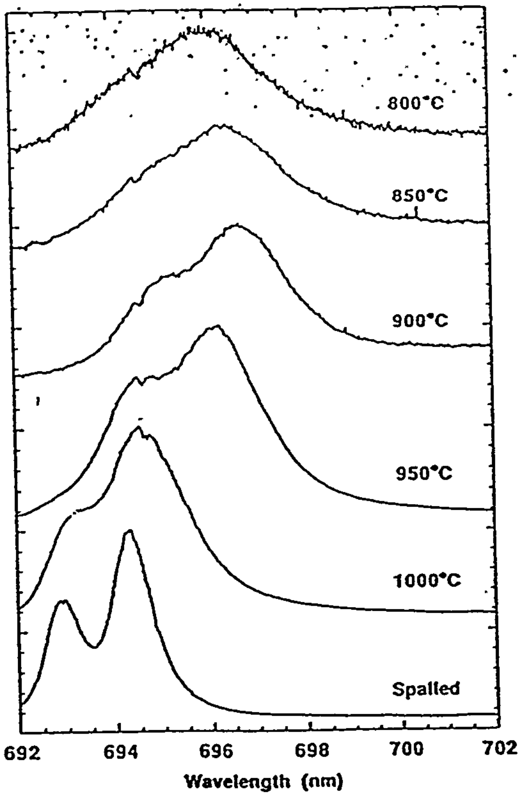

Fig 1. "Ruby" fluorescence spectra from an alumina scale grown on Fe-5Cr-28Al alloy (FAL) after one hour of (cumulative) oxidation at the indicated temperatures. The red shift indicates a compressive strain. The lower spectrum is from a strain relieved scale.

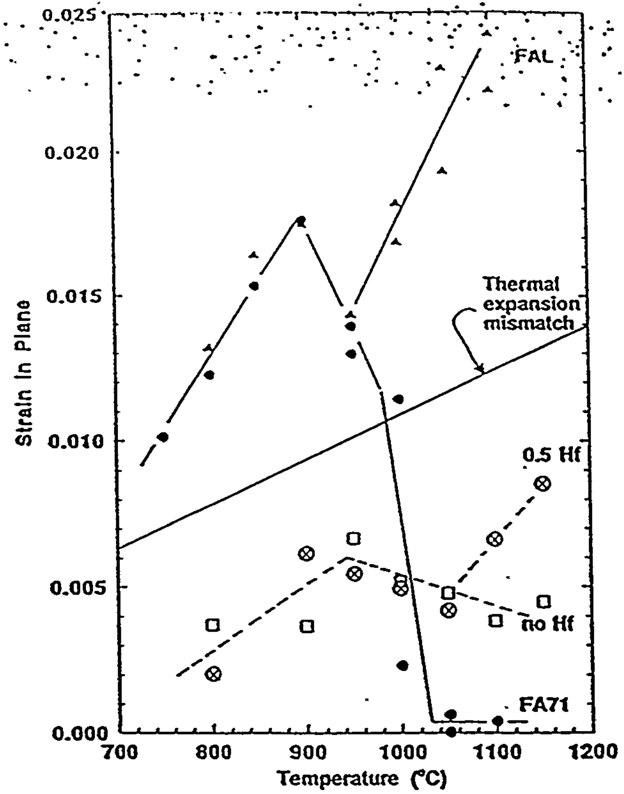

Fig 2. Strain in alumina scales thermally grown on several alloys as a function of exposure temperature. Solid dots FAL; solid triangles FA71; open squares Fe-18Cr-10Al; X's are Fe-18Cr-10Al-0.5Hf. Also shown is the strain calculated from thermal expansion mismatch between alumina and $AlFe_3$.

expected for an Al_2O_3 film on $AlFe_3$, assuming that the film is unstrained at the oxidation temperature. If the thermal expansion coefficient of the Fe-Cr-Al alloys is comparable to that of $AlFe_3$, then, for FA71 and FAL, substantial compressive strain beyond that attributable to thermal mismatch appears in the scales. Apparently a large compressive growth strain, comparable in magnitude to the thermal mismatch strain, develops in these scales.

Another possible explanation for the large strains observed in FAL and FA71 is that our model relating strain to the ruby shift is inaccurate. To test the validity of the model, we have performed a combined x-ray and ruby investigation of oxidized Fe - 18 Cr - 5 Al - 0.5 Hf. For this scale, the strain extracted from the ruby line is plotted in Fig 2 (as X's). A much smaller strain buildup is observed relative to that in FA71 or FAL scales (Fig 2). This reduced strain might be

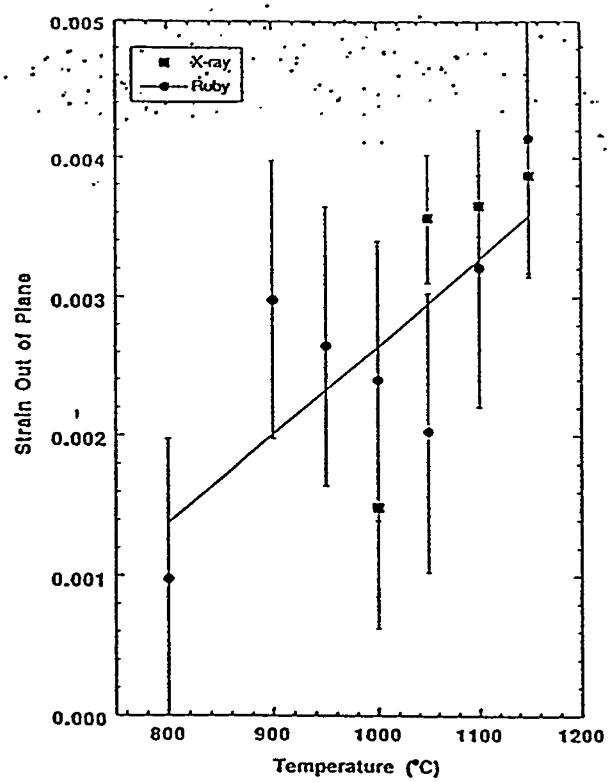

Fig 3. A comparison of out-of-plane strain, as determined by x-ray diffraction and by ruby fluorescence, for the two alloys Fe-18Cr-10Al and Fe-18Cr-10Al-0.5Hf after undergoing a series of oxidation treatments.

related to the peculiar interface morphology known to exist in the Fe - 18 Cr - 5 Al material [7]. Also, significantly less broadening is observed in the fluorescence peaks.

X-ray diffraction measurements were taken using the standard $\theta - 2\theta$ configuration. Because of the geometry of the experiment, only those crystallographic planes parallel to the sample surface were probed; ie, only the out-of-plane strain was measured. Fig 3 shows both the x-ray results and the out-of-plane strain obtained from the fluorescence lineshifts (using Eqs. 4 and 5) for the Fe - 18 Cr - 5 Al - 0.5 Hf scale. Both the x-ray and ruby measurements show a relaxation (expansion) normal to the sample surface as the oxidation temperature is increased. Within the large error bars, agreement between the x-ray and fluorescence results can be considered satisfactory; thereby validating the model used to interpret the fluorescence.

For all of the Fe-Cr-Al alloys, the luminescence line was first detected after heat treating at ~ 750 C, well below the usual formation temperature for the α-phase [eg, see ref. 8]. We believe that the ruby signal provides evidence that α-Al_2O_3 is present in the scales even at these low temperatures [also see ref. 2]. (We have observed that bulk γ-Al_2O_3 shows almost no ruby signal, but the ruby signal is strong after the sample is treated at 1200 C where it transforms to α-Al_2O_3.) A mechanism by which low temperature α-phase growth might occur involves the presence of transient phase Cr_2O_3 or Fe_2O_3 which could serve as templates for the direct formation of α-Al_2O_3. We have noted that, below ~ 900 C, the scales have a significant concentration of Fe_2O_3, and, in some cases, detectable Cr_2O_3. These phases are very similar to α-Al_2O_3; indeed α-Al_2O_3 forms a complete solid solution with Cr_2O_3. Consequently, possible"template phases" exist within the scales. The intensity of the fluorescence signal increases very rapidly with reaction temperature. The rapidly increasing intensity results, in part, from increasing scale thickness, but, more likely from (1) an increased growth rate of α-Al_2O_3 relative to other aluminum oxides and (2) from the conversion of some metastable oxide phase (possibly γ-Al_2O_3) to α-Al_2O_3.

In summary, the growth of alumina scales on several Fe-Cr-Al (alumina former) alloys was studied after samples were oxidized in air. We report room temperature measurements of the strain in thermally grown alumina scales using spectral lineshift measurements of the Cr^{3+} (ruby) fluorescence line and compare with x-ray strain measurements. We observed that, if samples contained a small amount of added "reactive element" (eg, Hf or Zr), the scales could support significantly larger strains. We observed the apparent growth of α-Al_2O_3 at oxidation temperatures as low as 750 C. Presumably, transient Fe_2O_3 or Cr_2O_3 serves as a "template" for the growth of α-Al_2O_3 at these low temperatures. The fluorescence technique provides a sensitive, rapid, and non-destructive method for measuring strains in alumina scales.

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