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The effect of Y and Ti on FeCrAl oxidation at 1400 °C

B.A. Pint, A.J. Garratt-Reed and L.W. Hobbs

H.H. Uhlig Corrosion Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.

Abstract. — Inco alloy MA956 (Fe-20wt%Cr-4.5%Al-0.35%Ti + 3vol% Y_2O_3 - Al_2O_3) was oxidized in 1 atm of dry, flowing O_2 at 1400 °C. Good scale-metal adhesion was observed. Some spalling occurred upon cooling, but it remained within the oxide, not through to the bare metal. Cyclic experiments showed good scale adherence. Y was found to segregate to the oxide grain boundaries and by implication to have modified oxidation behavior through a reactive element effect. However, while at lower temperatures Ti was also found to segregate, at 1400 °C very little segregation was detected. Instead, $\approx 0.5 \mu m$ TiN_x particles were observed in the scale. These particles appear to have cracked the surrounding oxide during cooldown. It is postulated that the spallation observed was due to these particles. MA956 was compared to Kanthal alloy APM (Fe-20%Cr-5.5%Al-0.03%Ti + $\approx 2 vol\% ZrO_2$ - Al_2O_3) and a conventionally-cast Fe-20%Cr-10%Al alloy, in order to study the effect of Y and Ti.

1. Introduction.

Because of its relatively low volatility, Al_2O_3 is of considerable importance in high temperature oxidation of corrosion-resistant alloys above 1000 °C. Applications continue to push these alloys to higher temperatures, but relatively little work has been done to examine the oxidation of primary alumina formers at temperatures above 1300 °C [1-7]. Studies of reactive elements (RE) have proven difficult at higher temperatures because of the problems with non-uniform distributions of Y as an alloy addition [8-9] and recent work demonstrating the extremely short-lived effects of an Y implant ($2 \times 10^{16} cm^{-2}$) at 1200 and 1500 °C [4, 7]. Thus, this study has turned instead to commercial oxide-dispersed FeCrAl alloys to study the reactive element effect (REE) at these higher temperatures, despite the close proximity to FeCrAl alloy melting points.

In the study of the REE, two important observations in the past decade have significantly constrained interpretations of these effects. The first was the identification of a detrimental role of sulfur on adherence [10-13]. The second was the observation of the segregation of RE ions to the oxide grain boundaries [14-20] and the metal-oxide interface [18]. The effect of sulfur pertains mainly to oxide adherence, but the segregation theory proposed by Przybylski and Yurek [15] for Cr_2O_3 and extended to Al_2O_3 -formers by Pint *et al.* [18], seeks to explain all of the experimentally observed effects.

Located at the grain boundaries and the alloy-oxide interface, a relatively small amount of RE can have a disproportionate effect on the oxidation mechanism (and thus the oxidation rate) by blocking the grain boundary diffusion of cations, leaving slower anion diffusion dominant [7, 17, 19-21]. At the alloy-oxide interface, the RE prevents the segregation of S by lowering the driving force for S segregation, thus improving the oxide adhesion. And finally, RE segregation to oxide grain boundaries has a solute drag effect which reduces oxide grain

growth and, combined with the change in oxidation mechanism, changes the overall oxide microstructure [18-20].

The initial thrust of this study was to determine if the segregation of the RE to the oxide grain boundaries would again coincide with improvements in the oxidation behavior. A subsequent, but no less important objective, was to look at the deleterious effect of TiN_x particles observed in the Al_2O_3 scale.

2. Experimental procedure.

Inco's MA956, a commercial Fe-20%Cr-4.3%Al-0.36%Ti alloy containing an oxide dispersion of Y_2O_3 - Al_2O_3 particles, was the initial focus of the investigation. For comparison, an undoped, conventionally-cast Fe-20%Cr-10%Al alloy and Kanthal's APM (Fe-20%Cr-5.5%Al-0.03%Ti-0.23%Si with a ZrO_2 - Al_2O_3 dispersion) were also studied. Alloy coupons were polished through 0.3 μm alumina and ultrasonically cleaned in acetone and alcohol prior to oxidation. Isothermal weight gain was measured with a Cahn model 1000 microbalance. Cyclic weight changes were measured after cooling to room temperature with a Mettler model AE163 balance. Isothermal experiments were performed at 1400 °C in a dry, flowing atmosphere of air or pure O_2 . Cyclic experiments were performed in the same apparatus using only dry, flowing O_2 .

After oxidation, specimens were characterized using glancing angle X-ray diffraction (GAXRD), scanning electron microscopy with X-ray energy dispersive spectroscopy (SEM/XEDS), transmission electron microscopy (TEM) and field-emission gun scanning-transmission electron microscopy (FEG-STEM) equipped with XEDS and electron energy-loss spectroscopy (EELS). The STEM work was done with a Vacuum Generators HB5 instrument with a ≈ 2 nm electron probe using a windowless XEDS detector. Specimens were sectioned parallel to the alloy-oxide interface and ion-milled so as to examine the oxide either near the gas interface or near the alloy interface [22].

3. Results.

Isothermal kinetic experiments were performed on the three FeCrAl materials at 1400 °C. Figure 1 shows the weight gain data plotted against the square root of time. The data have been corrected for the linear evaporation of the Pt-Rh hangdown wire. The kinetics generally obey a parabolic rate law indicative of growth via solid state diffusion. The FeCrAl without additions has a slightly higher rate than the two commercial alloys with a RE addition. The ODS alloys have essentially the same rate constant. The scales in each case were identified as primarily α - Al_2O_3 .

After isothermal exposure, it was noted that while APM (0.03%Ti) had visibly good oxide adherence, MA956 (0.36%Ti) appeared to spall slightly - not large flakes, but small sub-millimeter sections over less than 10% of the surface. Spallation was observed after exposures of 25 h or more but not after 1 h. SEM revealed that in fact the spalls had dimensions of 20-200 μm and extended not to the bare metal but were confined within the oxide (Figs. 2, 3). Based on the isothermal weight gains, all of the spalling occurred during cooldown. One of the spall regions contained a Ti-rich particle (identified by XEDS) while others contained Fe and Cr rich particles. These could be remnants of the initial transient period.

Parallel TEM sections of the oxide scale grown on MA956 were analyzed using STEM/XEDS. The initial analysis of the scale revealed that Y segregation to each boundary

Fig. 1. — Isothermal kinetic data from FeCrAl alloys oxidized at 1400 °C in O₂ showing parabolic behavior.

Fig. 2. — SEM secondary electron image of a region of spalled oxide after 25 h oxidation at 1400 °C in O₂.

was easily detected but that Ti was discernible in only very small amounts. This is distinctly different from the behavior observed at lower temperatures. Table I shows the ratios of Y and Ti to Al on Al₂O₃ grain boundaries near the gas-oxide interface at several temperatures from previous published studies and this work. Rather than strongly segregating at 1400 °C,

Fig. 3. — SEM secondary electron image of a region of spalled oxide after 25 h oxidation at 1400 °C in air showing the intragranular fracture.

Ti is observed to form TiN_x particles, 0.3-1.5 μm in diameter in a matrix 1-5 μm Al_2O_3 grains (Fig. 4). Figure 4 also reveals the apparent decohesion of the particle from the matrix in the lower right hand corner. The particles were identified first by XEDS then reconfirmed by EELS (Fig. 5). XEDS and EELS quantifications of the Ti/N ratio were not conclusive. Selected area diffraction of the particle was performed by conventional TEM but a specific structure has yet to be identified.

Table I. — *Apparent XEDS weight percentage ratios on Al_2O_3 grain boundaries near the oxide-gas interface in scales grown on MA956.*

Temperature	Y/Al ratio	Ti/Al ratio	Ti/Y ratio
1000 °C [16]	0.014	0.037	2.643
1200 °C [18]	0.049	0.071	1.431
1400 °C	0.017	0.003	0.184

In order to check the source of the nitrogen, MA956 was oxidized in air and in a carefully-flushed O_2 atmosphere. No significant difference in weight gain was observed, and both alloys spalled in the same way as described before (Figs. 2, 3).

To further investigate the effect of Ti on adherence, a relatively short 20-cycle adherence test was performed at 1400 °C (Fig. 6). On MA956, no spalling to the metal surface was observed, even though this alloy sample contained 110 ppm S. However, partial spallation by intragranular fracture again was observed within the Al_2O_3 scale, along with minor cracking along the sample edges. The conventional FeCrAl material began to exhibit massive exfoliation after a few cycles of relatively good adherence. Scales on APM (with 10 ppm S) exhibited

Fig. 4. — STEM annular dark-field image of TiN_x particle in the Al_2O_3 scale grown on MA956 after 25 h oxidation in O_2 at 1400 °C. The arrow indicates separation between the particle and the matrix.

Fig. 5. — EELS spectrum from TiN_x particle in the Al_2O_3 scale formed on MA956 after 25 h oxidation in pure O_2 . Only peaks for Ti and N are observed.

similar adherence to those on MA956, but after 20 cycles the scales looked very different. No intragranular fracture was observed, but macrocracking of the scale was observed similar to another study [3]. No macrocracking was observed for scales on MA956. Thus, while Ti appears to cause spallation, catastrophic exfoliation to the bare metal does not occur.

Fig. 6. — FeCrAl cyclic and isothermal kinetic data at 1400 °C in O₂. The connected data points are the cyclic data; the unconnected points with the same symbol are the isothermal exposure.

4. Discussion.

The primary reason for undertaking this work was to test the segregation theory at 1400 °C in a material without the problems associated with alloy additions or ion implantation. The driving force for segregation in Al₂O₃ is most likely a strain-relief mechanism for the larger Y and Ti cations. It is possible that, as the temperature is increased, foreign ions could be more easily accommodated into the lattice, thus limiting the extent of segregation. At this point, the REE would no longer be observed.

In this study, Y was found to segregate quite strongly, and improved performance customarily associated with the REE was observed. Very recently, Y also has been found to segregate to Al₂O₃ boundaries in scales grown on Y-implanted NiAl at 1500 °C [7]. Ti segregation at 1400 °C was significantly less than was observed in scales grown on MA956 at lower temperatures. However, Ti has not been found to exhibit the REE [23], even when added as an oxide dispersion [24]. Therefore, its absence on the boundaries is not expected to affect the oxidation behavior.

There is current disagreement about the effect of the RE on the oxidation rate of alumina-formers. While the rate reduction is nowhere near the 1-2 orders of magnitude found in chromia-formers containing a RE, there is a repeatable reduction in the oxidation rate for alumina formers containing a RE oxide dispersion [18]. The specific case of an oxide dispersion is cited because, in the cases of ion implantation or especially alloy additions, internal and external oxidation of the RE can represent a considerable weight gain. In both chromia- and alumina-formers, the reduction in rate constant is due to an observed reduction of cation boundary diffusion [7, 17, 21]. The reduced effect in alumina formers, as compared to chromia formers, is ascribed to the smaller difference between cation and anion transport in the former [18]. It appears that the reduction in oxidation rate decreases with temperature. At

1400 °C, the reduction is less than a factor of 2. This may be due to a reduction of the cation diffusion contribution in undoped Al_2O_3 or an increase in lattice diffusion relative to the boundary diffusion which dominates at lower temperatures.

The alloy addition of Ti appears to be the most likely reason for the observed spallation behavior of MA956. Stresses associated with very thick scales should have caused similar failure in each of the FeCrAl alloys, not just MA956. A similar argument applies to potential effects of Fe-, Cr- or RE-rich particles. However, it is difficult to make many direct comparisons between APM and MA956. While having less Ti than MA956, APM also has a 0.3%Si addition and a coarser oxide dispersion.

The effect of Y and Ti in this study appears to distinguish two different types of failure. The first type of failure is that associated with massive scale exfoliation, exposing the bare metal. There is considerable evidence to link this type of failure to the segregation of indigenous sulfur to the alloy-oxide interface. While S appears to weaken the oxide-metal bond, some source of stress, either due to growth of the oxide film or thermal mismatches during cooling, is also required to initiate failure. This type of failure was observed on the FeCrAl without a RE addition. As an aside, the spallation of this alloy at 1400 °C was less severe than at 1200 °C [19].

A second type of failure can also be observed which does not appear to be directly related to interfacial sulfur segregation. This type of failure typically occurs only during cooldown and involves a second phase particle which could have a thermal mismatch with the scale matrix or undergo a phase transformation. In certain cases, where the particle is particularly large, the spall can be all of the way to the metal interface [8]. In the present case, the relatively small ($\approx 0.7 \mu\text{m}$) TiN_x particles do not cause massive failure of the thick scale ($> 15 \mu\text{m}$ after 25 h), but appear to initiate microcracks (Fig. 4).

The source of the nitrogen is of considerable interest, as is the stability of a nitride within an oxide film. Changing the reaction environment from air to oxygen showed no noticeable effect. A more likely source is Inco's use of air as a mechanical alloying environment which may promote the formation of TiN_x which is a more stable nitride than Fe, Cr or Al nitrides. Nitrides present in the alloy may ripen in the growing scale and become more effective crack initiators, leading to eventual spallation.

At 1400 °C, TiN is stable with a nitrogen dissociation pressure of $\approx 10^{-11}$ atm; however both TiO and TiO_2 have a lower free energy of formation than TiN. While kinetic factors may limit the transformation to the more stable oxide, oxygen activity in the scale could represent a thermodynamic issue. Figure 7 illustrates a conventionally-envisaged oxygen gradient across the scale and a second, hypothetical one. If the oxygen activity were to drop precipitously near the gas interface, a TiN_x particle in an Al_2O_3 matrix would be below the dissociation pressure of TiO or TiO_2 . Al and Y, forming more stable oxides, would prevent TiO_x formation.

TEM cross-sectional analysis (XTEM) of the metal-oxide interface is an effective technique to probe for segregation there. Y in MA956 and Zr in APM have been found to segregate to this interface at 1000 and 1200 °C [18]. XTEM specimens are being prepared from MA956 oxidized at 1400 °C for future analysis.

5. Conclusions.

1) A slight reduction in oxidation rate is ascribed to the segregation of Y to the oxide boundaries, where it inhibits cation diffusion. The reactive element addition also improves oxide adherence at 1400 °C.

Fig. 7. — Schematic diagram of the oxygen activity across the scale thickness indicating the dissociation pressure of TiO_2 and Al_2O_3 at 1400 °C and the general location of the TiN_x particles found in the scale.

- 2) Unlike at lower temperatures, where Ti in the alloy segregates strongly to oxide grain boundaries, at 1400 °C Ti segregates only weakly. Instead, Ti is found in TiN_x particles in the scale.
- 3) After extended oxidation times, these TiN_x particles appear to initiate intragranular fracture within the oxide scale, but not spallation at the alloy-oxide interface.
- 4) In short-term cyclic testing at 1400 °C, these TiN_x particles do not appear to have any significant effect on adherence, and no spallation to the oxide-metal interface was observed.

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