Water vapor effect on high-temperature oxidation behavior of Fe$_3$Al intermetallics

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Abstract

Fe$_3$Al intermetallics (Fe$_3$Al, Fe$_3$Al-Zr, Fe$_3$Al-Zr,Mo and Fe$_3$Al-Zr,Mo,Nb) were oxidized at 950 °C in dry and humid (11 vol% water) synthetic air. Thermogravimetric measurements showed that the oxidation rates of the tested intermetallics were lower in humid air than in dry air (especially for Fe$_3$Al-Zr,Mo and Fe$_3$Al-Zr,Mo,Nb). The addition of small amounts of Zr, Mo or Nb improved the kinetics compared with that of the undoped Fe$_3$Al. Fe$_3$Al showed massive spallation, whereas Fe$_3$Al-Zr, Fe$_3$Al-Zr,Mo and Fe$_3$Al-Zr,Mo,Nb produced a flat, adherent oxide layer. The rapid transformation of transient alumina into alpha alumina may explain the decrease in the oxidation rate in humid air.

Keywords: intermetallic compounds, iron aluminides, water vapor, oxidation, transient alumina phases

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Intermetallic compounds [1–4], particularly iron aluminides [5–10], are resistant to oxidation, owing to the presence of a large Al ‘reservoir’ that enables the formation and maintenance of a protective alumina layer [11–15].

The addition of small amounts of alloy can significantly improve the mechanical and corrosion resistance properties. This is particularly true for reactive-element addition, whose effect on the high-temperature corrosion of alumina-forming materials was largely studied [16–27].

In many applications, humid air is corrosive [28]. The effects of water vapor on the oxidation behavior and mechanical properties of intermetallics have not been extensively studied [29–32]. Zeller et al [29] found that water vapor causes a significant increase in the oxidation kinetics accompanied by a change in the microstructure and morphology of the oxide layer in TiAl alloys. Pint et al [31] observed an increase in the level of spallation in NiAl intermetallics with increasing water vapor content, particularly if they do not contain small amounts of elements such as Y or Hf. Pérez et al [30] studied the effect of iron aluminide coatings on ferritic steels. The presence of the coating delayed the degradation of the steel by preventing the formation of Cr-containing volatile species. Similar results were obtained by Agüero et al for iron aluminide-coated ferritic steels [32] after a very prolonged exposure (32 000 h) to steam at 650 °C. According to a recent review by Saunders et al [33], water vapor strongly affects the high-temperature oxidation behavior of alumina-forming materials. Except for the paper of Regina et al [34], which deals with the effect of water on the oxidation of Fe(14–19)Al(2–5)Cr alloys in O$_2$/CO$_2$/N$_2$ atmosphere, we are not aware of any other study that deals with the effect of water vapor on iron aluminide intermetallics.

The goal of this study is to examine the effect of water vapor on the high-temperature oxidation behaviors of Fe$_3$Al intermetallic compounds. To test the effect of humidity in the
oxidizing atmosphere, a set of experiments was performed at 950 °C in synthetic air with a controlled water vapor pressure. The effect of the selected addition of Zr, Mo, Nb and Cr on the high-temperature corrosion (degradation) behavior of tested intermetallics in dry or humid air under isothermal conditions at 950 °C was examined.

2. Experimental procedure

The base materials used for the experiments were iron aluminide with the addition of supplementary elements (Cr, Zr, Mo, Nb, B and C) provided by the Military University of Technology in Warsaw (Poland). The chemical compositions of the Fe$_3$Al-modified elements are listed in table 1. The alloys were melted in a Balzers induction furnace in argon atmosphere and cast into graphite moulds (with a diameter of 25 mm and length of 500 mm). The samples were homogenized at 1100 °C for 5 h, followed by hot forging at 1100 °C and hot rolling at 650–750 °C, resulting in tapes 12 mm wide and 1 mm thick. The specimens consisted of grains with an average size of 200–250 µm. Specimens cut from the ingots were approximately 10 × 10 × 1 mm$^3$ in size. They were manually ground using SiC abrasive paper to 1200 grade. The samples were ultrasonically cleaned in ethanol, dried at room temperature, and weighed.

2.2. Water vapor experiments

For the water vapor experiments, synthetic air was enriched with 11 vol% H$_2$O; the experiments were conducted with a thermobalance (Setaram TGA 92) that was adapted for H$_2$O vapor atmosphere (figure 1). The synthetic air (carrier gas) was passed through boiling distilled water of a flow rate of approximately 50 ml min$^{-1}$. The H$_2$O fraction was controlled by bubbling synthetic air through a cooling tube maintained at a certain temperature (36 °C for 11 vol%), so that the H$_2$O partial pressure could be adjusted. The humidity content of 11 vol% was used for most ‘humid’ oxidation experiments, and this medium is called humid air thereafter. Figure 2 shows the relationship between the temperature of the cooling column and the water vapor content of air. The samples were oxidized for 24 h at 950 °C and continuously weighed. Their oxidation behavior was compared with that of the same samples oxidized in dry air.

![Figure 1. Equipment for the thermogravimetric measurements in humid atmosphere: (1) water bath thermostat, (2) gas inlet, (3) flow meter, (4) water bath/humidifier, (5) heating wire, (6) furnace, (7) thermobalance and (8) gas outlet.](image_url)

![Figure 2. Evolution of water vapor content in air as a function of cooling column temperature.](image_url)
The morphology, structure and chemistry of the oxidized specimens were investigated using a JEOL JSM-6400F scanning electron microscope (SEM) equipped with a field emission gun and an energy dispersive x-ray analyzer (EDX). The phase compositions of the produced surface oxides were identified by x-ray diffraction (XRD) using CuKα (λ = 0.154056 nm) radiation.

3. Results and discussion

3.1. Comparison of kinetics in dry and humid air

Figure 3 shows the specific mass gain as a function of oxidation time at 950 °C in humid air for Fe₃Al, Fe₃Al-Zr, Fe₃Al-Zr,Mo and Fe₃Al-Zr,Mo,Nb. The oxidation data of Fe₃Al, Fe₃Al-Zr, Fe₃Al-Zr,Mo and Fe₃Al-Zr,Mo,Nb were fitted by parabolic law except for the first 5 h of oxidation. The oxidation behavior is classified into two groups. Undoped Fe₃Al exhibits a higher weight gain and a kₚ value increase of about one order of magnitude compared with the kₚ values determined for the second group composed of Fe₃Al-Zr, Fe₃Al-Zr,Mo and Fe₃Al-Zr,Mo,Nb.

Fe₃Al-Zr appears slightly less efficient than Fe₃Al-Zr,Mo and Fe₃Al-Zr,Mo,Nb, as its weight gain and kₚ value are slightly higher than those of the two other intermetallics. Table 2 summarizes the parabolic rate constants kₚ at 950 °C for each Fe₃Al alloy.

Table 2. Parabolic rate constants obtained for the Fe₃Al alloys oxidized for 24 h at 950 °C in humid or dry synthetic air under isothermal condition.

| Alloy                | kₚ (g² cm⁻⁴ s⁻¹) | 950 °C, 24 h | dry air, 950 °C, 24 h |
|----------------------|------------------|--------------|-----------------------|
| Fe₃Al                | 2.6 × 10⁻¹⁴      |              | 3.0 × 10⁻¹⁴           |
| Fe₃Al-Zr             | 4.2 × 10⁻¹⁵      | 6.1 × 10⁻¹⁵  |                       |
| Fe₃Al-Zr,Mo          | 1.1 × 10⁻¹⁵      | 9.2 × 10⁻¹⁴  |                       |
| Fe₃Al-Zr,Mo,Nb       | 2.0 × 10⁻¹⁵      | 4.3 × 10⁻¹⁴  |                       |

Because the Mo-doped alloy exhibited a higher oxidation mass gain in dry air, but this gain became the lowest in humid air, it appears that Mo plays an important role in the oxidation behavior. As Mo is known to form hydroxide in humid atmosphere, the specific behavior of Mo-containing samples in humid air could be explained by the sufficiently high vapor pressure of molybdenum hydroxide that could cause mass loss during the oxidation.

The effect of water vapor is prominent during the first step of the oxidation. A steep weight gain curve is observed for the samples oxidized in dry air; it rapidly evolves toward a parabolic shape for humid air, whereas it transforms later when the oxidation is performed in dry air. The change in the slope of the weight gain curve is generally ascribed to the formation of transient alumina, which transforms into continuous and stable α-Al₂O₃ [35].

3.2. Surface morphologies and characteristics after oxidation in humid air

Figure 4 shows the surface morphologies of the oxide layers formed on Fe₃Al, Fe₃Al-Zr, Fe₃Al-Zr,Mo and Fe₃Al-Zr,Mo,Nb alloys at different magnifications after isothermal oxidation in humid air for 24 h at 950 °C.

![Figure 3](image-url) Comparison of isothermal oxidation kinetic curves for Fe₃Al, Fe₃Al-Zr, Fe₃Al-Zr,Mo and Fe₃Al-Zr,Mo,Nb alloys at 950 °C in dry air and humid air (11 vol% H₂O).
The oxide layer formed on the Fe₃Al alloy shows massive spallation in large sheets (figure 4(a)). The underlying metallic substrate is covered with α-Al₂O₃ nuclei and oxide imprints. The layer is composed of platelets, pores and cellular depressions (figure 4(b)). Moreover, grinding marks and cracks are visible.

A different morphology is observed in Fe₃Al-Zr. The layer is flat, uniform and spallation-free (figure 4(c)). An enhanced formation of fine oxide nodules aligned with polishing marks and accompanied by crater formation is observed at the layer surface. At the boundary regions of the oxide crater nodule, there is a radial arrangement of the
Water vapor can increase the level of the vaporization of water vapor increases the concentration of proton defects. The presence of water vapor results in the formation of the oxide layer with a structure close to that of the protective α-Al2O3 layer. Some investigators proposed that plasticity of oxide layers increases with the increased oxidation rates or improved adherence. Other investigators have proposed that plasticity of oxide layers increases with the increased oxidation rates or improved adherence.

No traces of transient alumina could be detected in our SEM observations. The presence of pores (ridge and cellular shape) in the Al2O3 layer is often described in the literature as the result of the rapid transformation of transient to alpha alumina owing to the huge volume contraction (around 14% [36]). This is confirmed by the absence of any evidence of transient alumina (needle or platelet) and by the steep kinetics that is usually proposed to result from a very rapid transformation of the initial transient alumina to α-Al2O3.

Analyses of the XRD patterns of all the specimens after oxidation at 950 °C in humid air revealed only α-Al2O3, the metallic substrate (figure 5). In air, a previous study clearly showed transient alumina morphology on the top of the alumina layers formed on Fe3Al and Fe2Al-Zr [37].

The transformation from transient alumina to α-Al2O3 appears much faster in humid air than in dry air. Similar observations were made by Buscail et al [38, 39] who noted a lower mass gain under humid conditions and a continuous layer with a structure close to that of the protective α-Al2O3. Götlind et al [40] reported that the presence of 40% water vapor in O2 increased the oxidation rate of FeCrAl steel during the first 72 h at 900 °C.

These preliminary results reveal the role played by water vapor. Data collected from the literature show that steam, or water in the gaseous state, can have various effects on the oxidation of alloys. These effects depend on the alloy under consideration, oxidation temperature, water vapor pressure and gas flow rate. Water vapor was found to affect the high-temperature oxidation of alloys in the following ways through the following mechanisms:

- The presence of water vapor results in the formation of H2–H2O in voids that facilitate a rapid inward transport of oxygen across the pores via dissociative gas transport (an oxidation–reduction process) [41, 42].
- Water vapor can affect the plasticity of oxide layers. Some investigators proposed that the plasticity of oxide layers decreases and, consequently, the spallation of layers increases [43]. Other investigators have proposed that plasticity of oxide layers increases with the increased oxidation rates or improved adherence [41, 44].
- The presence of water vapor adversely affects the selective oxidation of elements such as aluminum and chromium from iron-based alloys [45]. Water vapor also affects the selective oxidation of aluminum from TiAl [46].
- Water vapor can affect diffusion of species through oxides such as SiO2 [41] by changing the network structure [47].
- Water vapor can increase the level of the vaporization of some oxides because of the formation of hydrated species at high vapor pressures [48, 49].
- Water vapor increases the concentration of proton defects in oxide layers that can affect defect-dependent properties such as high-temperature creep and diffusion [50, 51].

The effects of water vapor observed in this study cannot be related to these proposed mechanisms. However, it was clearly observed that the kinetics rapidly transform from linear (more or less vertical) at the start of the oxidation tests to parabolic curves in the case of humid air. This
evolution was delayed for the oxidation in dry air, leading to prolonged formation of transient alumina. This observation correlates with the absence of any transient alumina in the oxide grown in humid air, whereas $\theta$-Al$_2$O$_3$ was detected after the oxidation in dry air. The ridges and pores observed in the SEM images can be related to the fast transformation from $\theta$ to $\alpha$-Al$_2$O$_3$. As suggested from the present results, the considerable acceleration of the transformation $\theta \rightarrow \alpha$ alumina in humid air could be responsible for the faster oxidation in humid air than in dry air. It is well known that transient alumina formation and/or transformation into alpha alumina is important for the high-temperature oxidation of alumina-forming alloys [52]. This result contradicts that of Götlind et al [40] who found that $\gamma$-Al$_2$O$_3$ did not transform at 900°C in O$_2$ + 40% H$_2$O, whereas it transformed in dry O$_2$. However, the comparison is difficult because Götlind et al used a FeCrAl substrate (known to form $\gamma$-Al$_2$O$_3$ and not $\theta$-Al$_2$O$_3$) like in the case of Fe$_3$Al) and the water vapor content was 40% instead of 11% used in this study. These parameters are important for the corrosion behavior and can explain the contradictory results found in the literature.

The still unanswered question is how and why the presence of water vapor can increase this transformation. Further investigations, such as, transmission electron microscopy observations and marker experiments on cross sections with concentration profiles of elements after prolonged oxidation, should be conducted to explain the growth mechanism of the alumina layer in humid air. Recent marker experiments using H$_2^{16}$O/H$_2^{18}$O [53] and $^{16}$O$_2$/$^{18}$O$_2$ [54] yielded interesting results on the growth mechanism of oxide layers in humid or dry air. Ongoing investigations on H$_2^{16}$O/H$_2^{18}$O/D$_2$O, the location of the oxygen isotopes, as well as that of deuterium in the alumina layers, should improve our understanding of the high-temperature oxidation in water vapor, which requires information on the role of OH and proton species in the growth of the alumina layer. Their location, using isotopes, could explain their effect on the transport properties in the thermally growing alumina layer. The transformation of transient phases to stable alpha alumina could then be directly related to the transport mechanism through the layer during its establishment in water vapor.

4. Conclusions

The weight gains and parabolic rate constants of the tested intermetallics were lower in air mixed with 11% H$_2$O than in dry air. The effect is dependent on the intermetallics, as the oxide layer growth rates for Fe$_3$Al and Fe$_3$Al-Zr did not appear to be strongly affected by the water vapor atmosphere in comparison with oxidation in air at the same temperature.

The presence of pores (ridge and cellular shape) in the Al$_2$O$_3$ layer, absence of transient alumina (needle or platelet) and steep kinetics at the start of the oxidation suggest a very rapid transformation of the initial transient alumina to $\alpha$-Al$_2$O$_3$.

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