INTERNAL STRESSES AND TEXTURE OF NANO-STRUCTURED ALUMINA SCALES GROWING ON Fe3Al POLYCRYSTALS

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ABSTRACT

The evolution of internal stresses in oxide scales growing on an Fe3Al polycrystal in atmospheric air at 700°C was determined using in-situ energy-dispersive synchrotron x-ray diffraction. Texture analyses were performed ex-situ after 5h of oxidation at 700°C. Under these conditions, the oxide scale thickness, as determined by x-ray photoelectron spectroscopy, lays between 80 and 100nm. 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 -300MPa.

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 [1, 2]. Important factors that affect the integrity of the protective oxide scale are growth stresses which 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 [3]. 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 [4-10]. 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 [11-14]. 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 [15] and not fully understood for a number of metal-oxide systems [12, 16-17].

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 that 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 [2, 18]. 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 of about 5-8% [19] which can induce tensile stresses into the first formed α-
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

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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 [20].

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-26at.%Al alloy. A low oxidation temperature (700°C) was applied in an attempt to favor the formation of metastable Al₂O₃ polymorphs.

**EXPERIMENTAL PROCEDURE**

The specimens used in the oxidation experiments were 8mm diameter discs of 1mm thickness cut from a polycrystalline Fe₃Al binary alloy ingot (Fe-26at.%Al). The as-cast samples had a grain size of a few hundred μm. Prior to oxidation, the samples were mechanically ground and polished to a 1μm 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-26at.%Al after 300min was characterized by applying X-ray Photoelectron Spectroscopy (XPS). XPS spectra and sputter depth profiles were taken using a monochromatic Al Kα X-ray source, step size of 0.8eV, pass energy of 93.90eV, 20 sweeps and a spot size of 100μm. The spectra were recorded within the binding energy range of 0 to 1200eV, sputter depth profiles were measured of the Fe 2p, Al 2p and O 1s photo lines and sputtering was performed with 2keV Ar⁺ ions in steps of approximately 10nm (calibrated according to a SiO₂ standard). The XPS data were analyzed using the CasaXPS software.

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

In-situ oxidation experiments for stress analyses were carried out at the beamline for Energy-Dispersive Diffraction (EDDI) of the Helmholtz-Zentrum Berlin, situated at the Berlin synchrotron radiation facility BESSY (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 10min. The energy-dispersive (ED) diffraction technique was applied [21] within an energy range of 15 to 85keV and the internal stresses in the growing oxide scale were determined using the sin²Ψ 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 [23].
In the present work the 20-angle was set to 5°. The acquisition time for an individual ED diffractogram amounted to 5min. The sin²Ψ measurements were performed using 7 ψ-tilts which resulted in a total measurement time, including sample movements, of 36min per stress analysis. Ex-situ texture analysis was also performed at the EDDI beamline on an Fe-26at.%Al sample previously oxidized for 300min 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 [25, 26] 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 [27].

RESULTS

The chemical composition gradient in the scale grown on Fe-26at.%Al after 5h oxidation at 700°C is presented in Figure 1 (sputter depth values increase in the direction of the substrate). Scale thickness ranges between 80 and 100nm 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 30nm at the oxide outer surface. It is worth noticing that the concentration of Al³⁺ 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 alumindes [20].

![Figure 1: XPS sputter depth profile in the oxide scale grown on Fe-26at.%Al substrate at 700°C after 5h oxidation time](image)

Phase analysis by grazing-incidence XRD was performed on samples oxidized for 2, 5, 10, 30 and 300min at 700°C. The diffraction data obtained for oxidation times of 5, 10 and 30 min are shown in Figure 2 (a), (b) and (c), respectively. The clear (220) diffraction line of the substrate, which appears for 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 shows that even at the onset of the oxidation process α-Al₂O₃ is the predominant oxide
phase in the scale, with only minor quantities of $\alpha$-$\text{Fe}_2\text{O}_3$ and metastable $\theta$-$\text{Al}_2\text{O}_3$. $\theta$-$\text{Al}_2\text{O}_3$ appears to vanish already after 30 min of oxidation, even though the development of the stable $\alpha$-$\text{Al}_2\text{O}_3$ is usually associated with oxidation temperatures of over 1000°C [18, 20]. However, it has been noted that other oxides with trigonal crystal lattices, such as $\alpha$-$\text{Fe}_2\text{O}_3$ or $\text{Cr}_2\text{O}_3$, may form at earlier stages and act as templates for the growth of $\alpha$-$\text{Al}_2\text{O}_3$, thus favoring the earlier development of stable corundum at lower temperatures [22, 24]. The results suggest, therefore, that the formation of $\alpha$-$\text{Al}_2\text{O}_3$ occurs not only by transformation from $\theta$-$\text{Al}_2\text{O}_3$ but also spontaneously as a consequence of the presence of $\alpha$-$\text{Fe}_2\text{O}_3$ in the oxide scale.

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

Experimental pole figures were determined for the (104), (110), (113) and (116) diffraction lines of the $\alpha$-$\text{Al}_2\text{O}_3$ 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 $\alpha$-$\text{Fe}_2\text{O}_3$ in the oxide scale, the only pole figure that could be measured for this phase was the one corresponding to the (104) reflection, which represents the strongest diffraction line. For this reason, it was not possible to determine the ODF or inverse pole figures for $\alpha$-$\text{Fe}_2\text{O}_3$. 
The experimental pole figure measured for the (104) diffraction line of α-Al₂O₃ is presented in Figure 3(a). The correspondent re-calculated pole figure obtained from the ODF is shown in Figure 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 (m.r.d). 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 [28, 29]. Furthermore, Sun et al [30] have 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 [31], while observing that this template effect is stronger for α-Al₂O₃ developing on the (10-14) of α-Cr₂O₃, have also reported the growth of textured (0001) α-Al₂O₃ on α-Cr₂O₃ (0001).

The inverse pole figure of α-Al₂O₃ in the direction normal to the scale surface (ND) is plotted in Figure 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 (EBSD) study which also revealed a (0001) fiber texture in the ND of thermally grown α-Al₂O₃ scales [32]. The texture strength of the oxide scale is, however, weak, thus allowing e.g. for unrestricted sin²Ψ measurements. This agrees with the predictions of Blâchere et al. [33], that the ion mobility inside an oxide is low for oxidation temperatures below Tₘ/2 (Tₘ is the melting point of the oxide, here 2054°C for α-Al₂O₃), 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 α-Al₂O₃ grains without a strong crystallographic preferred orientation.

Figure 5 shows the evolution of the internal stresses in the oxide scale growing on Fe-26at.%Al. The stresses were determined for the (012) and (104) diffraction lines. From the first stress analysis performed, at 45min, to approximately 200min of oxidation, the scale undergoes a continuous increase in the level of compressive stresses until a maximum average value of -630 ± 200MPa (-720 ± 70MPa, as determined for the (012) reflection, and -550 ± 200MPa, 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 [16, 34]. According to this model, Al³⁺ and O²⁻ 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 [14, 17, 35], and the stress level in the oxide scale approaches a steady state condition which, in the present case, is close to -300MPa.
Figure 3: (a) Experimental (104) pole figure of $\alpha$-Al$_2$O$_3$, (b) recalculated (104) pole figure of $\alpha$-Al$_2$O$_3$ and (c) experimental (104) pole figure of $\alpha$-Fe$_2$O$_3$ after 5h oxidation of a Fe-26at.%Al polycrystal at 700°C. Texture strength is given in terms of multiples of random distribution (m.r.d.).

Fig. 4: ND inverse pole figure of the $\alpha$-Al$_2$O$_3$ grown on Fe-26at.%Al after 5h oxidation at 700°C. Texture strength is given in terms of multiples of random distribution (m.r.d.).

The strain evolution during the first 45min 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.
[14, 36] in which it was observed that the first formed $\alpha$-$Al_2O_3$ grains are under tensile stresses due to the development of metastable $\theta$-$Al_2O_3$ and subsequent transformation of $\theta$-$Al_2O_3$ to $\alpha$-$Al_2O_3$. The extrapolation of the initial stress values (represented by the dotted line in Figure 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 $-10 \pm 100$MPa to $-70 \pm 100$MPa, show. As displayed in Figure 1(c), the $\theta$-$\alpha$ transformation is completed before 30min of oxidation time. After the metastable $\theta$-$Al_2O_3$ 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 $Al_2O_3$ formation on the binary Fe-26at.%Al alloy is restricted to the beginning of the oxidation process.

![Figure 5: Evolution of growth stresses, determined for the (012) and (104) diffraction lines of $\alpha$-$Al_2O_3$, with increasing oxidation times at 700°C.](image)

**CONCLUSIONS**

The oxidation behavior of polycrystalline $Fe_3Al$ in atmospheric air at 700°C was studied. At this temperature, an oxide scale of approximately 80-100nm forms on the metal surface. The scale is composed mostly of $\alpha$-$Al_2O_3$ with minor quantities $\alpha$-$Fe_2O_3$. A small amount of $\theta$-$Al_2O_3$ was also shown to be present in the first minutes of oxidation. Texture analyses of the oxide scales formed after 5h oxidation show that $\alpha$-$Al_2O_3$ 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 $\alpha$-$Fe_2O_3$ and $\alpha$-$Al_2O_3$ reflect the template effect of $\alpha$-$Fe_2O_3$ for the nucleation of $\alpha$-$Al_2O_3$ at lower temperatures. In-situ stress analyses using ED synchrotron XRD showed that compressive stresses build up in the oxide scale after 45min of oxidation as a result of new oxide growth inside the scale. In the first minutes, it is believed that the stress state is governed by the transformation of metastable $\theta$-$Al_2O_3$ to $\alpha$-$Al_2O_3$. 
REFERENCES