

INTERNAL OXIDATION OF Fe_3Al DURING HIGH TEMPERATURE OXIDATION^①

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ABSTRACT The oxidation behavior of Fe_3Al at 1 000 °C in air was studied by thermobalance, scanning electron microscope (SEM) and X-ray diffraction (XRD). It was found that the oxidation kinetics approximately follows the parabolic law; the oxide scale consists of Al_2O_3 and a little amount of Fe_2O_3 ; and there occurs transgranular internal oxidation. Based on the analyses of the oxide scale and the matrix, an internal oxidation model was proposed, which considers the effect of the long-range ordered structure of Fe_3Al on its high temperature oxidation. The long-range ordered structure reduces the activity of Al in Fe_3Al , thus reducing the diffusion coefficient of Al in the matrix. Consequently, in the oxidation process, the matrix surface will be seriously depleted in Al and then there occurs internal oxidation.

Key words Fe_3Al oxidation internal oxidation corrosion

1 INTRODUCTION

The high-temperature oxidation behavior of the intermetallics Fe_3Al has drawn more and more attention. It is generally thought that the oxidation mass gain of Fe_3Al at high temperatures is small, but the adhesion of the oxide scale is poor, thus the oxide scale shows a serious crack and massive spallation in the cooling process^[1, 2]. Therefore, the previous work focused on improving its high-temperature oxidation resistance by alloying^[3], and no reports concerning its internal oxidation can be found. However, the internal oxidation not only affects the adhesion of the scale and the resistance to oxidation of the alloy, but seriously deteriorates the high-temperature mechanical properties of the alloy.

There are wide differences between different literatures^[4-7] about the minimum aluminum content necessary for the formation of Al_2O_3 external oxide scale in the Fe-Al alloy at 1 000 °C. Tomaszewicz *et al*^[5] reported that

9.84% Al (mole fraction) is enough to form protective external Al_2O_3 oxide scale, Sykos *et al*^[4] claimed that the minimum aluminum content is 11.69% (mole fraction) for the formation of protective external oxide scale of Al_2O_3 , Nakayama^[6] indicated that there still exists a large amount of $\alpha\text{-Fe}_2\text{O}_3$ when the aluminum content is 17% (mole fraction), and Kynnikov *et al*^[7] even gave a minimum aluminum content high up to 30% (mole fraction).

Following the oxidation behaviour of Fe_3Al at 1 000 °C in air^[2, 3], it can be seen that the aluminum content in Fe_3Al is as high as 28% (mole fraction), but the oxide scale is not single phase, it consists of Al_2O_3 and a little amount of Fe_2O_3 . In our study, we also found the internal oxidation phenomenon in Fe_3Al as being reported in this paper.

2 EXPERIMENTAL

The test Fe_3Al alloy was melted in vacuum

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and drop cast. After a homogenization treatment of 1 000 °C, 5 h, 1 mm × 10 mm × 20 mm slices were prepared. The specimens were ground to 1 000[#] abrasive paper, cleaned and dried. The analytical chemical composition of the alloy is Fe-27.8% (mole fraction).

The continuous oxidation test (1 000 °C, 10⁵ Pa) was carried out on a SETARAM TG85 thermobalance. The morphologies, compositions and structures of the oxide scale and the internal oxides were analysed by SEM, EDX and XRD.

3 EXPERIMENTAL RESULTS

It can be seen from Fig. 1 that the oxidation kinetics of Fe₃Al at 1 000 °C in air shows an obvious parabolic change. XRD analysis indicated that the oxide scale after oxidation at 1 000 °C for 100 h consists of Al₂O₃ and a little Fe₂O₃ (Fig. 2), which is consistent with Ref. [3]. The SEM observations indicate that the oxide scale seriously cracks and spalls off (Fig. 3(a)) and the matrix under the oxide scale forms a concave-convex structure. EDX analyses demonstrate that the oxide scale contains a little Fe and the matrix is depleted in Al (Table 1). The convex surface of the matrix contacts with the oxide scale is relatively rich in Al while the concave surface is very depleted in Al. The internal oxidation occurs at the convex points (Fig. 3(b)) and the internal oxides extend into the matrix and

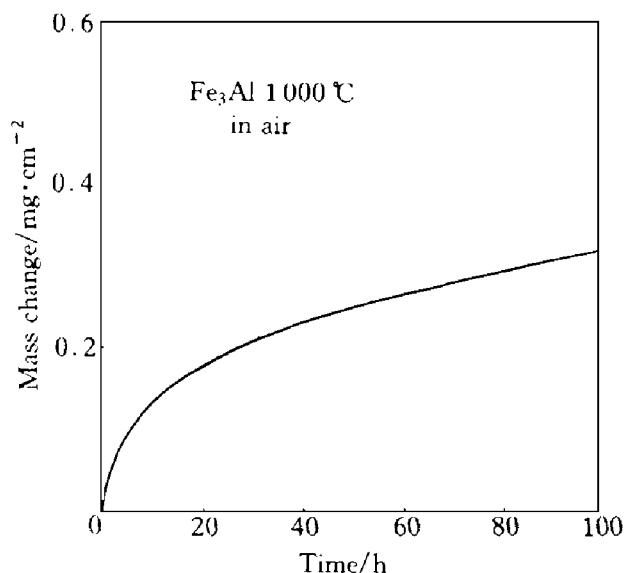


Fig. 1 Oxidation kinetics of Fe₃Al at 1 000 °C in air

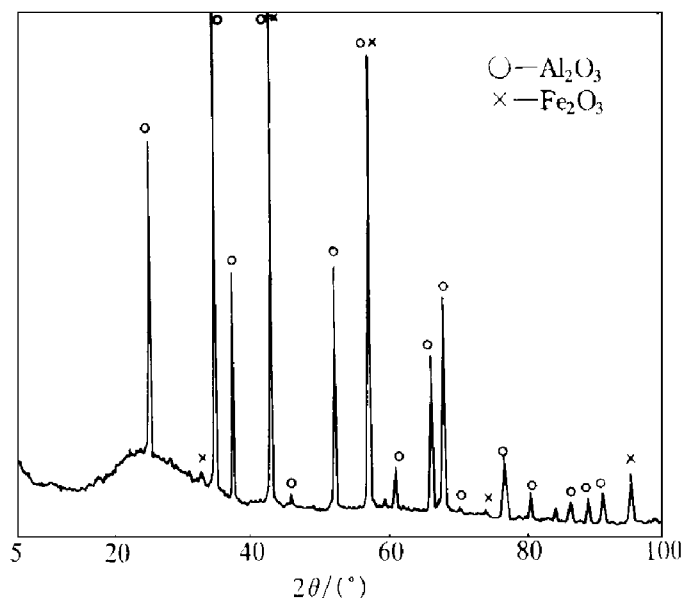


Fig. 2 XRD pattern of oxide scale on Fe₃Al after 1 000 °C, 100 h oxidation

Table 1 EDX analyses of Fe₃Al after 1 000 °C, 100 h oxidation (mole percent)

Location	Al	Fe
Oxide scale	98.65	1.35
Convex points	21.20	78.80
Concave points	6.60	95.40
Internal oxides	99.71	0.29

produce cavities around them.

4 DISCUSSION

The above experimental results show that no single Al₂O₃ oxide scale is formed at 1 000 °C in air, which indicated that although the Al content is high in Fe₃Al, the activity of Al, a_{Al} , is relatively low; the matrix/oxide scale interface is seriously depleted in Al and rich in Fe, which indicates that the diffusion of Al is slow.

The Fe₃Al intermetallics has a long-range ordered structure, which generally greatly deviated from the ideal solid solution. Stener *et al*^[8] and Eldridge *et al*^[9] indicated that the activities of the constituents in the ordered structures display great negative deviations. Fig. 4 shows the change of a_{Al} with Al content in the Fe-Al alloy. It can be seen that the actual a_{Al} shows a large negative deviation from the disordered structure.

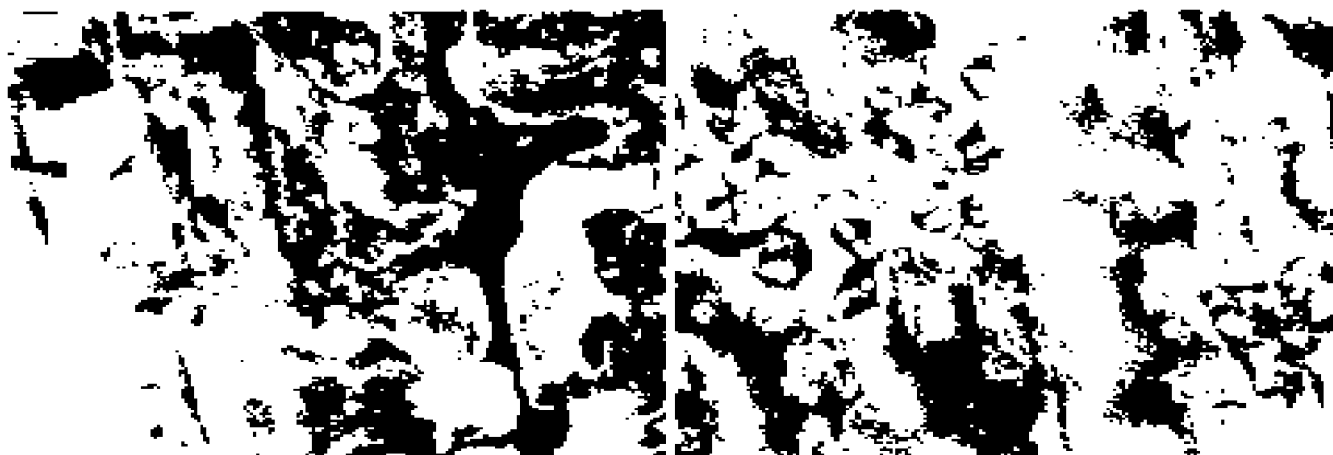


Fig. 3 Morphologies of oxide scale (a) and matrix (b) after 1000 °C, 100 h oxidation

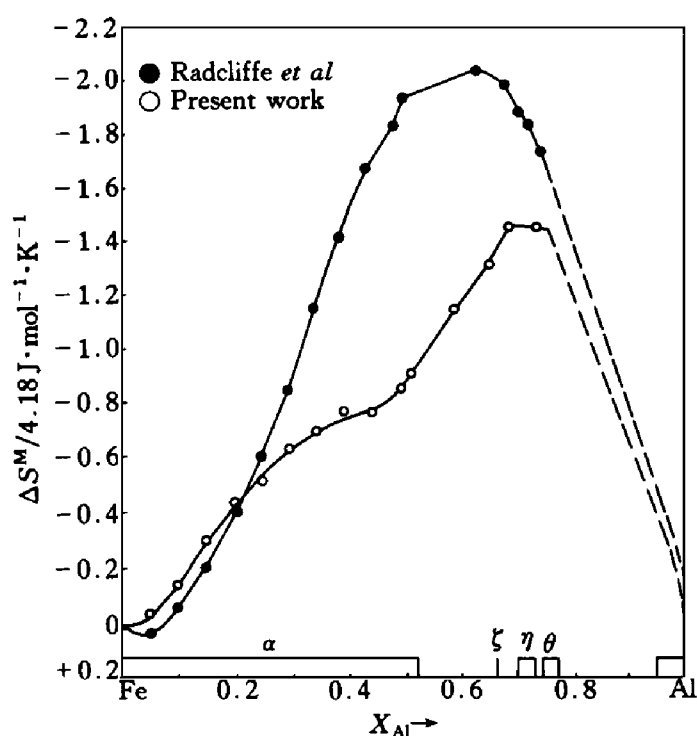


Fig. 4 Change of mixing entropy of Fe-Al alloy with Al content^[9]

From the point of view of thermodynamics, this kind of activity reduction is not very important for common metals and alloys, because in almost all cases, the oxygen activity at the oxide/metal or oxide/gas interface is large enough to make the aluminum oxidize to form stable Al_2O_3 . However, a minimum flux for the Al atoms to diffuse to the surface must be ensured so as to form and maintain an integrated and stable Al_2O_3 scale. The ordered structure has great

influence on diffusion^[10] and this kind of influence can be reflected through the self-diffusion coefficient^[11] as

$$D_i^I = D_i^* \left[1 + \frac{\partial \ln \gamma_i}{\partial \ln N_i} \right]$$

where D_i^* , γ_i and N_i are the tracing diffusion coefficient, activity coefficient and mole fraction of constituent i , respectively. Therefore, the negative deviation of the activity is reflected by the decrease of the diffusion coefficients of the solvent in the matrix.

Based on the experimental results and the above analyses, a mechanism of internal oxidation of Fe_3Al at 1000 °C in air is proposed, as shown in Fig. 5. Because the activity of Al in the alloy is relatively small and cannot reach the critical value for the formation of single Al_2O_3 external scale. Therefore, although the aluminum selectively oxidizes to form the Al_2O_3 scale, there is still a little Fe_2O_3 . Because the oxidation temperature is high, the selective oxidation rate is big. The ordered structure impedes the diffusion of Al in the matrix to the oxide/matrix interface, the depletion of Al in the matrix beneath the oxide scale is gradually accelerated (Fig. 5 (a)). Because the grain boundaries are rapid diffusion paths, the vacancies aggregate at the oxide scale/matrix interface to form cavities (Fig. 5 (b)). The cavity surface (concave points) is rich in Fe, while the matrix surface (convex points) in contact with the oxide scale is relatively rich in Al, therefore, the internal

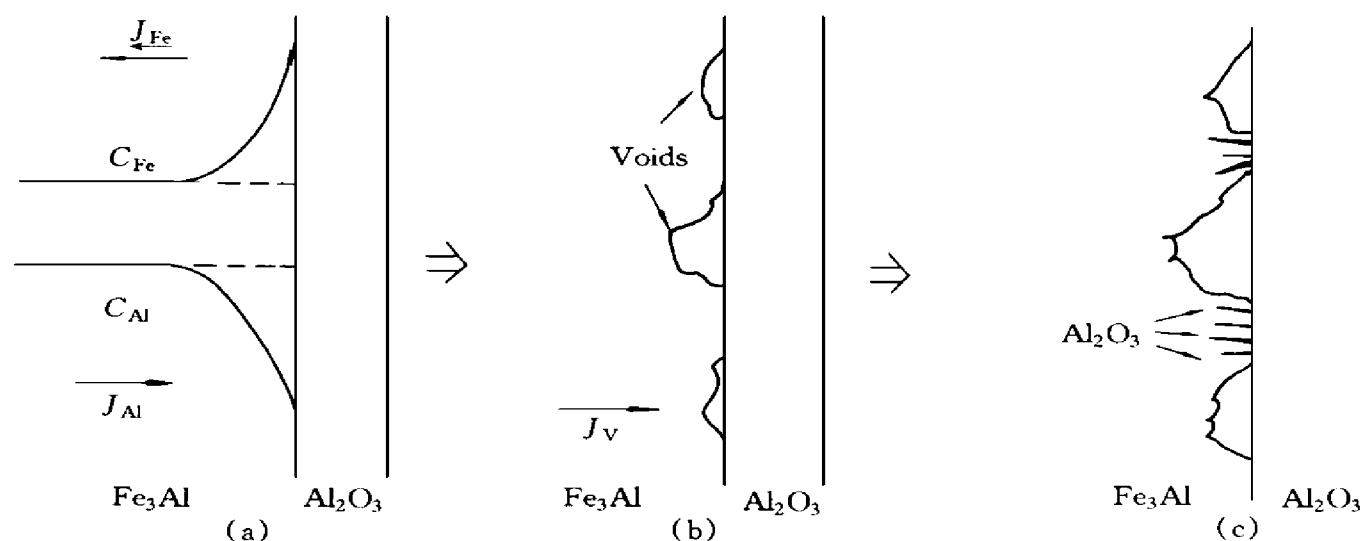


Fig. 5 Schematic diagram of internal oxidation of FeAl at 1 000 °C in air

oxidation is selective to occur at the convex points when the oxygen atoms are transferred through the oxide scale to the oxide scale/matrix interface.

5 CONCLUSIONS

(1) When Fe₃Al is oxidized at 1 000 °C in air, its oxidation kinetics approximately obeys the parabolic law. Due to the effect of the ordered structure of the intermetallics, the activity of Al in the alloy is relatively low, therefore no exclusive Al₂O₃ scale is formed, but an oxide scale mainly of Al₂O₃ with a little Fe₂O₃ is formed.

(2) When Fe₃Al is oxidized at 1 000 °C in air, there occurs transgranular internal oxidation, which is because the ordered structure of the alloy decreases the diffusion rate of Al, thus causing the depletion of Al at the oxide scale/matrix interface.

REFERENCES

- 1 Devan J H *et al.* Corrosion Science, 1993, 35: 1065 – 1069.
- 2 Wang Yonggang, He Yedong and Ma Tiejun *et al.* Ordnance Material Science and Engineering, (in Chinese), 1995, 18(6): 15– 18.
- 3 Sun Chao, Guo Jianting and Wang Shuhe *et al.* Corrosion Science and Protection Technology, (in Chinese), 1993, 2(5): 1093– 113.
- 4 Sykos C and Bampfylde J W. J Iron Steel Inst Adv Copy, 1934, 12(1): 22– 26.
- 5 Tomaszewicz P and Wallwork G R. Rev High Temp Mater, 1978, 4(1): 75– 105.
- 6 Nakayama T. Report of Castings Research Laboratory, Waseda University, 1958, 9: 71.
- 7 Kynikov B S *et al.* Protection Met, 1981, 17: 290 – 296.
- 8 Stener A and Komarek K L. Trans Met Soc AIME, 1964, 230: 786– 791.
- 9 Eldridge J, Komarek K L. Trans Met Soc AIME, 1964, 230: 226– 231.
- 10 Larikov L N *et al.* In: Diffusion Process in Ordered Alloys. New Delhi: Oxonian Press Pvt Ltd, 1981: 144.
- 11 Maning J R. In: Diffusion Kinetics for Atoms in Crystals. Princeton: D Van Nostron Co Inc, 1968: 44.

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