Internal stresses and textures of nanostructured alumina scales growing on polycrystalline Fe(3)Al alloy
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The evolution of internal stresses in oxide scales growing on polycrystalline Fe₃Al alloy in atmospheric air at 700 °C was determined using in situ energy-dispersive synchrotron X-ray diffraction. Ex situ texture analyses were performed after 5 h of oxidation at 700 °C. Under these conditions, the oxide-scale thickness, as determined by X-ray photoelectron spectroscopy, lies between 80 and 100 nm. The main phase present in the oxide scales is α-Al₂O₃, with minor quantities of metastable θ-Al₂O₃ detected in the first minutes of oxidation, as well as α-Fe₂O₃. α-Al₂O₃ grows with a weak (0001) fiber texture in the normal direction. During the initial stages of oxidation the scale develops, increasing levels of compressive stresses which later evolve to a steady state condition situated around −300 MPa. © 2010 International Centre for Diffraction Data. [DOI: 10.1154/1.3402764]

Key words: oxidation, alumina, energy-dispersive diffraction, internal stress, texture

I. INTRODUCTION

Iron aluminides are considered as candidate materials for high-temperature applications due to their low cost, elevated strength to weight ratio, and excellent oxidation resistance. The oxidation resistance of these alloys relies upon the formation of a stable and protective α-Al₂O₃ scale that adheres to the metal surface and acts as a diffusion barrier for the underlying substrate against potentially hazardous corrosive environments (Prescott and Graham, 1992; Grabke, 1999). The important factors that affect the integrity of the protective oxide scale are growth stresses that develop within the scale, intrinsic to the oxidation process, and also the residual stresses that result after cooling to room temperature from the differences in thermal expansion between the metal substrate and the oxide (Tolpygo and Clarke, 1999). For this reason, much effort has been put forth in the past years to characterize the evolution of growth stresses in oxide scales during oxidation (Schumann et al., 2000; Messaoudi et al., 2000; Mennicke et al., 2001; Clarke, 2002; Eschler et al., 2004; Huntz et al., 2007). In the specific case of Al₂O₃ forming alloys, recent studies have focused on the in situ determination of growth stresses during high-temperature oxidation (above 1000 °C) of Ni-Al and Fe-Cr-Al alloys using synchrotron radiation (Specht et al., 2004; Veal et al., 2006; Reddy et al., 2007; Veal and Paulikas, 2008). However, in spite of these successful attempts to determine internal stresses in growing oxide scales, the mechanisms of strain formation during oxide growth are manifold (Evans, 1995) and not fully understood for a number of metal-oxide systems (Veal et al., 2006; Clarke, 2003; Panicaud et al., 2006).

Another important issue that affects the oxidation resistance of iron aluminides is the appearance of less protective Al₂O₃ polymorphs, generally monoclinic θ-Al₂O₃ or cubic γ-Al₂O₃, which only later transform into the stable α-Al₂O₃. These phases are formed when iron aluminides are subjected to low oxidation temperatures (below 1000 °C) and have a detrimental impact on the oxidation resistance of the alloy (Grabke, 1999; Levin and Brandon, 1998). The development of transition Al₂O₃ may also modify the stress state in the oxide layer since the transformation to α-Al₂O₃ is accompanied by a volume contraction (Rybicki and Smialek, 1989) which can induce tensile stresses into the first formed α-Al₂O₃ grains. Nevertheless, the evolution of phase composition in thermally growing alumina scales, especially in the early oxidation stages of Fe-Al alloys, remains yet to be clarified (Pötter et al., 2005).

In order to further enhance the understanding on the mechanisms of internal strain formation during oxidation, the present work aims at the study of the microstructure (in terms of chemical composition, phase development, and crystallographic texture) and the stress evolution in oxide scales forming in atmospheric air on an intermetallic Fe–26 at. % Al alloy. A low oxidation temperature (700 °C) was applied in an attempt to favor the formation of metastable Al₂O₃ polymorphs.

II. EXPERIMENTAL

The specimens used in the oxidation experiments were 8-mm-diameter disks of 1 mm thickness cut from a polycrys-
talline Fe-26 at. % Al. The as-cast samples had grain sizes of a few hundred μm. Prior to oxidation, the samples were mechanically ground and polished to a 1 μm finish and thoroughly cleaned in ethanol. All oxidation experiments were performed at 700 °C in atmospheric air at ambient pressure.

The chemical composition in the oxide scales grown on Fe-26 at. % Al after 300 min was characterized by applying X-ray photoelectron spectroscopy (XPS). XPS spectra and sputter depth profiles were taken using a monochromatic Al Ka X-ray source, step size of 0.8 eV, pass energy of 93.90 eV, 20 sweeps, and a spot size of 100 μm. The spectra were recorded within the binding energy range of 0 to 1200 eV, sputter depth profiles of the Fe 2p, Al 2p, and O 1s photo-lines were measured, and sputtering was performed with 2 keV Ar+ ions in steps of approximately 10 nm (calibrated according to a SiO2 standard). The XPS data were analyzed using the CASA-XPS software.

In order to assess the conditions for the appearance of metastable Al2O3 polymorphs, ex situ phase analyses applying grazing-incidence X-ray diffraction (XRD) at an incidence angle (ω) of 1° were carried out using a laboratory Co Ka source for samples produced after different oxidation times, ranging from 2 to 300 min at 700 °C. Under these conditions, the penetration depth is estimated to be approximately 400 nm.

Ex situ oxidation experiments for stress analyses were carried out on the beamline for energy-dispersive diffraction (EDDI) of the Helmholtz-Zentrum Berlin, situated at the Berlin synchrotron radiation facility Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung. The samples were oxidized in atmospheric air using an air-cooled resistance furnace. The time required to reach the desired oxidation temperature of 700 °C was approximately 10 min. The ED diffraction technique was applied (Genzel et al., 2007) within an energy range of 15 to 85 keV and the internal stresses in the growing oxide scale were determined using the sin2 ψ method. In contrast to time-consuming angle-dispersive diffraction with monochromatic radiation, ED diffraction uses a polychromatic X-ray beam, thus allowing for the acquisition of complete ED diffractograms at a fixed 2θ angle. This enables the determination of stress values for several diffraction lines simultaneously (Juricic et al., 2010).

In the present work the 2θ angle was set to 5°. The acquisition time for an individual ED diffractogram amounted to 5 min. The sin2 ψ measurements were performed using seven ψ tilts which resulted in a total measurement time, including sample movements, of 36 min/stress analysis. An ex situ texture analysis was also performed at the EDDI beamline on an Fe-26 at. % Al sample previously oxidized for 300 min at 700 °C. Pole-figure data were recorded for a ψ range of 0° to 75° in 5° steps and for an azimuthal ϕ range of 0° to 345° in 15° steps. Corrections of the pole-figure intensities were performed for absorption and geometrical aberrations (Welzel and Leoni, 2002) by measuring a randomly oriented W powder sample deposited on the oxidized sample. Complete pole figures and inverse pole figures were computed using the BEARTEX software, version 3.4 (Wenk et al., 1998).

III. RESULTS AND DISCUSSION

The chemical composition gradient in the scale grown on Fe-26 at. % Al after 5 h oxidation at 700 °C is presented in Fig. 1 (sputter depth values increase in the direction of the substrate). Scale thickness ranges between 80 and 100 nm and the scale appears to be formed exclusively by Al oxides except for a small concentration (lower than 10%) of Fe oxides which is restricted to the first 30 nm at the oxide outer surface. It is worth noticing that the concentration of Al2O3 in the oxide scale, approximately 35%, is well above the nominal Al content in the base material (26%). This is an indication that oxide-scale growth occurs by outward diffusion of Al3+ cations as well as by the inward diffusion of O2−, as it has been previously reported for the oxidation of other binary iron aluminides (Pöter et al., 2005).

Phase analyses by grazing-incidence XRD were performed on samples oxidized for 2, 5, 10, 30, and 300 min at 700 °C. The diffraction data obtained for oxidation times of 5, 10, and 30 min are shown in Figs. 2(a)–2(c), respectively. The clear (220) diffraction line of the substrate, which appears in some of the samples, results from the coarse-grained substrates, which were prepared from different cast ingots. In spite of the low oxidation temperature applied, the XRD data show that even at the onset of the oxidation process α-Al2O3 is the predominant oxide phase in the scale, with only minor quantities of α-Fe2O3 and metastable θ-Al2O3. θ-Al2O3 appears to vanish already after 30 min of oxidation even though the development of the stable α-Al2O3 is usually associated with oxidation temperatures of over 1000 °C (Levin and Brandon, 1998; Pöter et al., 2005). However, it has been noted that other oxides with trigonal crystal lattices, such as α-Fe2O3 and α-Cr2O3, may form at earlier stages and act as templates for the growth of α-Al2O3, thus favoring the earlier development of stable corundum at lower temperatures (Renusch et al., 1997; Asteman and Spiegel, 2008). The results suggest, therefore, that the formation of α-Al2O3 occurs not only by transformation from θ-Al2O3 but also spontaneously as a consequence of the presence of α-Fe2O3 in the oxide scale.

Experimental pole figures were determined for the (104), (110), (113), and (116) diffraction lines of the α-Al2O3 developed after 5 h oxidation at 700 °C. These data were used for calculating the orientation distribution function (ODF) and inverse pole figures. Owing to the lower volume fraction of α-Fe2O3 in the oxide scale, the only pole figure that could be measured for this phase was the one corresponding to the

Figure 1. XPS sputter depth profile in the oxide scale grown on Fe-26 at. % Al substrate at 700 °C after 5 h oxidation time.
(104) reflection, which represents the strongest diffraction line. For this reason, it was not possible to determine the ODF or inverse pole figures for α-Fe₂O₃.

The experimental pole figure measured for the (104) diffraction line of α-Al₂O₃ is presented in Fig. 3(a). The corresponding recalculated pole figure obtained from the ODF is shown in Fig. 3(b). Figure 3(c) displays the experimental pole figure measured for the (104) diffraction line of α-Fe₂O₃. The texture strength is given in terms of multiples of a random distribution (mrd). The α-Fe₂O₃ pole figure is similar to the one of α-Al₂O₃ in the sense that in both cases the maximum texture strength occurs between polar distances of 20° to 40°. This suggests that the texture formation of both oxides is equivalent and could be a consequence of α-Fe₂O₃ acting as a crystallographic template for the formation of α-Al₂O₃. This observation is in agreement with studies of the epitaxy relation between α-Fe₂O₃ films grown on α-Al₂O₃, which show that the (0001) surfaces of both phases remain parallel to each other (Wang et al., 2002; Lee et al., 2005). Furthermore, Sun et al. (2006) suggested that the (0001) plane of another trigonal structured oxide, α-Cr₂O₃, provides favorable conditions for the template growth of α-Al₂O₃. Eklund et al. (2008), while observing that this template effect is stronger for α-Al₂O₃ developing on the (10-14) of α-Cr₂O₃, also reported the growth of textured (0001) α-Al₂O₃ on α-Cr₂O₃ (0001).

The inverse pole figure of α-Al₂O₃ in the normal direction (ND) of the scale surface is plotted in Fig. 4. It can be noticed that the (0001) basal planes of the corundum structure grow with a certain preferential orientation parallel to the surface of the sample. These results are in agreement with a previous electron backscattered diffraction study which also revealed a (0001) fiber texture in the ND of thermally grown α-Al₂O₃ scales (Karadge et al., 2006). The texture strength of the oxide scale is, however, weak, thus allowing, e.g., for unrestricted \( \sin^2 \psi \) measurements. This

Figure 2. Grazing-incidence XRD patterns showing the oxide phases developed on Fe–26 at. % Al after (a) 5, (b) 10, and (c) 30 min of oxidation.

Figure 3. (a) Experimental (104) pole figure of α-Al₂O₃, (b) recalculated (104) pole figure of α-Al₂O₃, and (c) experimental (104) pole figure of α-Fe₂O₃ after 5 h oxidation of a Fe–26 at. % Al polycrystal at 700 °C. Texture strength is given in terms of mrd.
agrees with the predictions of Blachère et al. (2003) that the ion mobility inside an oxide is low for oxidation temperatures below \( T_m/2 \) (\( T_m \) is the melting point of the oxide, here 2054 °C for \( \alpha\)-Al\(_2\)O\(_3\)), causing a competitive oxide grain growth in the direction of the ion flux, i.e., parallel to the direction of the surface normal. This produces oxide scales which consist of stacks of \( \alpha\)-Al\(_2\)O\(_3\) grains without a strong crystallographic preferred orientation.

Figure 5 shows the evolution of the internal stresses in the oxide scale growing on Fe–26 at. % Al. The stresses were determined for the (012) and (104) diffraction lines. From the first stress analysis performed, at 45 min, to approximately 200 min of oxidation, the scale undergoes a continuous increase in the level of compressive stresses until a maximum average value of −630 ± 200 MPa [−720 ± 70 MPa, as determined for the (012) reflection, and −550 ± 200 MPa, as determined for the (104) reflection] is reached. The occurrence of compressive growth stresses during oxidation is attributed to the lateral growth mechanism of the oxide scale (Clarke, 2003; Rhines and Wolf, 1970). According to this model, \( \text{Al}^{+3} \) and \( \text{O}^{-2} \) diffusing in opposite directions combine to form new oxide grains along grain boundaries of the scale, which are oriented vertically to the surface. Since this new oxide is laterally constrained by the surrounding oxide grains as well as by the underlying substrate, high compressive stresses develop. After a maximum compressive stress level is reached in the scale, creep-induced stress relief begins to balance the intrinsic oxide growth stresses (Veal and Paulikas, 2008; Panicaud et al., 2006; Limarga et al., 2004), and the stress level in the oxide scale approaches a steady state condition which, in the present case, is close to −300 MPa.

The strain evolution during the first 45 min of oxidation could not be characterized because of the long measurement times, which were necessary given the reduced thickness of these oxide scales. Thus, the impact of the appearance of \( \theta\)-Al\(_2\)O\(_3\) on the growth stress level could not be directly verified. However, the results obtained here appear to be consistent with previous studies (Veal and Paulikas, 2008; Hou et al., 2007) in which it was observed that the first formed \( \alpha\)-Al\(_2\)O\(_3\) grains are under tensile stresses due to the development of metastable \( \theta\)-Al\(_2\)O\(_3\) and subsequent transformation of \( \theta\)-Al\(_2\)O\(_3\) to \( \alpha\)-Al\(_2\)O\(_3\). The extrapolation of the initial stress values (represented by the dotted line in Fig. 5) suggests the possibility of tensile stress formation during the first minutes of oxidation since it is rather unlikely that the oxide scale grows initially nearly stress-free, as the first determined stress values, ranging between −10±100 and −70±100 MPa, show. As displayed in Fig. 1(c), the \( \theta\)-\( \alpha\) transformation is completed before 30 min of oxidation time. After the metastable \( \theta\)-Al\(_2\)O\(_3\) is consumed, the compressive stress generation mechanism via new oxide growth inside the scale becomes predominant and the internal stresses change from tensile to compressive. The absence of tensile stresses in the scale during the later stages of oxidation further corroborates that metastable \( \text{Al}_2\text{O}_3 \) formation on the binary Fe–26 at. % Al alloy is restricted to the beginning of the oxidation process.

IV. CONCLUSION

The oxidation behavior of polycrystalline Fe\(_3\)Al in atmospheric air at 700 °C was studied. At this temperature, an oxide scale of approximately 80 to 100 nm forms on the metal surface. The scale is composed mostly of \( \alpha\)-Al\(_2\)O\(_3\) with minor quantities \( \alpha\)-Fe\(_2\)O\(_3\). A small amount of \( \theta\)-Al\(_2\)O\(_3\) was also shown to be present in the first minutes of oxidation. Texture analyses of the oxide scales formed after 5 h oxidation show that \( \alpha\)-Al\(_2\)O\(_3\) grows with a weak preferential orientation of the (0001) basal planes parallel to the oxidizing surface. It is also suggested that the similarities in texture between \( \alpha\)-Fe\(_2\)O\(_3\) and \( \alpha\)-Al\(_2\)O\(_3\) reflect the template effect of \( \theta\)-Al\(_2\)O\(_3\) to \( \alpha\)-Al\(_2\)O\(_3\).


