HIGH-TEMPERATURE OXIDATION PROPERTIES OF IRON ALUMINIDES WITH Zr ADDITION

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Abstract

Iron aluminides are known for their excellent oxidation and corrosion resistance. If they are exposed to hostile environment, a protective Al_2O_3 layer creates on its surface. Through an addition of Zr, their high temperature mechanical properties could be enhanced, however, their oxidation resistance is also affected. A small amount of Zr enhances the high temperature oxidation resistance, but at higher concentration it creates ZrO_2 which has a detrimental effect on the oxidation behaviour.

Keywords: Intermetallics, oxidation, structure, iron aluminides

1. INTRODUCTION

Remarkable oxidation and corrosion resistance of iron aluminides makes them potential candidates to replace nickel-chromium-based stainless steels in high-temperature structural applications [1-6]. However, iron aluminides suffer also from some disadvantages, e.g. insufficient mechanical strength at elevated temperatures (over 600 °C), brittleness at room temperature and the associated poor machinability.

In the last years, considerable research effort has been devoted to an attempt to increase the high temperature mechanical properties [7-11]. It has been shown, that increase in yield stress could be achieved for example by a third element addition. A suitable method to improve the mechanical strength of the iron aluminides appears hardening by secondary phases such as carbides, nitrides, oxides or intermetallic phases. Significant increase in strength was achieved through alloying with elements involved in the formation of very hard and stable Laves phases [12-15].

Due to very limited solubility of Zr in Fe-Al, even a small addition of Zr leads to precipitation of Laves phase and/or τ_1 phase [16-18]. Presence of these phases enhances mechanical strength but however, it reduces ductility and machinability [19-22]. It has been shown, that a small amount of Zr can eliminate the Al_2O_3 scales spalling, but higher amount of Zr showed detrimental effect on high temperature oxidation resistance due to formation of ZrO_2 which disrupts the Al_2O_3 barrier protective function [20, 23-26].

In the present paper the oxidation resistance at 900 °C of Fe-30Al-xZr alloys (where x = 0.4, 0.9 and 5.2 at. %) was evaluated and compared to the results obtained for similar alloys. Also the structure of alloys after 500 exposition was studied and described.

2. EXPERIMENTAL

The chemical composition of the materials is given in **Table 1**.

Table 1 Chemical composition of investigated alloys

Alloy	Al [at. %]	Zr [at. %]	Fe [at. %]
30_0	29.3	0.4	Bal.
30_1	29.2	0.9	
30_5	30.1	5.2	

Cylindrical samples with diameter of 7 mm and height of 19 mm for testing of oxidation resistance were cut by the electro-discharge machining, their surface was subsequently manually polished by SiC paper grit 1200.

Cyclical oxidation tests were performed in an electric furnace at 900 °C in alumina crucibles. Heating and cooling between individual cycles was realized slowly in the furnace to minimize spallation of the oxide scales. The samples were weighted before tests and after 25, 50, 100, 200, 300, 400 and 500 hours. Measured weight increases were then related to the area units. The oxidation resistance was then calculated as a parabolic rate constant (k_p) according to equation (1):

$$(\Delta m/A)^2 = k_p\, t, \quad (1)$$

where Δm [mg] is a mass increase, A [cm^2] is the sample surface area, t [s] is time. The k_p values were calculated from t = 200 h.

The structure of samples in both, in the as cast state and after 500 h oxidation, was evaluated using optical microscope and scanning electron microscope equipped with an energy-dispersive detector.

3. RESULTS

3.1 Structure

The initial structure of alloys in as cast state was described in detail in [21, 22]. The as cast structure was composed of a lamellar eutectic Fe-Al/Laves phase in a Fe-Al matrix.

The structure after 500 h of oxidation at 900 °C is shown in **Fig. 1**. Long-time exposition to 900 °C led to coarsening and coagulation of LP, a part of LP transformed to τ_1 phase according to equilibrium Fe-Al-Zr diagram [16, 17]. It is obvious, that preferential selective oxidation occurs in Zr-rich Laves phase (bright areas in SEM images). In both, OM and SEM images, the depth of oxidation ingress is visible; the depth grows with Zr content.

In the case of 30_5 alloy four different areas are clearly visible (see **Fig. 2**). Area I is composed of oxides (Fe_2O_3, Al_2O_3 and ZrO_2) and shows the depth of oxide penetration. Area II is composed of Fe-Al and shows the depth from which Zr atom diffused into the oxide layer. Two-phase area III is composed of Fe-Al and Laves phase. Quantitative EDS analysis showed lower Al-concentration compared to the three phase IV area. Lower Al content could be explained through the Al-diffusion into the oxide layer similarly as Zr-absence in area II. The difference in Al and Zr diffusion depths corresponds to their different atom diameter.

3.2 Oxidation kinetics

Table 2 Parabolic rate constants

Alloy	k_p (g^2 cm^{-4} s^{-1}), 900 °C
30_0 (Fe-29.3Al-0.4Zr)	6.4 x 10^{-13}
30_1 (Fe-29.2Al-0.9Zr)	5.8 x 10^{-13}
30_5 (Fe-30.1Al-5.2Zr)	4.1 x 10^{-11}
Fe-20Al-0.1Zr[a]	9 x 10^{-14} [20]
Fe-32Al-0.8Zr[a]	4 x 10^{-13} [20]
Fe-25Al[a]	1.0 x 10^{-13} [27]

The calculated parabolic mass constants were calculated for a time interval from 200 to 500 hours and are summarized in **Table 2**. For comparison, in the table are also listened values from [20, 27]. It is obvious, that alloys with lower Zr content show very low values of k_p, while increase in Zr concentration leads to considerable increase in k_p, what indicates its detrimental effect on the high temperature oxidation resistance. From the k values it is obvious, that the oxidation resistance grows also with the Al content.

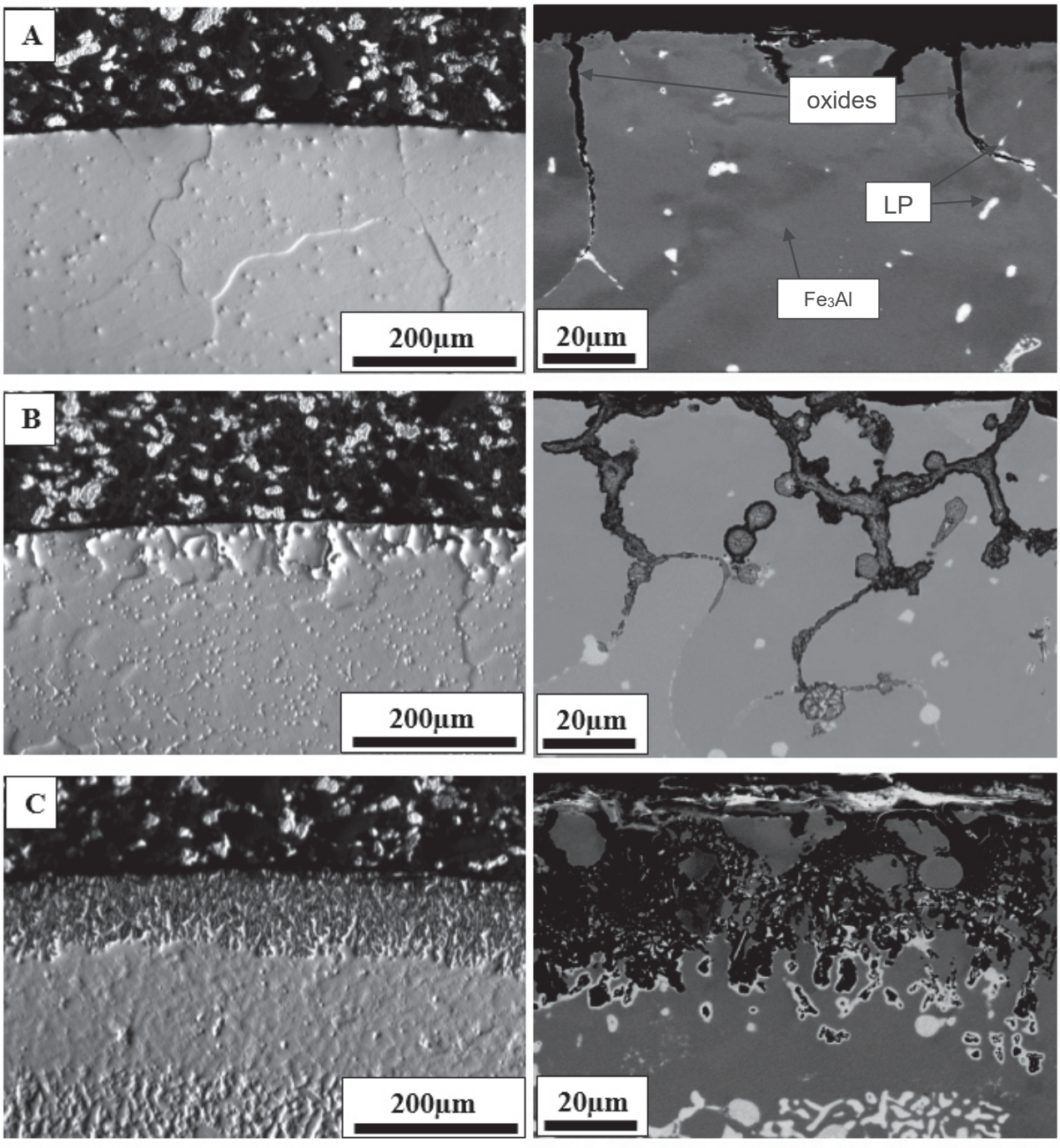

Fig. 1 Structure of samples oxidized at 900 °C for 500 h. In the left column are images taken by optical microscope, on the right side are SEM images taken in Z-contrast. A) 30_0 alloy; B) 30_1 alloy; C) 30_5 alloy. From the images the ingress of oxidation into the alloys is obvious. The oxidation affects preferentially Zr-containing Laves phase (bright phase in SEM). The depth oxidation ingress grows with Zr content

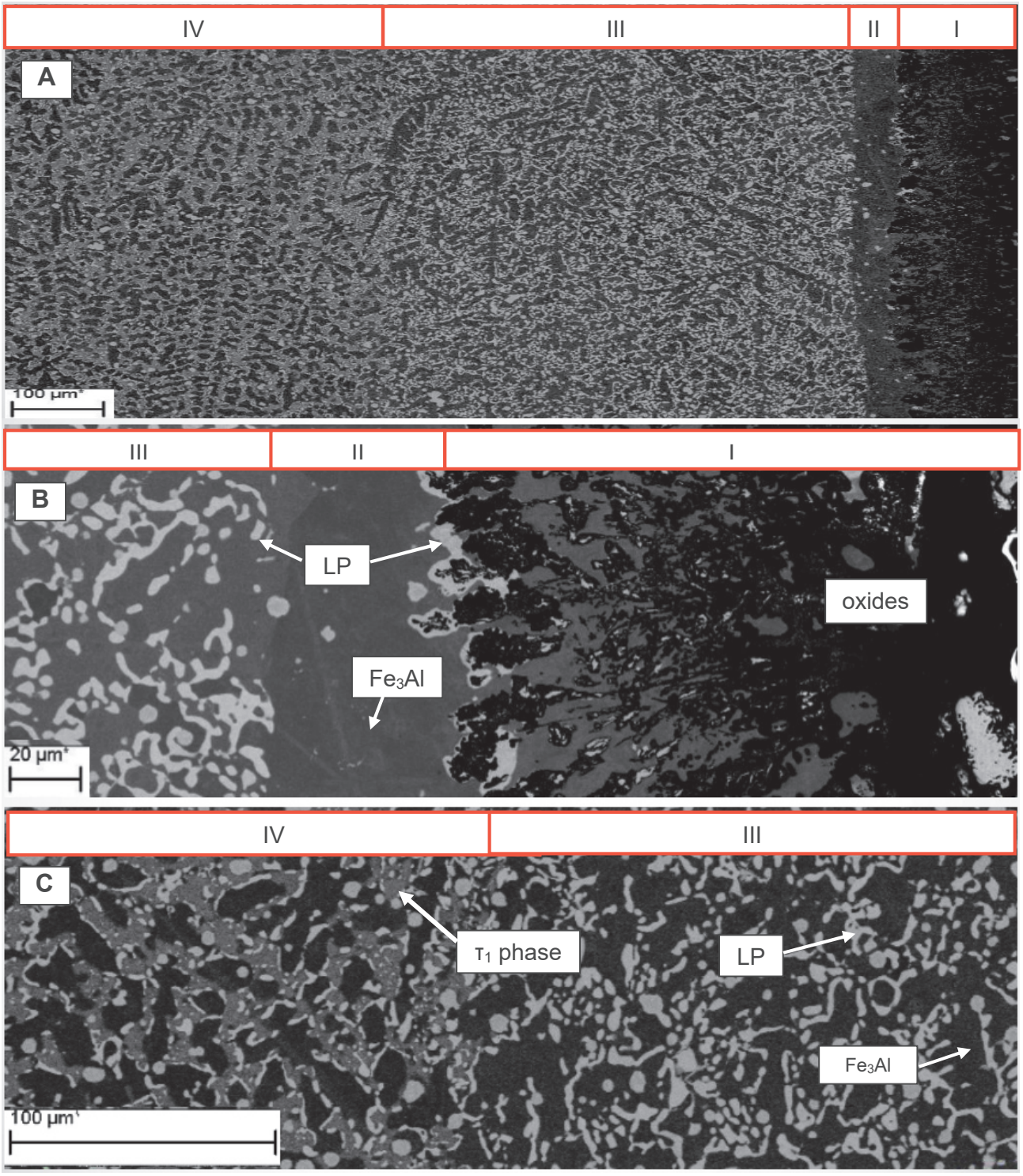

Fig. 2 Structure of 30_5 alloy after 500 h at 900 °C
A) Four areas are marked: I. oxidic layer Al_2O_3 + ZrO_2; II. Fe-Al; III. Fe-Al + LP; IV. Fe-Al + LP + τ_1
B) a detail of I/II and II/III boundary
C) Detail of III/IV boundary

CONCLUSION

After oxidation at 900 °C the inner structure is three-phase. In the Fe-Al matrix occur Laves phase and τ_1 phase.

With increasing amount of Zr grows the depth of oxidation ingress into the material. The Zr containing Laves phase is oxidized preferentially.

Near the sample surface, four areas were observed. Under the top oxide layer there is Fe-Al area. Then follows a two phase area Fe-Al + LP with lower Al content compared to the inner three phase material where FeAl + LP + τ_1 phases were identified. Absence of Zr in II-zone and decrease of Al in III-zone could be explained through the diffusion of Zr and Al atoms to the surface to form the oxides.

During the oxidation Al_2O_3 oxide layer forms on the surface. With increasing Zr concentration ZrO_2 appears in the oxide layer. The presence of ZrO_2 in low concentration enhances the Al_2O_3 adhesion, however, in higher amount disrupts its protective/barrier effect and dramatically decreases the high temperature oxidation resistance.

Parabolic rate constants were calculated. While increase of Zr content from 0.4 to 0.9 led to insignificant change in k_p, the 30_5 alloy shows nearly two orders of magnitude higher k_p value what indicates a sharp drop in oxidation resistance.

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