Oxygen Permeability through Internal Oxidation Zone in Fe–Cr Alloys under Dry and Humid Conditions at 973 and 1 073 K

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Internal oxidation of Fe–Cr alloys were investigated in dry and humid atmospheres at temperatures of 973 and 1 073 K in order to clarify the effect of humidity on the oxygen permeability in internal oxidation zone. The oxygen partial pressure in the chamber was fixed by Fe/FeO powder mixture. The calculated oxygen permeability increases linearly with increasing Cr concentration in the alloys, both at 973 and 1 073 K. Moreover, the presence of humidity enhanced the oxygen permeability compared with that under dry condition. The oxygen permeability through IOZ in humid atmosphere is larger than that in dry atmosphere as a factor of 1.2.

KEY WORDS: internal oxidation; Fe–Cr alloys; oxygen permeability.

1. Introduction

The reduction of the CO₂ emission and awareness of global warming has pushed forward the development of advanced power plants with higher efficiencies. The most obvious route to increase the efficiency of power plants is to increase the steam temperature. Now the target has been set to achieve a goal of 973 K at pressures around 38 MPa.1) A number of high strength 9–12% Cr ferritic steels have been developed as construction materials in advanced power plant. Understanding the steam oxidation behavior of these steels is very important.

It is well known that the oxidation behavior of Fe–Cr ferritic alloys in the atmosphere containing water vapor (humid atmosphere) is very different from that without water vapor (dry atmosphere). The oxidation rates are usually larger in the humid atmosphere. It is well known that the oxidation behavior of Fe–Cr ferritic alloys in the atmosphere containing water vapor (humid atmosphere) is very different from that without water vapor (dry atmosphere). The oxidation rates are usually larger in the humid atmosphere. However, the mechanism responsible for this observation is still unclear. Kurokawa et al.2) and Nakagawa et al.3) have reported that hydrogen permeates through oxide scales into Fe–Cr alloys during oxidation. Recently, Hanafi et al.4) have clarified that water vapor in humid atmosphere might give hydrogen dissolving in the alloys, enhance the oxygen permeability and retard the formation of protective external scale.

In the present work, oxygen permeability through internal oxidation zone (IOZ) in dry and humid atmospheres was investigated in dilute Fe–Cr alloys at temperatures of 973 and 1 073 K.

2. Internal Oxidation

Consider a planar specimen of a binary alloy A–B as shown in Fig. 1, in which B is a dilute solute. The element of B is less noble than A. Internal oxidation is the process where oxygen diffuses into the alloys, reacts with B and forms precipitated oxide of B in the A matrix. Assuming that the ambient oxygen pressure is low enough not to oxidize the element A and the diffusion of oxygen is the rate determining step, Wagner5) provides the depth of internal oxidation zone to be given by:

\[ x^2 = 2k_p t = 2 \left( \frac{N_o^{(i)} D_o}{v N_B} \right) t \]  

where \( k_p \) is parabolic rate constant and \( t \) is the oxidation time. \( N_o^{(i)} \) is the solubility of oxygen in the alloy for given oxidizing atmosphere, \( D_o \) is the diffusivity of oxygen in the alloy, \( v \) is the ratio of oxygen atom to solute atom in the precipitated oxide, \( B_{o} \) and \( N_B \) is the mole fraction of B of the alloy.

Fig. 1. Schematic illustration of internal oxidation in binary alloy A–B.
3. Experimental Procedure

3.1. Sample Preparation

The samples of Fe–0.5, –2.5 and –5mass%Cr were prepared from Fe (purity 99.99%) and Cr (purity 99.9%) by an arc melting technique. The button alloys after arc melting were annealed at 1473 K for 43.2 ks in vacuum. Then, the buttons were sliced into plates of 1 mm in thickness. The plates were ground with abrasive paper of up to #2000 grits and polished with diamond paste of 4 μm. Finally, the plates were ultrasonically washed in ethanol and dried at room temperature. The chemical composition of the sample was analyzed using an electron probe micro analyzer (EPMA). The analyzed compositions are shown in Table 1.

X-Ray Diffraction (XRD) confirmed the sample to be a single phase of solid solution with bcc structure.

3.2. Internal Oxidation of Fe–Cr Alloys

The internal oxidation was carried out at temperatures of 973 and 1073 K for up to 691.2 ks in the apparatus shown in Fig. 2. The oxygen partial pressure in the chamber was fixed by the Fe/FeO powder mixture which contains a small amount of ZrO2 powders to minimize sintering among powders. The corresponding value of oxygen partial pressure was 4.3 × 10^-17 Pa at 973 K and 1.1 × 10^-14 Pa at 1073 K.

In dry oxidation, the chamber was evacuated using a rotary pump for 1.8 ks and closed. Then, the sample was heated to the oxidation temperature and held for up to 691.2 ks (8 d). In humid oxidation, Ar–5%H2 gas of 3 × 10^5 Pa was filled after evacuation of the chamber. At 973 K, the oxygen partial pressure is 4.3 × 10^-17 Pa and the water vapor pressure is 7.7 × 10^7 Pa. At 1073 K, the oxygen partial pressure is 1.1 × 10^-14 Pa and the water vapor pressure is 3.3 × 10^8 Pa. Two thermocouples were used to monitor the temperatures of the sample and the Fe/FeO powder mixture during oxidation. The temperature variation during the experiment was ±3 K at most. After oxidation, the samples were cooled to room temperature in the furnace.

4. Results

4.1. Phase Identification

Figure 3 shows the XRD patterns from the sample surface after oxidation at 973 K for up to 172.8 ks (2 d) in dry and humid atmospheres. The XRD patterns are similar in both dry and humid atmospheres. The peak for α-Fe appears in all samples. The oxide phase is FeCr2O4 both in dry and humid atmospheres because the formation of iron oxide is prevented at the dissociation pressure of FeO. Similar phase composition was also detected after oxidation at 1073 K.

4.2. Internal Oxide Morphology

Figure 4a shows the cross sections of Fe–Cr alloys after internal oxidation at 973 K in dry and humid atmospheres under PO2 = 4.3 × 10^-17 Pa for 604.8 ks (7 d). Meanwhile Fig. 4b shows the cross section of Fe–Cr alloys after internal oxidation at 1073 K in dry and humid atmospheres under PO2 = 1.1 × 10^-14 Pa for 345.6 ks (4 d).

In the both figures, oxide particles precipitated in IOZ are identified to be FeCr2O4 by XRD. At 973 K and 1073 K, the oxide precipitates formed discrete particles. The oxide precipitates in Fe–0.5mass%Cr is spherical in shape, both in dry and humid atmospheres. Meanwhile, the oxide precipitates in Fe–2.5mass%Cr and Fe–5mass%Cr alloys are acicular in shape, both in dry and humid atmospheres. The thickness of IOZ in humid atmosphere was slightly thicker compare to that in dry atmosphere. There is no indication of preferential precipitation along grain boundaries in the alloys.

4.3. Thickness of IOZ

From the cross sectional images of Fe–0.5mass%Cr, Fe–2.5mass%Cr and Fe–5mass%Cr alloys, the thickness of...
IOZ after oxidation was measured and plotted in Fig. 5. The growth of IOZ in dry and humid atmospheres obeys the parabolic rate law of Eq. (1). The values of \( k_p \) were summarized in Table 2. The parabolic rate constant under humid condition is larger than that in dry atmosphere. The increase of Cr concentration in the alloys decreases the growth rates of IOZ.

5. Discussion

5.1. Oxygen Permeability in \( \alpha \)-Fe

Figure 5 has shown that the oxidation kinetics for the growth of IOZ obeys a parabolic rate law. This indicates that the oxygen transport from the Fe/FeO mixture to the specimen is rapid enough and the rate determining step is oxygen diffusion in IOZ. The permeability of oxygen in IOZ under dry and humid conditions was calculated by Eq. (2) as shown in Fig. 6.

\[
k_p = \frac{N^{(i)}_O D_O}{\nu V_{Cr}}
\]

The calculated oxygen permeability increases linearly with...
increasing Cr concentration in the alloys, both at 973 and 1073 K. The oxygen permeability in humid atmosphere is larger than that in dry atmosphere. The intercept gives the bulk permeability \((N_{\text{Cr}})_{\text{bulk}}\). Intercepts for dry and humid conditions exhibit almost the same value. This indicated that the oxygen permeability in bulk \(\alpha\)-Fe is not sensitive to the atmosphere. The value of \((N_{\text{O}}D_{\text{O}})_{\text{bulk}}\) in bcc iron is calculated to be \(3 \times 10^{-18} \text{ m}^2\text{s}^{-1}\) at 973 K, and \(5 \times 10^{-17} \text{ m}^2\text{s}^{-1}\) at 1073 K.

The temperature dependence of oxygen permeability in bulk \(\alpha\)-Fe is shown in Fig. 7. The oxygen permeability reported by other researchers \(^6\) is also shown in the same figure. The value of \((N_{\text{O}}D_{\text{O}})_{\text{bulk}}\) obtained in this work shows a good agreement with the reported values. The temperature dependence of oxygen permeability in \(\alpha\)-Fe could be expressed as follows,

\[
(N_{\text{O}}D_{\text{O}})_{\text{bulk}} = 3 \times 10^{-7} \exp \left( \frac{-200 \text{ kJ mol}^{-1}}{RT} \right) \text{ m}^2\text{s}^{-1} \quad (3)
\]

### 5.2. Effect of Solute Concentration on the Oxygen Transport in Internal Oxidation Zone

Several works have shown that the oxygen permeability increases with increasing the solute concentration in IOZ of Ni–Al\(^{8-10}\) and Fe–Al\(^{7,11}\) systems. In these alloys, the oxides form acicular, rods or laths aligned with the diffusion direction. On the contrary, in Fe–Cr\(^{12}\) and Ni–Cr\(^{8-10}\) alloys, the internal oxides were discrete particles, often relatively spherical. Due to the accelerated inward oxygen diffusion along the particle-matrix interface in the Al-bearing alloys, the elongated aluminum oxides developed much more rapidly than the spherical chromium oxides.

Stott \(^9\) has proposed a model of internal oxidation involving enhanced oxygen diffusion as shown in Fig. 8. They reported that the effective flux of oxygen through the IOZ as the sum of the fluxes of oxygen through the alloy lattice, along internal oxide/metal interface, and through the internal oxide precipitate in the alloys. The increase of oxygen permeability is associated with enhanced oxygen transport along precipitated oxide/metal interfaces.

In this work, the internal oxide precipitates in Fe–Cr alloys are spherical in shape both in dry and humid atmospheres. This fact indicates that the enhancement of oxygen permeability along the internal oxide/metal interface is not so large, but noticeable enhancement was appeared as shown in Fig. 6. The dependency of oxygen permeability on Cr concentration, \(N_{\text{Cr}}\) could be stated as follows:

\[
(N_{\text{O}}D_{\text{O}}) = BN_{\text{Cr}} + \left(N_{\text{O}}D_{\text{O}}\right)_{\text{bulk}} \quad \text{(4)}
\]

where \(B\) is the slope of the line. Thus, it is postulated that the enhancement of oxygen transport with the increase of alloying concentration is due to rapid transport of oxygen along the oxide precipitates/metal interfaces.

### 5.3. Effect of Water Vapor on the Oxygen Transport in Internal Oxidation Zone

The oxygen permeability in IOZ was further enhanced in
the humid atmosphere, as shown in Fig. 6. The enhancement factor \( (f_E) \) is defined by the ratio of \( B \) in dry and humid atmospheres as follows:

\[
f_E = \frac{B_{\text{humid}}}{B_{\text{dry}}} \tag{5}
\]

where \( B_{\text{humid}} \) and \( B_{\text{dry}} \) are slopes of the lines in Fig. 6. At 973 K, the value of \( B_{\text{dry}} \) is \( 2.59 \times 10^{-16} \text{m}^2 \text{s}^{-1} \) and \( B_{\text{humid}} \) is \( 3.15 \times 10^{-16} \text{m}^2 \text{s}^{-1} \). The enhancement factor at 973 K is 1.2. At 1073 K, the value of \( B_{\text{dry}} \) is \( 3.04 \times 10^{-15} \text{m}^2 \text{s}^{-1} \) and \( B_{\text{humid}} \) is \( 3.75 \times 10^{-15} \text{m}^2 \text{s}^{-1} \). The enhancement factor at 1073 K is 1.2.

In the humid atmosphere, hydrogen may dissolve into the IOZ. The dissolved hydrogen may segregate at the oxide precipitate/metal interface and enhances oxygen permeability. However, the mechanism on the enhancement of oxygen transport along the interface is still unknown and needs further investigations.

6. Conclusion

Internal oxidation of Fe–0.5 to 5 mass%Cr alloys was investigated in dry and humid atmospheres under the oxygen partial pressure of the Fe/FeO coexistence at temperatures of 973 and 1073 K. The growth of internal oxidation zone (IOZ) obeyed the parabolic rate law, indicating that oxygen permeation in IOZ was the rate determining step. Oxygen permeability increased linearly with increasing Cr concentration. Furthermore, humidity enhanced the oxygen permeability compared with that in dry atmosphere.

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