Magnetic effect on oxide-scale growth of Fe-5Cr alloy

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Abstract. The oxidation behaviour of Fe-5Cr alloy was investigated at 650°C in the presence of magnetic field. Results indicated that the oxide scales were both consisted of an outer Fe-oxide scale and an inner mixed-oxide scale in the presence or absence of magnetic field. The oxide-scale growth of Fe-5Cr alloy, gained by measuring the oxide-scale thickness, was verified to follow parabolic lawyer. And the oxidation kinetics showed that the applied magnetic field retarded the oxide-scale growth of Fe-5Cr alloy.

1. Introduction

The development of superconducting magnet techniques promote the material researches in a high magnetic field [1]. Many investigations have focused on the magnetic effect on the annealing [2], grain growth [3, 4], phase transformation [5, 6], texture [7], and interfacial reaction [8-14]. Most of these studies are related to the atom diffusion behaviour in a magnetic field. Earlier, Youdelis [8] reported that the diffusion of Cu in Al was retarded by a 3T magnetic field. And many subsequent investigations about the magnetic effect on the diffusion behaviour in the diffusion couple systems were in agreement with the result [9-11]. However, some other studies have found different magnetic effect on the diffusion behaviour. Nakajima [12] pointed out that the diffusion of Ni in Ti was not affected by an applied 4T magnetic field. Zhao [13, 14] reported that the growths of intermetallic compounds at Sn-3Ag-0.5Cu/Cu and Sn1.5Cu/Cu interface were increased by the applied magnetic field. Therefore, it can be seen that the magnetic effect on the diffusion behaviour is still unclear.

Difference with atom diffusion in a diffusion couple system, the diffusion behaviour during oxidation/corrosion of alloys is closely related to the ion diffusion. Lu [15] reported that the electrochemical corrosion behaviour of metal in aqueous solutions was significantly affected by an applied magnetic field. Zhou [16] pointed out that the subscale growth of Fe-20Ni alloy was retarded by an applied magnetic field. Nevertheless, it is hard to explain the magnetic field effect on the ion diffusion based on the recently investigations More investigations are still needed to explore the magnetic effect mechanism on the ion diffusion. The oxide-scale growth of Fe-Cr alloys is a typical case which is controlled by ion diffusion [17]. And many investigations have been carried out to study the ion diffusion behaviour during oxidation of Fe-Cr alloys [18-20]. In the present work, the authors investigated the oxidation behaviour of Fe-5Cr alloy in a series of magnetic fields, the objective was to give some evidences on the magnetic effect on the ion diffusion behaviour during the oxide-scale growth of Fe-5Cr alloy.
2. Experimental materials and procedures
The alloy with nominal composition of Fe-5Cr was used. It was prepared by vacuum arc-melting using appropriate mixtures of high purity metals (Fe 99.97 wt.%, Cr 99.7 wt.%). And the actual composition determined by energy dispersive X-ray spectroscopy (EDX) was Fe-5.45Cr (in wt.%). The samples with dimensions about $1 \times 6 \times 12$ mm$^3$ were ground with SiC papers down to 2000 polishing grit (2.5 $\mu$m), and then cleaned with acetone and ethanol. Discontinuous oxidation tests were carried out, which means that the samples were exposed to the conditions of high temperature and magnetic field for a given time, and then were fetched out from the furnace. And the average oxide-scale thicknesses oxidized at different time were measured by using Q500IW image analysis meter to plot a fully oxidation kinetics curve. And at least 5 SEM images were used. The mean thickness of oxide scales was the mean value measured by different SEM images.

The magnetic field apparatus was introduced by many investigations [9-11]. During the oxidation in the uniform magnetic field, the samples were placed in a flat quartz capsule, and the main oxidation surface was parallel to the magnetic field direction, as shown in figure 1. The oxidation test was carried out in air at 650 $^\circ$C and the applied magnetic field intensity was 0 T, 2 T and 6 T. After the tests, the samples were mounted in resin and the oxide-scale cross-sections were examined using a JSM-5600LV scanning electronic microscopy.

![Figure 1. Schematic diagram of the oxidized samples in the magnetic field.](image)

3. Experimental materials and procedures

3.1. Cross-sectional morphologies
Figure 2 shows the cross-sectional morphology of Fe-5Cr alloy oxidized at 650 $^\circ$C for 7 h. It can be seen that the oxide scale was composed of three distinguishable zones, i.e., the outmost dark layer, the intermediate gray layer and the inner dark layer. The element composition of every layer was detected by EDX, as indicated in table 1. It is indicated that the outmost layer marked by number 1 and 2 in figure 2 only contained Fe and O elements and the ratio of Fe/O is approximately 1, which implies the outmost layer is FeO. Though Cr element existed in the intermediate layer marked by number 3, its content is lower and the ratio Fe(Cr)/O is also about 1. It is implied that the main oxide of intermediate layer is also FeO. However, the Cr content at the location 4 and 5 was up to 6.86% and 6.61% which is somewhat higher than that of the alloy substrate. It may be FeO and dispersed Fe-Cr-oxide. The microstructures of oxide scales on an Fe-5Cr alloy were in accordance with previous investigations [17]. In order to clear the oxidation mechanism of Fe-5Cr alloy under a high magnetic field, the oxide scale was divided to two parts. The location numbered by 1-3 was defined as Fe-oxide scale and the location numbered by 4 and 5 was called mixed-oxide scale.
Figure 2. Cross-sectional morphologies of Fe-5Cr alloy oxidized at 650 °C for 7 h.

Figure 3 displays the cross-sectional morphologies of Fe-5Cr alloy oxidized at 650 °C for 5 h under a series of magnetic field intensities. It can be seen that the cross-sectional morphologies of samples under different magnetic field are nearly same, which means that all of them were composed of an Fe-oxide layer and a mixed-oxide layer. The difference is that the oxide-scale thickness in the absence of magnetic field is thicker than those in the presence of magnetic field, which implies that the applied magnetic field induced a decrease of oxide-scale growth. Moreover, it can be found that the difference of oxide-scale thicknesses for 2 T and 6 T are almost indistinguishable in this magnification.

Figure 3. Cross-sectional morphologies of Fe-5Cr alloy oxidized at 650 °C for 5 h under a magnetic field of (a) 0 T; (b) 2 T; (c) 6 T.

3.2. Growth of oxide scale

Figure 4(a) represents the oxide-scale thickness as a function of oxidation time for Fe-5Cr alloy oxidized at 650 °C with and without magnetic field. It can be obviously gained that the application of magnetic field decreases the oxide-scale growth, which is in agreement with the current investigations about the magnetic effect on the diffusion in diffusion couple systems and high temperature oxidation process [8-11, 16]. The variation of oxidation kinetics affected by magnetic field is attributed to a change of the growths of Fe-oxide layer and mixed-oxide layer.

The relation between square of oxide-scale thickness and time is shown in figure 4(b), which is implied that it followed a parabolic law. Calculations of quantifying the oxide rate constant were performed. And the oxide rate constants for Fe-5Cr alloy oxidized at 0 T, 2T and 6 T were $1.43 \times 10^{-7}$ cm$^2$•s$^{-1}$, $1.98 \times 10^{-8}$ cm$^2$•s$^{-1}$ and $1.67 \times 10^{-8}$ cm$^2$•s$^{-1}$, respectively. It can be seen that the decreased effect of 2 T magnetic intensity on the oxidation kinetics constant of oxide scale by a factor of approximately
7. Under 6 T, the decreased effect can be by a factor of more than 9. It is confirmed that the application of magnetic field strongly affects the oxide-scale growth of Fe-5Cr alloy.

3.3. Growth of mixed-oxide scale
As indicated in figure 3, the thicknesses of mixed-oxide scales oxidized under magnetic field were somewhat similar. To further clear the magnetic effect on the growth of mixed-oxide scale, the thicknesses of mixed-oxide scales were measured and curves of the relation between thicknesses of the mixed-oxide scale and time were plotted in figure 5. It can be seen that the growth of mixed-oxide scale approximatively obeyed a linear law, which is related to the lower Cr content in Fe-5Cr alloys. At low Cr contents, some Cr will enter solution in the FeO phase but, due to the stability of spinel, the solubility is limited, so Cr-rich oxides dispersed in FeO layer [17]. Since the diffusion distance for solution formation is short, Cr-rich oxides can be fast generated, then the formation of mixed-oxide scale is also fast, consequently the growth kinetics displays a linear law. As for the magnetic effect on the growth of mixed-oxide scale, it can be attributed to the restrained effect of magnetic field on the diffusion of iron ions. The rate constants of mixed-oxide scale were calculated. And the oxide rate constants at 0 T, 2T and 6 T were $1.28 \times 10^{-6}$ cm$\cdot$s$^{-1}$, $3.11 \times 10^{-7}$ cm$\cdot$s$^{-1}$ and $2.42 \times 10^{-7}$ cm$\cdot$s$^{-1}$, respectively. It can be seen that the decreased effects of 2T, 6T magnetic intensities on the rate constants of mixed-oxide scales by a factor of more than 4 and 6, respectively.

Figure 4. The oxidation kinetics of the Fe-5Cr alloy.
(a) oxide-scale thicknesses as a function of time. (b) square of oxide-scale thickness as a function of time.

Figure 5. Thickness of the mixed-oxide scales as a function of time for samples oxidized with and without magnetic field.
4. Discussion

The magnetic effects on the diffusion process, such as grain growth, interfacial reaction, were intensively investigated [3, 4, 8-14]. Under magnetic field, a physical explanation of the magnetic effect on the diffusion coefficient of charged particle is usually identified as [8, 21, 22]:

\[
D_\perp \approx \frac{1}{1 + \omega_C \tau^2} D \quad \text{and} \quad D_\parallel = D
\]

(1)

where \(\tau\) is the mean collision time of the charged particle, \(D\) is the diffusion coefficient without magnetic field, \(\omega_C = qB/m\), \(q/m\) is the charge-mass ratio of the charged particle, subscripts \(\perp\) and \(\parallel\) indicate the direction perpendicular and parallel to the magnetic field, respectively. Based on equation (1), it is indicated that the diffusion is suppressed in the direction perpendicular to the magnetic field, by which a large volume of reports about magnetic field retarded effect on diffusion were demonstrated [8-11, 16]. During the oxide-scale growth of Fe-5Cr alloy, the diffusion of Fe cations is perpendicular to the magnetic field. Such process must be retarded by the magnetic field according to the equation (1).

Moreover, the diffusion coefficient \(D\) is depended on the lattice parameter and the jump rate of atom, as indicated in equation (2).

\[
D = n \beta d^2 \Gamma
\]

(2)

where \(n\) is the number of the nearest neighbor interstitial positions, \(2 \beta\) the probability when an interstitial atom jumps into a new interstitial position, and \(d\) the projected length onto the diffusion direction. Symbol \(\Gamma\) in Equation 2 represents the jump rate [23]. When the anions or cations diffuse in the high magnetic field, they are affected by the magnetic field in the form of Lorentz force, and the Lorentz force \(\vec{f}\) is expressed by [24, 25]:

\[
\vec{f} = q\vec{V} \times \vec{B}
\]

(3)

where \(\vec{V}\) is the average velocity of ions in the absence of magnetic field, \(\vec{B}\) is the magnetic field intensity. During the growth of oxide scale of Fe-5Cr alloy, the diffusion of Fe cations perpendicular to the magnetic field is retarded by the Lorentz force, and then the probability when an atom jumps into a new interstitial position is decreased. Meanwhile, the jump rate for Fe cations perpendicular to the magnetic field is also decreased by the Lorentz force. Those magnetic effects on the diffusion behavior of Fe cations result in the decreased diffusion coefficient of high temperature oxidation of Fe-5Cr alloy.

As an oxidation process, the oxidation rate is controlled by the cations and anions diffusion. Once the ion diffusion behavior is changed, the oxidation rate is also changed. Wagner proposed the high temperature oxidation model based on the ions-electron theory, as indicated in equation [17].

\[
k_p = \frac{2M_{\text{ox}} \sigma n_e (n_c + n_a)}{nF \rho_{\text{ox}}}\]

(4)

where \(k_p\) the parabolic oxidation rate constant, \(M_{\text{ox}}\) molar mass of oxide, \(E\) electric field intensity, \(\sigma\) oxide scale conductivity, \(n_e\) electron transport number, \(n_c\) cation transport number, \(n_a\) anion transport number, \(n\) valence, \(F\) faraday’s constant, \(\rho_{\text{ox}}\) oxide density, \(n_c + n_e + n_a = 1\). According to aforementioned analysis on the effect of magnetic field on the ion diffusion in equation (1), (2), (3), the effective \(n_c, n_e, n_a\) along the oxide-scale growth direction are all retarded by the applied magnetic field during the oxidation of Fe-5Cr alloy. In addition, the oxides formed in all experimental conditions are not changed as indicated in figure 2 and figure 3, i.e. \(M_{\text{ox}}, \rho_{\text{ox}}\) and \(\sigma\) are not changed by the applied magnetic field. Then the decreased \(n_c, n_e, n_a\) result in oxidation parabolic rate constant decreasing, as shown in figure 4.
5. Conclusion
Fe-5Cr alloy was subjected to oxidation under magnetic field at 650 °C. The cross-sectional morphologies and the oxide-scale growth were examined. The major conclusions from this investigation are as follows:

- The oxide-scale structures, consisted of outer Fe-oxide layer and inner mixed-oxide layer, were not changed by the applied magnetic field.
- The application of magnetic field retarded the oxide-scale growth.
- The applied magnetic field did not change the oxidation kinetics law.

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