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by

K. Natesan, K. L. Klug, D. Renusch, M. Grimsditch, and B. W. Veal
Argonne National Laboratory
Argonne, IL 60439

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MICROSTRUCTURAL AND MECHANICAL CHARACTERIZATION OF ALUMINA SCALES THERMALLY DEVELOPED ON IRON ALUMINIDE ALLOYS*

K. Natesan, K. L. Klug, D. Renusch, M. Grimsditch, and B. W. Veal
Argonne National Laboratory
Argonne, IL 60439

ABSTRACT

An understanding of the underlying phenomena when characterizing material performance requires knowledge in several areas, including the chemistry and physics of the early stages of oxidation, chemistry and bonding at the substrate/oxide interface, effect of segregants on the strength of bonding, transport processes through the scales that are formed during corrosion, mechanisms of residual stress generation and relief, and fracture behavior at the oxide/substrate interface. Specific objectives of the program described here are to (a) systematically investigate the relationships among substrate composition and properties and scale/coating adherence, damage tolerance, and micromechanical properties; (b) use results from the investigation to prevent scale/coating failure at elevated temperatures; and (c) identify conditions that lead to more damage-tolerant coatings and scales that are amenable to legitimate synthesis routes. The paper presents experimental data on microstructural characteristics of alumina scales that have been thermally developed on several Fe-based alumina-forming intermetallic alloys. In addition, adhesion data developed on the scales are presented, along with determinations of strain from data obtained by ruby fluorescence.

INTRODUCTION

Protection from corrosion and environmental effects arising from reactions with gases and condensed products is required to fully exploit the potential of advanced high-temperature materials designed to improve energy efficiency and minimize deleterious environmental impact. This protection is best afforded either by formation of stable surface oxides that are slow-growing, sound, and adherent to the substrate or by deposition of coatings that contain or develop oxides with similar characteristics. The benefits of certain alloying additions on the growth and adherence of protective oxide scales on metallic substrates are well known, but there remains the need for a detailed understanding of the mechanisms by which scale properties and coating integrity are improved by compositional, microstructural, and processing modifications.
The ultimate objective of this program is to systematically generate a scientific basis for designing and synthesizing improved protective oxide scales/coatings (slow-growing, adherent, sound) on high-temperature materials without compromising the requisite properties of the bulk materials. Specific objectives are to (a) systematically investigate the relationships among substrate composition and properties and scale/coating adherence, damage tolerance, and micromechanical properties; (b) use such information to predict scale/coating failure; and (c) identify conditions that lead to more damage-tolerant coatings and scales that are amenable to legitimate synthesis routes. The objectives of the ANL program are to correlate actual oxidation performance with stresses, voids, segregants, interface roughness, initial stages of oxidation, and microstructures; study such behavior in growing or as-grown films; and define prescriptive design and synthesis routes to mechanically reliable surface oxides.[1,2] Several techniques are used in the studies, including Auger electron spectroscopy, X-ray diffraction, X-ray grazing incidence reflectance, grazing-angle

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X-ray fluorescence, optical fluorescence, and Raman spectroscopy. The project has selected Fe-25 wt.% Cr-20 wt.% Ni and Fe-Cr-Al alloys, which are chromia- and alumina-formers, respectively, for the studies. This paper presents selected results on alumina scale morphologies that develop on several Fe-Al based intermetallic alloys, their adhesion strength, and stresses in scales that can lead to spallation of the scales.

EXPERIMENTAL PROCEDURE

The experimental study has focused on iron aluminide (Fe-Al) intermetallic alloys, which are of interest for application in coal-gasification and coal-combustion systems. Iron aluminide alloys, which are alumina-formers, are in various stages of development under the sponsorship of the DOE. These alloys can be used as either structural material or cladding to protect structural material against corrosion. Sheets of several Fe_3Al-based alloys were procured from Oak Ridge National Laboratory. Table 1 lists the compositions of the alloys used in the study. Alloy FA 186 is a ternary alloy that contains Fe, Cr, and Al and is considered a base alloy. Alloy FA 129 is designed to exhibit high ductility at room temperature while retaining its strength at high temperatures, whereas FAL is designed for improved oxidation resistance through addition of Zr. Alloy FAS is designed to resist sulfidation, and FAX is designed for improved resistance in aqueous environments by deliberate addition of Mo. Coupon specimens were cut from sheet material for thermogravimetric oxidation experiments and for spectroscopic studies.

Specimens of the intermetallic alloys were oxidized at 1000°C for up to 100 h in oxygen bubbled through water at room temperature to examine the morphologies of the alumina scales that form on alloys with different bulk compositions. Thermogravimetric experiments were performed with an electrobalance having a sensitivity of 0.1 µg, to evaluate the rate of oxidation in different alloys and to establish the scaling kinetics. Specimens were suspended from the balance in a vertical furnace and held for the desired exposure period. Upon completion of the oxidation test, the furnace was opened and the specimens were rapidly cooled to room temperature. Following thermogravimetric measurement of oxidation, scale surfaces and cross sections of specimens were examined with a scanning electron microscope equipped with an energy-dispersive X-ray analyzer. Further, the oxidized specimens were cooled to liquid nitrogen temperature and fractured to examine the fracture morphologies of the scales and to evaluate the scale/metal interface.

A Sebastian-Five multipurpose tester (fromQuad Group Inc.) was used to evaluate the strength of the scale/substrate interface of each oxidized specimen. In this technique, an epoxy-coated pin is attached to the surface of interest at a temperature sufficient to cure the epoxy. The pin is subsequently separated from the sample at room temperature by applying a tensile load. Prior to testing the oxidized samples, the

Table 1. Nominal composition (wt.%) of alloys used in corrosion tests

Material	Cr	Al	Fe[a]	Other
FA 186	2.2	15.9	Bal.	-
FAS	2.2	15.9	Bal.	B 0.01
FA 129	5.5	15.9	Bal.	Nb 1.0, C 0.05
FAL	5.5	15.9	Bal.	Zr 0.1, B 0.05
FAX	5.5	15.9	Bal.	Nb 1.0, Mo 1.0, Zr 0.15, B 0.04

[a] Bal. = balance.

the procedure was evaluated using several flat unoxidized 316 stainless steel samples. This was done to establish the reliability of the technique and the absolute strength of the epoxy. In addition, epoxy-coated pins that had been at room temperature for varying lengths of time (as opposed to being in a freezer, where they are normally held) were used to evaluate the effect of this variable (room temperature degradation of the epoxy) on the strength data. Strength data from these tests were consistent; the maximum strength that could be measured by this procedure was ≈71±3 MPa. No significant variation in data was noted for pins exposed to room temperature for up to four days. Adhesion testing was then performed on each of the oxidized Fe-Al specimens.

The oxidized samples were also examined by a ruby luminescence at room temperature. By exploiting the strain dependence of the ruby fluorescence line, strains in the thermally grown oxides were determined for scales that developed on different substrates.[3,4] 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 but very weakly dependent on Cr concentration. Depending on scale-growth conditions, the doublet shifts and broadens, apparently as a consequence of varying strains in the alumina scale. The shifts provide a sensitive measure of strain accumulation in the scales and clearly indicate when strain relief occurs.

RESULTS AND DISCUSSION

Oxidation Behavior

Oxidation weight change of the intermetallic alloys was generally parabolic for ≈20 h, followed by much slower weight change for the rest of the exposure period. However, the scales in FA 186 and FAS exhibited significant spallation during oxidation at 1000°C and therefore, no weight change data could be obtained. For example, FA 186 showed a small weight gain up to 60 h of exposure, after which the weight of the sample decreased and showed a loss after 100 h of exposure. Assuming a parabolic behavior for the alloys with no spallation, rate constants calculated for FA 129, FAL, and FAX at 1000°C were 6.0×10^{-5}, 4.2×10^{-5}, and 4.2×10^{-5} $\mu g^2/mm^4s$, respectively. X-ray diffraction data showed α-Al_2O_3 as the scale in all of the oxidized samples.

Microstructures of Oxide Scales

The surfaces of the oxidized samples were examined by scanning electron microscopy (SEM). Subsequently, the specimens were cooled to liquid nitrogen temperature and fractured. The freshly fractured surfaces of scale and substrate were then analyzed by SEM. Figures 1 and 2 show SEM photomicrographs of the fractured and oxidized surfaces of specimens. The fracture microphotograph of FA 186 shows a wavy oxide structure and the oxidized surface of the structure also indicates a fine distribution of oxide crystals or nodules. The fracture photomicrograph of the FAS specimen has an appearance similar to that of FA 186 but the surface shows a few large particles of oxide surrounded by a fine distribution of oxide precipitates. The morphologies in these specimens indicate that the scale is bonded to the substrate, probably at these large particles, and a two-dimensional bonding between the scale and substrate may not be present. In contrast, the fracture surface of the FA 129 alloy shows a dense, ≈2-μm-thick oxide scale, bonded well to the

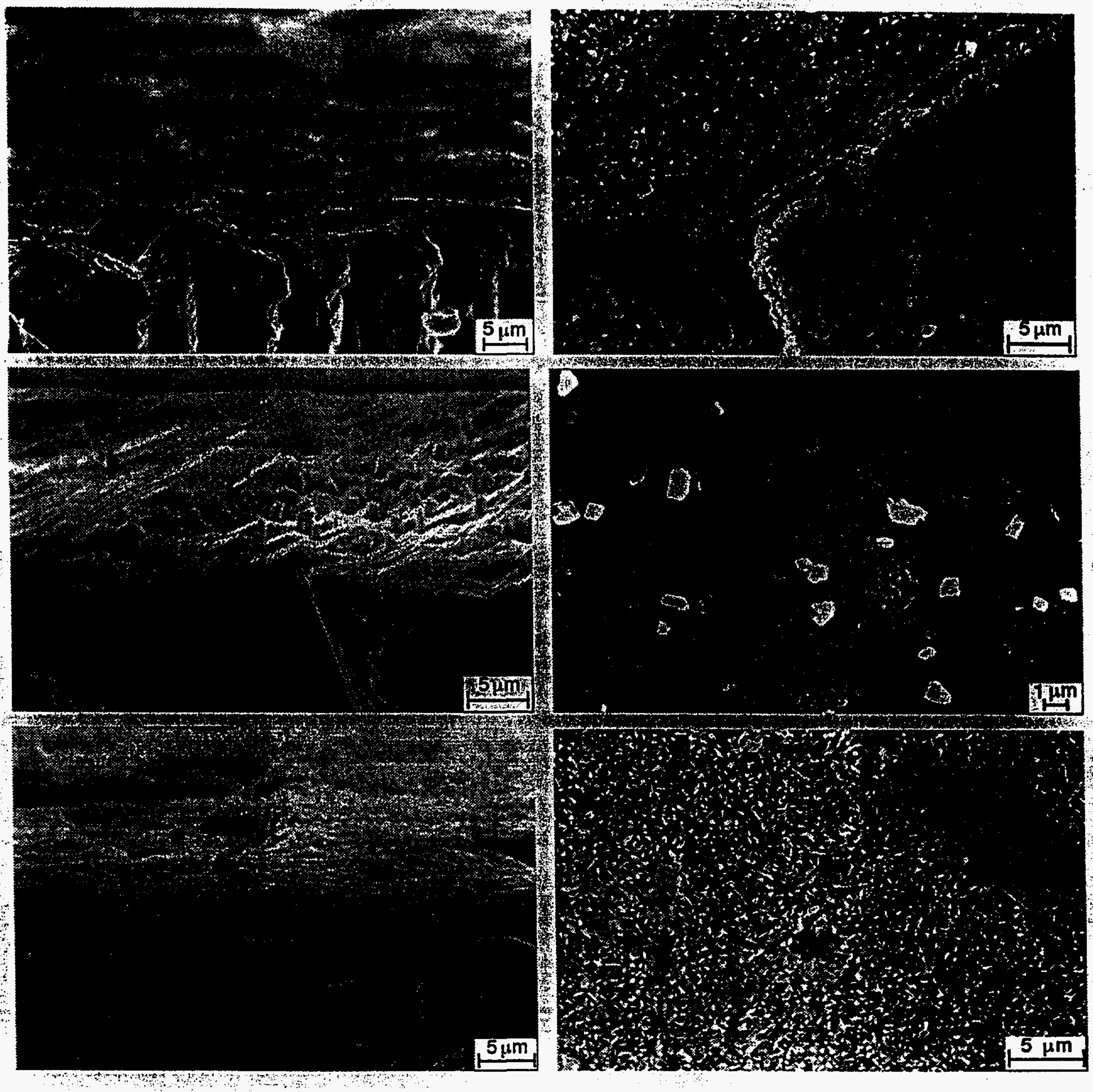

Fig. 1. SEM photomicrographs of (left) fracture surfaces and (right) oxidized surfaces of (top) FA 186, (middle) FAS, and (bottom) FA 129 alloys oxidized for 100 h at 1000°C

substrate. However, the surface of oxide exhibits some clumps of oxide, but not as many as in FAS alloy. The oxide morphology in FAL differs significantly from the morphologies of FA 186, FAS, and FA 129 alloys. Oxide growth is much more uniform and a distribution of fine oxide particles is present rather than spikes or clumps of oxide as observed in other samples. The oxide morphology in the FAX sample is much like that of the FAL sample but the fracture photomicrograph shows some voids at the scale/metal interface, which may be detrimental in the long run from an adhesion standpoint.

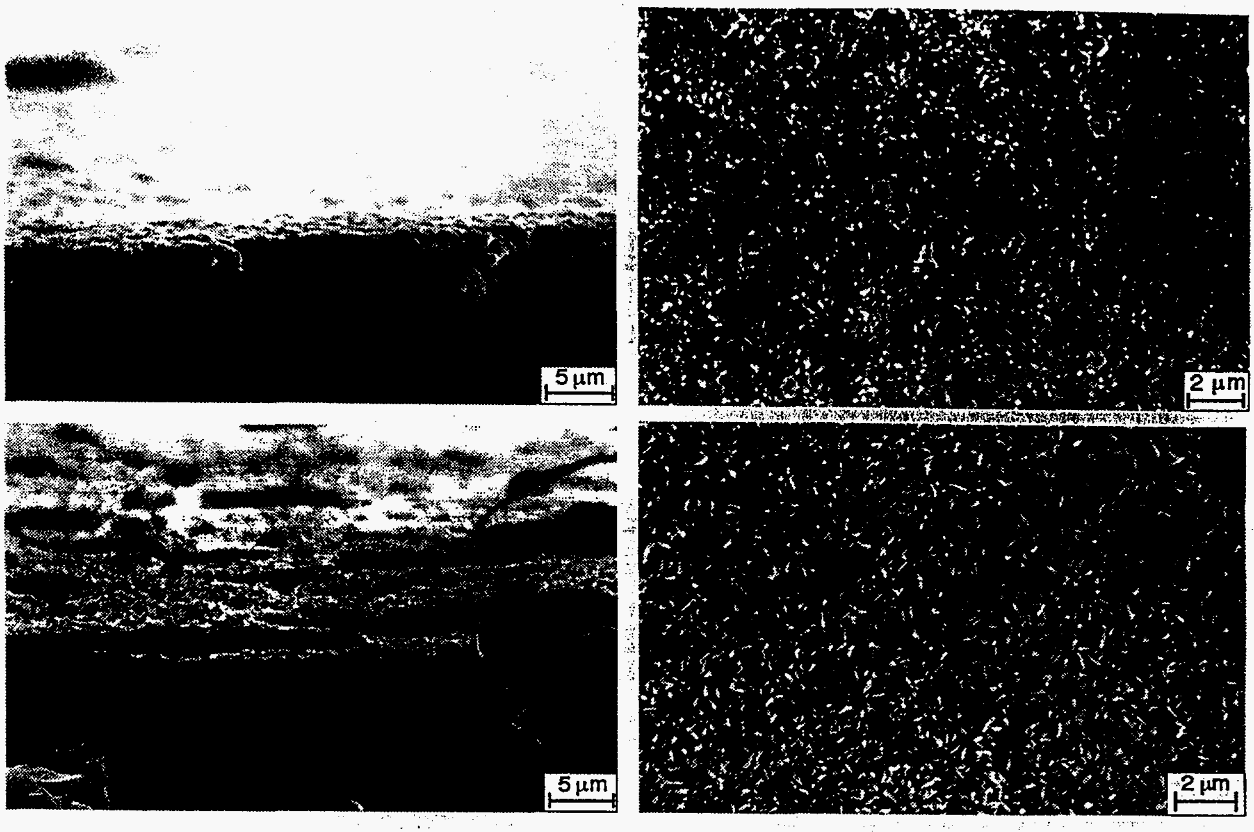

Fig. 2. SEM photomicrographs of (left) fracture surfaces and (right) oxidized surfaces of (top) FAL and (bottom) FAX alloys oxidized for 100 h at 1000°C

Adhesion of Scale to Substrate

To examine the adhesion characteristics of the thermally grown scales to the substrate, a Sebastian multipurpose tester was used to apply a tensile pull to separate the scale from the substrate. The surfaces of pulled pins were examined to assess whether the debonding occurred in the scale itself or at the scale/metal interface. Five measurements were taken for each specimen. The highest and lowest values for the load were discarded, and an average of the other three values and deviations from the mean were calculated. Knowing the pin area of contact, the stresses needed to pull the scale from the substrate were calculated. Figure 3 shows plots of the maximum stress endured by scale for the alloys oxidized at 800, 1000, and 1200°C as a function of alloy exposure temperature. The results show that Alloys FAS, FA 186, and FA 129 exhibit a peak in maximum stress value for specimens exposed at 1000°C. On the other hand, maximum stress values for FAL and FAX specimens are almost independent of exposure temperature. Even though the total exposure time of 100 h was used for all the specimens at all temperatures, the rates of disappearance of transient oxides and development of stable alumina scale will be different for different exposure temperatures and may be influenced by the composition of the bulk alloy, especially by the presence of reactive elements such as Zr and Nb.

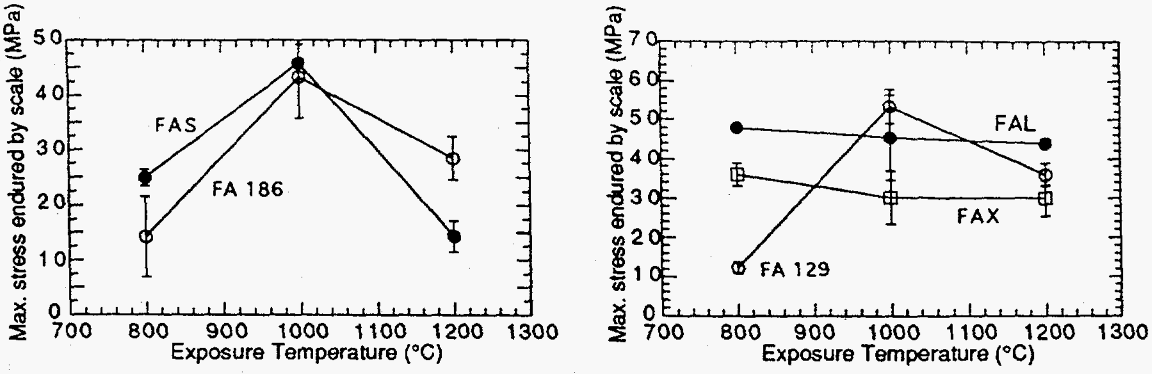

Fig. 3. Maximum sress endured by oxide scales on Fe-Al alloys determined by adhesion tests

Fluorescence Spectroscopy - Strain Analysis

Stress determination in thermally grown alumina scales by ruby luminescence has been recently addressed.[3,4] The technique has shown potential to elucidate our understanding of the strains that develop in thermally grown scales. The basic premise is that one can quantitatively assess the shift in the peaks of a relatively sharp fluorescence doublet obtained from the alumina scale, and, assuming a plane strain condition, calculate the strain in the scale. It is difficult to assess the importance of the measured strain values in scale fracture because little or no quantitative data are available for films of alumina in the literature. Nonetheless, the technique can be used to compare the strain values for specimens that have received differing treatment or compare the values obtained for different alloy specimens that have been oxidized under the same conditions. The trends identified in such an approach can shed light on the important variables responsible for the observed microstructure, alloying-element effect, adhesion, and time-dependent variations in the scale and at the scale/metal interface. The frequency shift ($\Delta\nu$ in cm^{-1}) is related to the in-plane strain by the expression

$$\Delta\nu = 2810\,\varepsilon_{in}.$$

Figure 4 shows the fluorescence spectra for various alloys oxidized for 100 h at 1000°C. The three spectra for each alloy are measurements taken at three different locations on the same specimen. The extreme variability in the spectra of FA 186 and FAS specimens indicates that the scale has spalled from various areas of the specimen. The spectra for FA 129, FAL, and FAX are fairly consistent. Figure 5 shows the in-plane strain, calculated from the peak shifts, for the five alloys oxidized for 100 h at 1000°C. The results show low strain values for FA 186 and FAS alloys, indicating significant spallation of the scale. This observation confirms the SEM analysis of the fracture surfaces and thermogravimetric test data for these alloys. The in-plane strain values for FA 129, FAL, and FAX are consistently high and indicate that the scales developed in these alloys can accommodate the deformation, as evidenced by the lack of spalling in the oxidized alloys.

A comparison of the stress needed to pull the scale away from substrate and the strain that was accommodated in the scale of various oxidized specimens is attempted in Fig. 6. It is evident that the maximum stress needed to pull the scale from various alloys is in the range of 30-52 MPa and the

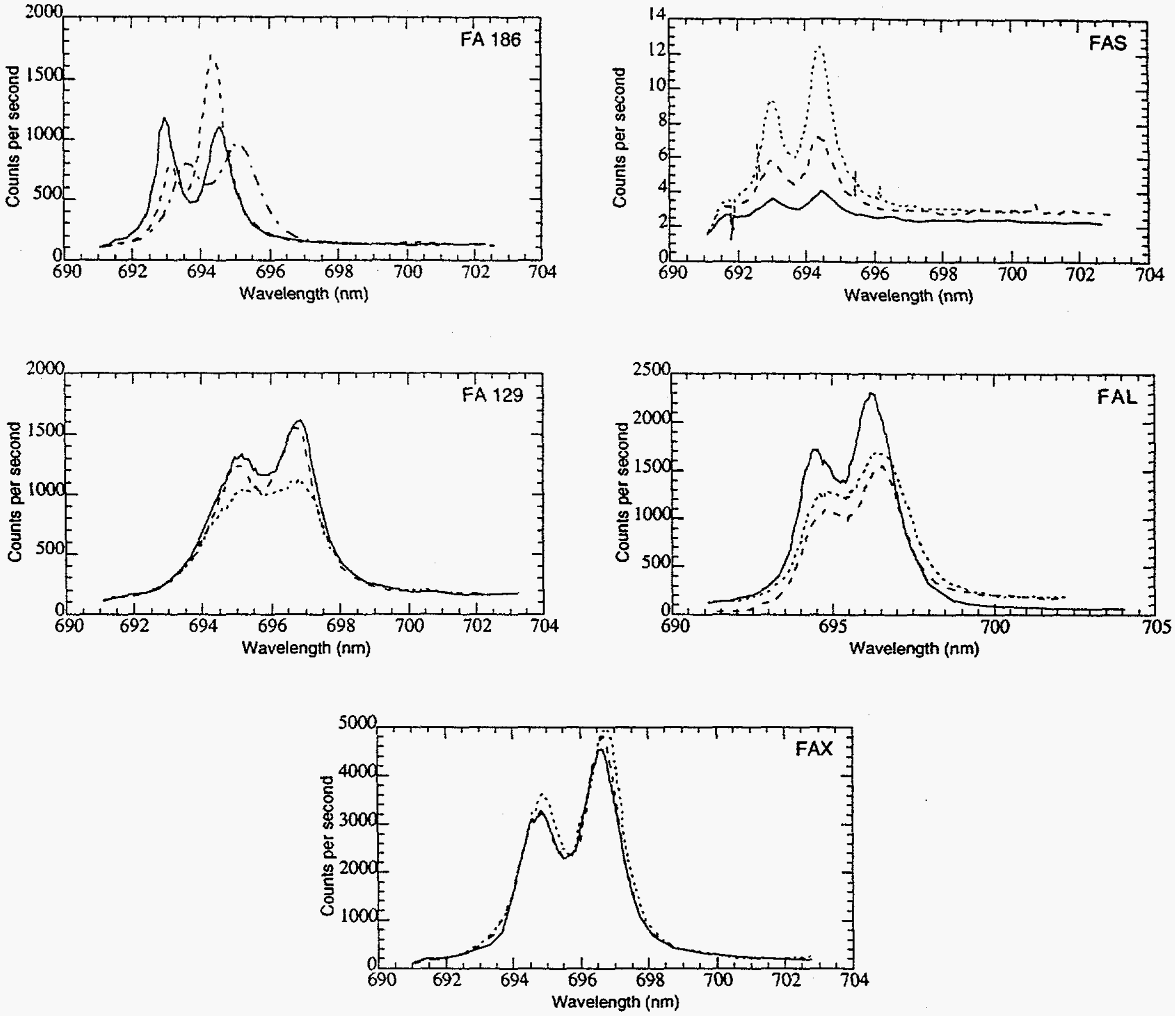

Fig. 4. "Ruby" fluorescence spectra for several Fe-Al alloys after oxidation for 100 h at 1000°C

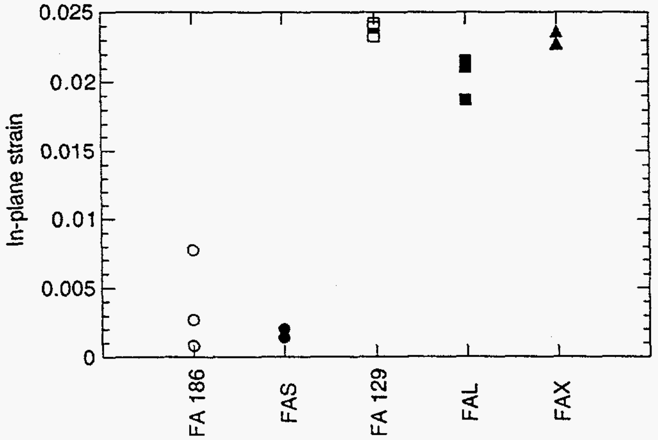

Fig. 5. In-plane strain values for oxide scales calculated from peak shifts in fluorescence spectra

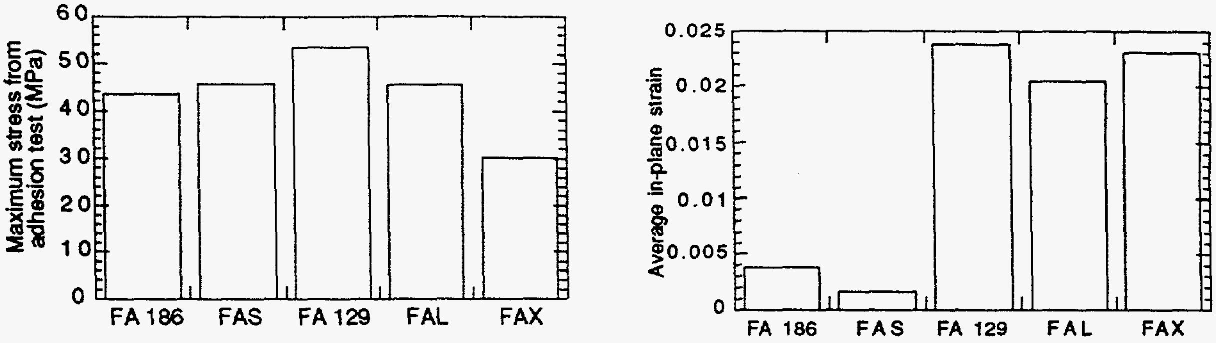

Fig. 6. Comparison of maximum stress needed to pull scale from substrate, and in-plane strain values for oxides that developed on several Fe-Al alloys

microstructural characteristics cannot be correlated with the stress values from the limited adhesion tests. Additional tests are underway with specimens exposed at 800 and 1200°C to develop a better understanding of scaling kinetics, adhesion of scale to substrate, and scale failure.

SUMMARY

Several alumina-forming Fe-Al intermetallic alloys have been oxidized in oxygen for 100 h at 1000°C to elucidate our understanding of the scaling kinetics, scale morphology, scale adhesion characteristics, and strain accommodation in the scales. Oxidation studies were conducted by the thermogravimetry technique, followed by detailed analyses of the surfaces of oxide scales. In addition, samples were cooled to liquid nitrogen temperature and then fractured; subsequently, their scale/metal interfaces were analyzed. Some of the scales were adhesion-tested by applying a tensile load to pull the scale away from the substrate. Finally, ruby fluorescence was used to measure in-plane strains in the oxide scales and the values were correlated with the scale microstructures.

REFERENCES

1. K. Natesan, B. W. Veal, M. Grimsditch, D. Renusch, and A. P. Paulikas, "Mechanically Reliable Surface Oxides for High-Temperature Corrosion Resistance," Proc. 9thAnnual Conf. on Fossil Energy Materials, CONF-9505204, ORNL/FMP-95/1, p. 225 (1995).

2. K. Natesan, C. Richier, B. W. Veal, M. Grimsditch, D. Renusch, and A. P. Paulikas, "Chemical and Microstructural Characterization of Thermally Grown Alumina Scales," Argonne National Laboratory Report ANL/FE-95/02 (1995).

3. D. Renusch, B. W. Veal, I. Koshelev, K. Natesan, M. Grimsditch, and P. Y. Hou, "Stress Determination in Thermally Grown Alumina Scales Using Ruby Luminescence," Proc. Spring Meeting of MRS Society, San Francisco, CA, April 8-12, 1996.

4. D. M. Lipkin and D. R. Clarke, "Measurement of the Stress in Oxide Scales Formed by Oxidation of Aluminum-Containing Alloys", Oxid. Metals (in press), and Q. Ma and D. R. Clarke, "Stress Measurement in Single and Polycrystalline Ceramics using Their Optical Fluorescence", J. Am. Ceram. Soc., 77 (2), 298-302 (1994).