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Oxidation behavior of FeAl alloys with and without titanium

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The influence of Ti addition on the high temperature oxidation behavior of FeAl intermetallic alloys in air at 1000°C and 1100°C has been investigated. The oxidation kinetics of FeAl alloys was examined by the weight gain method and oxide products were examined by XRD, SEM, EDS and EPMA. The results showed that the oxidation kinetic curves of both Ti-doped and binary Fe-36.5Al alloys could be described as different parabolas that followed the formula: $(\Delta W/S)^2 = K_p t + C$. The parabolic rate constant, K_p values are approximately 2.4 and 3.3 mg^2 cm^{-4} h^{-1} for Fe-36.5Al alloy and about 1.3 and 2.0 mg^2 cm^{-4} h^{-1} for Fe-36.5Al-2Ti alloy when oxidizing at 1000°C and 1100°C respectively. The difference between Fe-36.5Al and Fe-36.5Al-2Ti alloy is not only in the surface morphology but also in the phase components. In the surface there is only α-Al$_2$O$_3$ oxide for Fe-36.5Al alloy while there are α-Al$_2$O$_3$ and TiO oxides for Fe-36.5Al-2Ti alloy. The effects of Ti addition on the oxidation resistance of FeAl alloy were addressed based on the microstructural evidence.

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1. Introduction

Intermetallic FeAl alloy is considered as a potential structural material for use at high temperature. Along with a low cost, FeAl alloys posses reasonably high specific modulus, strength-to-weight ratio, excellent oxidation, sulfidation and other corrosion resistance [1–4]. These characteristics make FeAl alloy an attractive candidate for high temperature application in harsh environments. Binary FeAl alloy has a B2 crystal structure which exists over a wide range of compositions, from about 36at.%Al to 50at.%Al at room temperature and maintains its B2 structure to its melting point [5]. These characteristics allow considerable solubility for third element additions and offer a potential of producing an acceptable material by alloying. However, different alloying elements will play different roles in the oxidation resistance of FeAl alloy. The investigations on the effect of some alloying elements, such as Hf, Zr, Y, Si, B, on the oxidation behavior of FeAl alloy have been reported by some researchers [6, 7], but some of other elements which have beneficial effects on improving the mechanical properties of FeAl alloys have not been reported. (Although it was reported that cyclic oxidation screening studies had been performed on some of Fe-40Al-5X and Fe-45Al-5X alloys at 1200°C, where $X =$ Ti, Cr, Co, Ni, Zr, Nb, Mo, Ta, W or Re, the experimental data have not been open published so far [6].) In our laboratory, it was found that FeAl alloy containing titanium exhibits superplasticity phenomenon [8–10]. This suggests that titanium can improve the high temperature mechanical properties of FeAl alloys. In the present investigation the effect of titanium alloying element on the oxidation behavior of FeAl alloys at high temperature has been carried out.

2. Experimental

The Fe-36.5Al and Fe-36.5Al-2Ti (atomic volume throughout) alloys were prepared by arc melting under argon using pure iron (99.0%), pure aluminum (99.99%) and pure titanium (99.9%). The alloy buttons were remelted three times to improve their homogeneity. After homogenizing for 24 hours at 1000°C, these buttons were clad in a stainless sheet and hot rolled by about 50–60% reductions at 1050–950°C. Oxidation specimens with the size of space 10.0 × 10.0 × 2.0 mm were cut from these bars using a spark machine, and then polished to a 600 grade emery paper finish. The static oxidation was performed in a tube furnace at 1000 and 1100°C in air for different times and specimens were then weighed. Thermogravimetry measurements were conducted to study the oxidation kinetics. The weight gains of the oxidized specimens were measured in an electronic balance with an accuracy of ±0.1 mg. After the static oxidation, the oxidized surfaces were examined in a HITACHI S-520 scanning electron microscope (SEM) with energy dispersive spectrum (EDS) operated at 20 kV and a D/MAX-IIIA X-ray diffractometer (XRD). Electron probe microanalysis (EPMA) was used to examine the distribution of some elements across the oxide and substrate interface in oxidized specimens using the JEOL Superprobe 733.

3. Results and discussion

3.1. Oxidation kinetics

Specific weight change versus time curves of FeAl alloys exposed at 1000°C and 1100°C, respectively, are shown in Fig. 1. From the figure, it is found that the weight gain of Fe-36.5Al alloy is significantly higher than that of Fe-36.5Al-2Ti alloy at the same temperature. The fitting curves of these two plots of weight gain versus time followed the law described by the parabolic equation:

$$(\Delta W/S)^2 = K_p t + \mathrm{C} \qquad (1)$$

where K_p is the parabolic rate constant; ΔW is the weight change; S is the total surface area, t is the exposure time and C is a constant. The relation shows that an oxide film with protective effect has formed on the surface of FeAl alloys. The oxidizing rate is determined by the growth rate of oxide film. When specimens were exposed at 1000°C, the K_p values of Fe-36.5Al and Fe-36.5Al-2Ti alloys are 2.4, 1.3 mg^2 cm^{-4} h^{-1}, respectively. When specimens were exposed at 1100°C, the K_p values of Fe-36.5Al and Fe-36.5Al-2Ti alloys are 3.3 and 2.0 mg^2 cm^{-4} h^{-1}. The K_p value of Fe-36.5Al alloy is much higher than that of Fe-36.5Al-2Ti alloy at the same experimental temperature. The K_p values show that the oxide film on the surface of Fe-36.5Al-2Ti alloy has a better protective effect than that of Fe-36.5Al alloy. So it can be thought that Ti addition has a beneficial effect on improving the oxidation resistance of FeAl alloy.

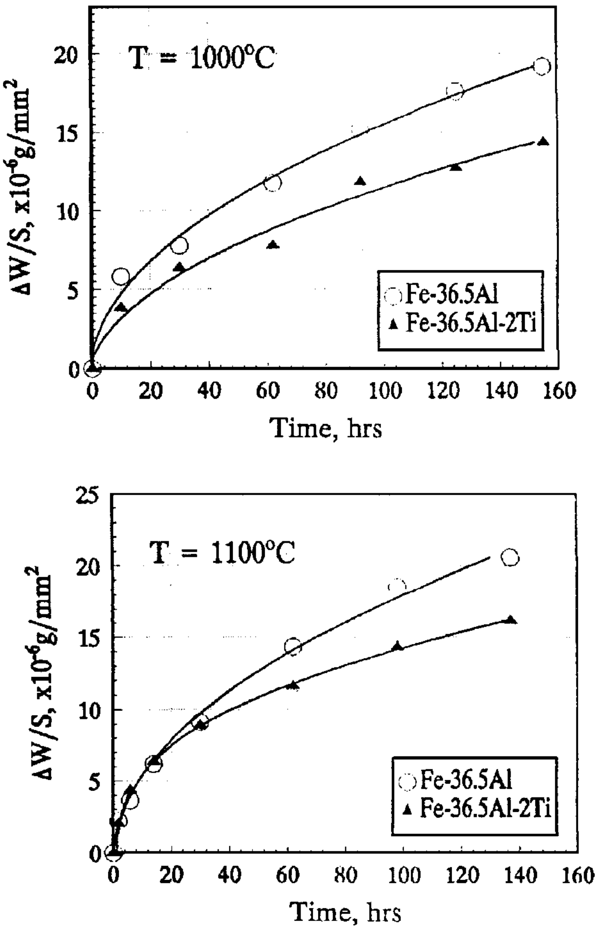


Figure 1 Oxidation kinetic of FeAl alloys at 1000°C and 1100°C.

3.2. Oxide products

Fig. 2 shows a typical X-ray diffraction spectrum of Fe-36.5Al-2Ti alloy that oxidized at 1100°C for 137 hours. From the spectrum it can be found that there are two phases, α-Al_2O_3 and TiO on the surface of oxidized Fe-36.5Al-2Ti alloy. The distance of diffraction planes, d values and corresponding diffraction plane indices of these two oxides are listed in Table I. The resultant enthalpies, ΔH of α-Al_2O_3, TiO and FeO are 266.8, 246.3 and 126.5 (×4, 184J) respectively [11]. Among these data, ΔH of α-Al_2O_3 and ΔH of TiO is approximate, which suggests that on the surface, both α-Al_2O_3 and TiO formed preferentially for Fe-36.5Al-2Ti alloys while only α-Al_2O_3 oxide formed preferentially for Fe-36.5Al alloy.

3.3. Surface morphology

The surface morphology of the FeAl alloy varied considerably depending on the alloy compositions. Both tested FeAl alloys show a little powder spallation after about 130–140 hours exposure at 1000°C or 1100°C. Surface oxide morphology of two FeAl alloys after 137 hours exposure at 1100°C are shown in Fig. 3. The surfaces consist of white and dark parts. The compositions of them measured by EDS are listed in Table II. It can be found that the white part is Al_2O_3 phase and the dark part is the phase of base alloy. It is also shown that in Fe-36.5Al alloy the size of Al_2O_3 oxide scale are much finer than that in Fe-36.5Al-2Ti alloy. The fact that oxide surface of Fe-36.5Al is much rough shows its characteristics of repeated oxidation. It is also found that oxide scales in the Fe-36.5Al-2Ti alloy are more compact than that in the Fe-36.5Al alloy. Because an important factor that determines the growth rate of Al_2O_3 film is the diffusive rate of oxygen into substrate along the boundary of Al_2O_3 [12], the fine Al_2O_3 scales no doubt accelerate the diffusion rate and results in the fast growth of Al_2O_3 film.

Fig. 4 shows EPMA spectra of the transverse sections in the oxide layer for FeAl alloys. Both for Fe-36.5Al and Fe-36.5Al-2Ti alloys the outer layer is Al rich and Fe depleted while the inner layer is Al depleted. The Ti is rich in the outer layer and depleted in the inner layer of the Fe-36.5Al-2Ti alloy. However, the oxygen is concentrated in the outer layer of the FeAl alloys.

As the Al_2O_3 film is a very good barrier for further oxidation and has a good chemical stability, it

TABLE I The measured *d* values and corresponding values of oxides from JPDCF

Measured	*d*	5.36	2.58	2.40	2.10	2.06	1.76	1.69	1.61	1.52	1.45	1.41	1.38	1.24	1.19
α-Al_2O_3	*d*	3.48	2.55	2.38	2.09		1.74		1.60	1.51		1.40	1.37	1.24	1.19
	hkl	012	104	110	113		024		116	122		124	030	1.0.10	220
TiO	*d*			2.39	2.10	2.07	1.76	1.69		1.52	1.46			1.23	1.20
	hkl			$1\bar{2}1$	220	$002,2\bar{4}0$	$3\bar{1}\bar{1}$	$3\bar{3}1$		$042,2\bar{6}0$	$4\bar{2}0,2\bar{4}2$			$2\bar{4}2,420$	$4\bar{2}2$

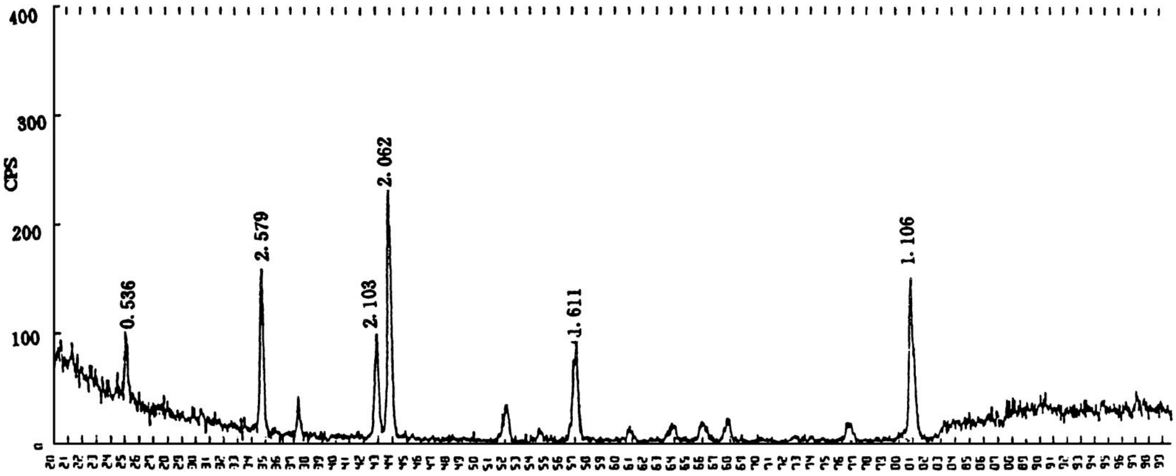
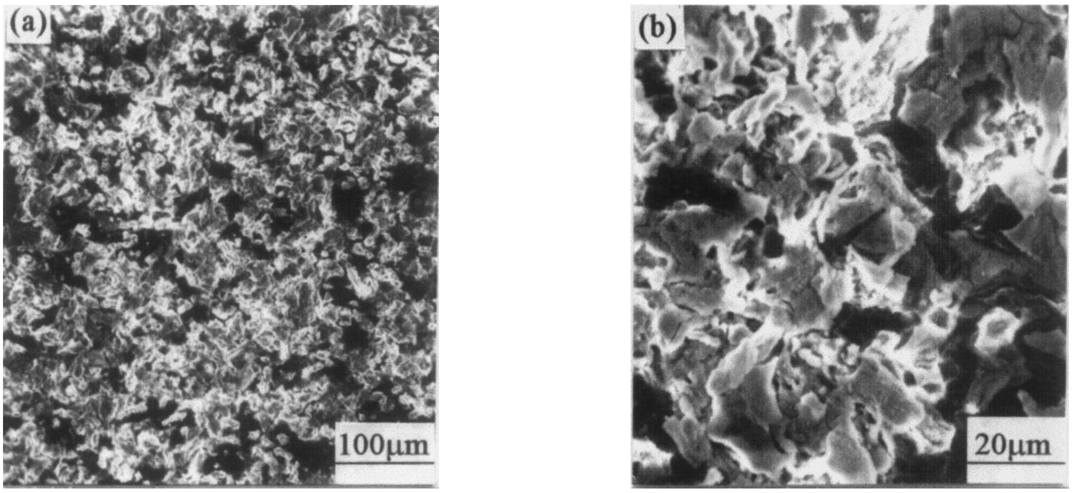
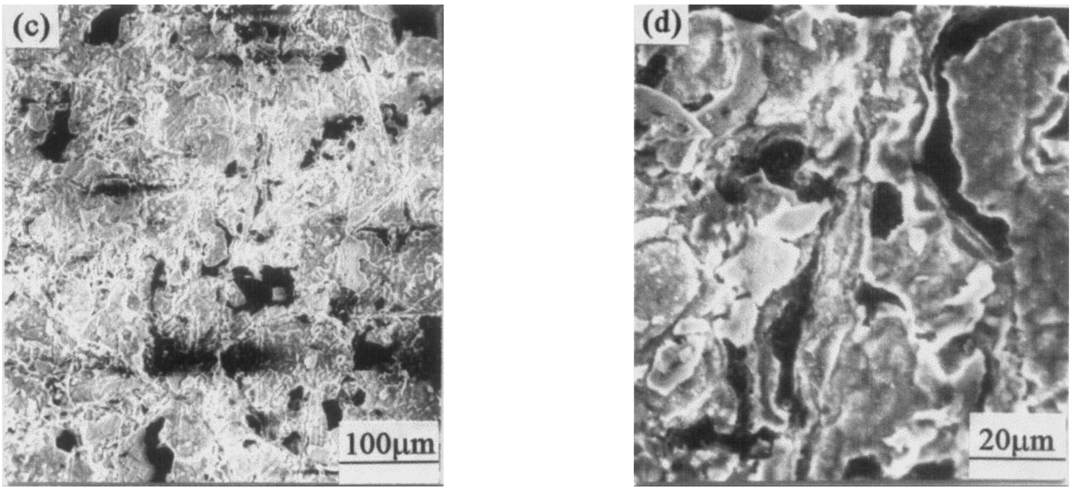


Figure 2 An X-ray diffraction spectrum of oxidation products on the surface of Fe-36.5Al-2Ti alloy after total 137 hours exposure at 1100°C.



Fe-36.5Al alloy

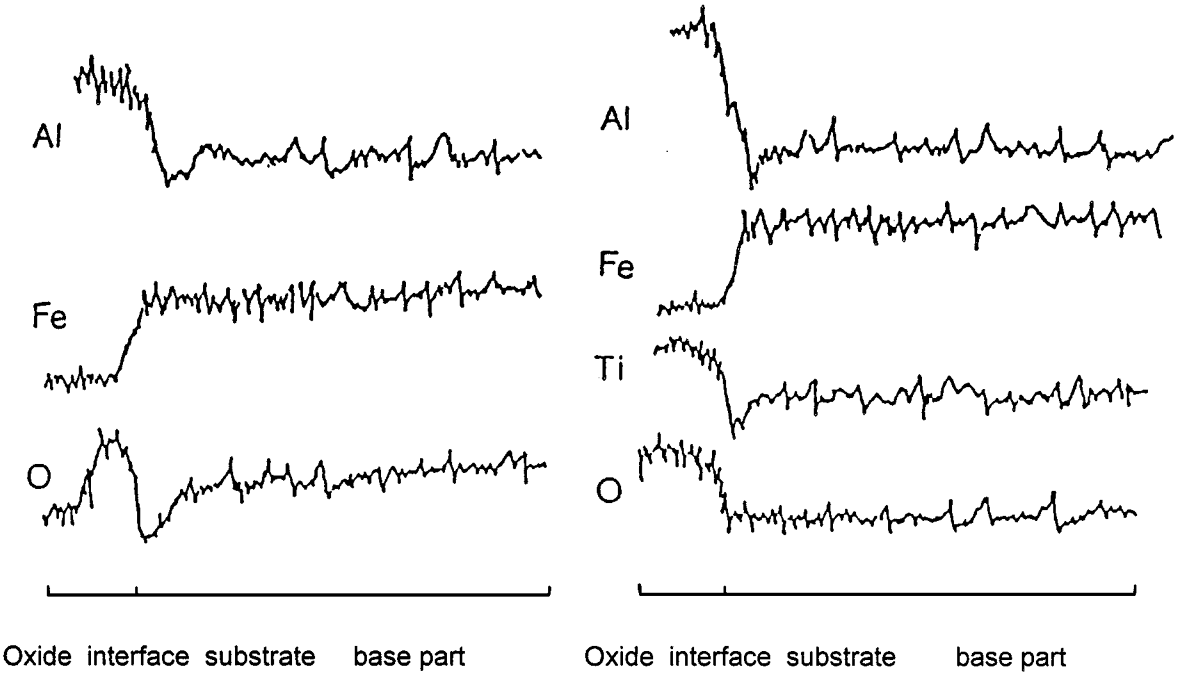


Fe-36.5Al-2Ti alloy

Figure 3 Surface morphology of FeAl alloys after 137 hours oxidation at 1100°C.

TABLE II Microanalysis of metallic elements (at.%) in FeAl alloy after 137 hours oxidation at 1100°C

	surface			white phase			dark phase		
Alloy	Fe	Al	Ti	Fe	Al	Ti	Fe	Al	Ti
Fe-36.5Al	43.58	56.42		6.93	93.07		65.27	34.73	
Fe-36.5Al-2Ti	29.51	69.35	1.14	5.74	97.11	0.22	65.40	32.37	2.24



(a) Fe-36.5Al alloy; (b) Fe-36.5Al-2Ti alloy

Figure 4 EPMA line profiles of FeAl alloys after 137 hours oxidation at 1100°C.

formed on the surface of FeAl alloys will result in their having excellent oxidation resistance at high temperature. α-Al_2O_3, however, may mechanically crack and spall under thermal or growth stresses. Therefore, restraining the spallation tendency of α-Al_2O_3 scale is the key task to increasing the resistance against oxidation [7]. The general mechanism for scale spallation involves the stress development and stress relief in the oxide film. The stresses in an oxide scale mainly include growth stress and thermal stress. The stress relief can be achieved by plastic deformation of the substrates or the oxide film, or crack of the oxide film and can be also achieved by separation of the oxide scale from the substrates. So any factor that can restrain the tendencies of crack of the oxide film and scale or/and the tendencies of separation of the oxide scale from the substrates, or/and enhance the tendencies of plastic deformation of the substrates will reduce scale spallation and increase the oxidation resistance [7].

Based on the above analysis, the improvement of the oxidation resistance of FeAl alloy by Ti addition can be rationalized as follows:

(1) Ti addition can improve significantly the compactness of oxide scales in the surface of FeAl alloy, which leads to a better protective effect; (2) TiO has a better adherence to the substrate of FeAl alloy, so the scale spalls with more difficulty; (3) The coefficient of thermal expansion of TiO ($\sim$10 × 10-6/°C) is between α-Al_2O_3 ($\sim$6 × 10-6/°C) and FeAl ($\sim$21 × 10-6/°C). Therefore TiO in the oxide scale can reduce the thermal expansion difference between oxide and base alloy, resulting in reduced thermal stress when specimens were repeatedly heated up and cooled down; (4) The Ti addition may improve the toughness of the oxide film scales, therefore reducing the possibility of oxide film or scale fracture.

4. Conclusion

By weighing the weight gains of Fe-36.5Al and Fe-36.5Al-2Ti alloy specimens after static oxidation performed at 1000°C and 1100°C in air for different times, the oxidation kinetic curves of both Fe-36.5Al and Fe-36.5Al-2Ti alloys were described as parabolas following the formula: $(\Delta W/S)^2 = K_\mathrm{p} t + \mathrm{C}$. The parabolic rate constants, K_p are about 2.4 and 3.3 mg^2 cm^{-4} h^{-1} for Fe-36.5Al alloy and about 1.3 and 2.0 mg^2 cm^{-4} h^{-1} for Fe-36.5Al-2Ti alloy when oxidized at 1000°C and 1100°C respectively. The difference between Fe-36.5Al and Fe-36.5Al-2Ti alloy is not only in the surface morphology but also in the phase components. In the surface there is only α-Al_2O_3 oxide for Fe-36.5Al alloy while there are α-Al_2O_3 and TiO oxide for Fe-36.5Al-2Ti alloy. In Fe-36.5Al alloy the Al_2O_3 oxide grains are much finer than those in the Fe-36.5Al-2Ti alloy, which leads to the fast growth of Al_2O_3 scale. In a word, 2at.%Ti addition can improve the oxidation resistance of Fe-36.5Al alloy because of TiO forming in the surface.

Acknowledgments

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