The Effect of Water Vapor on High Temperature Oxidation of Fe-Cr Alloys at 1073 K

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The effect of water vapor on high temperature oxidation was studied based on Wagner’s theory of binary alloy oxidation. The oxidation of Fe-Cr alloys was carried out at 1073 K in dry and humid conditions. The oxidation was conducted in a closed apparatus at 1073 K and the oxygen partial pressure of 1.1 × 10⁻¹⁴ Pa, which was fixed by a Fe/FeO buffer. To prepare the humid condition, Ar-5% H₂ gas mixture of 3 × 10⁸ Pa was filled in the apparatus, which provided the water vapor pressure of 3.3 × 10⁹ Pa. The transition of internal and external oxidation was observed in Fe-8Cr in the dry condition and in Fe-12Cr in the humid condition.

Interdiffusion experiment of Fe/Fe-16Cr diffusion couples in dry and humid environments showed that the diffusion coefficient of Cr was not influenced by dissolved hydrogen.

The oxygen permeability in α-Fe was determined by means of internal oxidation of Fe-5Cr alloy at 1073 K and the oxygen partial pressure of 1.1 × 10⁻¹³ Pa in a dry and two humid conditions with water vapor of 1.1 × 10² Pa and 3.3 × 10² Pa. The oxygen permeability in humid condition increases by a factor of 1.4. Dissolved hydrogen increases the oxygen permeability, thus increases the minimum concentration of Cr to form external scales in humid conditions. The presence of dissolved hydrogen changes the oxide shape from discrete spherical particle to spike-like precipitates, which enhances the oxygen transport along the metal/oxide precipitates interface.

Keywords: steam oxidation, internal oxidation, external oxidation

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1. Introduction

There is an essential demand to increase the operation temperature in steam-power generation in order to improve the efficiency of energy conversion. Higher efficiency results in lowering the CO₂ emission and suppressing the global warming. The target temperature is 973 K. The operation temperature in current power plants is 883 K at 31 MPa.¹ Fe-Cr ferritic alloys with Cr composition of 9 to 12 mass% have been currently in service. The formation of protective Cr₂O₃ scale in the steam oxidation is a key issue because the scale lowers the oxidation rate dramatically.

The presence of water vapor in oxidation environment greatly affects the formation of oxide scales on Fe-Cr alloys. Many studies have shown that oxidation rates in humid environment are relatively higher than in dry environment.²⁻⁶ A possible mechanism is that water vapor retards the formation of protective scale. Extensive works have been done to understand the role of water vapor in impeding the formation of protective Cr₂O₃ scale, but the explanations remain in qualitative manner. Segerdahl et al.⁷ summarized that presently there is no consensus regarding the cause of accelerated oxidation in humid environment.

Oxidation in the early stage plays important roles in the formation of protective scale. For general A-B alloy, where B is more stable than lowest oxide of A, Wagner⁸ has proposed a minimum concentration of B in a binary A-B alloy required to form continuous protective scale of oxide of atom B. In case of Fe-Cr alloys, Cr concentration required to form external Cr₂O₃ scale is shown as below.

\[ N_{Cr}^{(s)} > \left[ \frac{\pi g^{*} N_{Cr}^{(s)} D_{O} V_{Alloy}}{2v D_{Cr} V_{CrO_{3}}^{*}} \right]^{\frac{1}{2}} \]  

where \( N_{Cr}^{(s)} \) is the mole fraction of oxygen at the metal surface, \( D_{O} \) and \( D_{Cr} \) are diffusion coefficients of oxygen and Cr in the alloy, respectively. \( V_{Alloy} \) and \( V_{CrO_{3}}^{*} \) are molar volumes of alloy and CrO₃, \( v \) is the atomic ratio of O to Cr in Cr₂O₃ (\( v = 1.5 \)). \( g^{*} \) is the volume fraction of internal oxide precipitates when external oxidation takes place. Rapp⁹ has evaluated the transition from internal to external oxidation in Ag-In binary alloys and proposed that the value of \( g^{*} \) is 0.3.

Below this critical concentration the internal oxidation may show up and above this value the external scale will form. Equation (1) shows that the permeability of oxygen in Fe-Cr alloy, \( N_{Cr}^{(s)} D_{O} \), and the diffusion coefficient of chromium, \( D_{Cr} \), plays an important role in the formation of continuous Cr₂O₃ scale. When water vapor presents in the oxidation atmosphere, it may retard the formation of protective Cr₂O₃ scale. The question is how water vapor affects these two parameters of \( N_{Cr}^{(s)} D_{O} \) and \( D_{Cr} \). The presence of water vapor provides an excessive supply of hydrogen, which is dissociated from water vapor. In a metallic phase, a possible hydrogen state is a neutral atom. The aim of this study is to clarify the effects of dissolved hydrogen atoms in the alloy on the formation of continuous Cr₂O₃ scale based on Wagner’s eq. (1).

In this paper, high temperature oxidation experiments in dry and humid conditions were conducted on Fe-Cr alloys with Cr concentrations ranging from 5 to 17 mass% at 1073 K to clarify the critical concentration of Cr to form external scale on dry and hydrogen containing environment. The experiment was purposely conducted at higher temperature than existing operation temperature of 883 K to accelerate the oxidation and remarks the water vapor effects. The change in precipitates oxide and oxygen permeability of Fe-5Cr alloy was meticulously inspected. Furthermore, interdiffusion experiment of Fe/Fe-16 mass% Cr diffusion
couple in dry and humid condition was conducted in order to evaluate the effect of dissolved hydrogen on Cr diffusivity in Fe-Cr alloy.

In this manner, the effects of dissolved hydrogen on oxygen permeability and Cr diffusivity in α-Fe was quantitatively clarified.

2. Experimental

2.1 Oxidation of Fe-Cr alloys

Fe-Cr alloys were prepared from high-purity Fe (99.99%) and Cr (99.9%) plates by arc melting in Ar gas. The alloys were in form of 20 g buttons and were annealed for 86.4 ks at 1373 K in vacuum. Then, the alloys were sliced into coupons were in form of 20 g buttons and were annealed for 86.4 ks at 1373 K in vacuum. Then, the alloys were sliced into coupons and was calculated by the standard Gibbs energy change of the reaction below.

\[
0.947 \text{Fe} + 1/2\text{O}_2 \rightarrow \text{Fe}_0.947\text{O} \quad (2)
\]

FeO was known as a non-stoichiometric substance, having a chemical composition of Fe_{0.947}O at 1073 K. The standard Gibbs energy change of the eq. (2) at 1073 K is \(-194.7 \text{kJmol}^{-1}\) from thermodynamic data compiled by Barin. \(^\text{13}\) The calculated equilibrium oxygen partial pressure is \(1.1 \times 10^{-14} \text{Pa}\).

The calculated equilibrium oxygen partial pressure finally polished with 4 of 1 mm thick and ground with an emery paper of # 2000, and 1373 K in vacuum. Then, the alloys were sliced into coupons couple in form of 20 g buttons and were annealed for 86.4 ks at 1373 K in vacuum. Then, the alloys were sliced into coupons and was calculated by the standard Gibbs energy change of the reaction below.

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For the oxidation in dry environment, the apparatus was evacuated using a rotary pump for 1.8 ks and closed. The sample was heated to 1073 K and hold for 172.8 ks. For the oxidation in humid environment, the apparatus was evacuated, filled with Ar-5% H\(_2\) gas of \(3 \times 10^4 \text{Pa}\) and closed. The sample was heated to 1073 K and hold for 172.8 ks. Hydrogen in the chamber reacts with oxygen to form water vapor as the following manner,

\[
\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O} \quad (3)
\]

At 1073 K, the measured total pressure of the apparatus was \(4 \times 10^4 \text{Pa}\). Using the standard Gibbs energy change of \(-188.7 \text{kJmol}^{-1}\) at 1073 K compiled by Barin, the water vapor pressure is calculated to be \(3.3 \times 10^2 \text{Pa}\). After oxidation, the samples were cooled to room temperature in the furnace.

Oxide phases formed were analyzed by X-ray diffraction (XRD) using the divergence slit of 1 degree. A fluorescence plate was used to estimate the irradiation area of the X-ray. At low diffraction angle of 20° the irradiation area is \(19 \text{mm} \times 14 \text{mm}\), and at high diffraction angle of 80° the irradiation area is \(6 \text{mm} \times 14 \text{mm}\). To examine the oxide phases in the internal oxidation zone, a sample was tilted 2 degree and polished. Distribution of elements was analyzed by EPMA. Surface morphology was observed by scanning electron microscopy (SEM).

2.2 Interdiffusion of Fe/Fe-16 mass% Cr

The Fe/Fe-16 mass% Cr diffusion couple was employed. Fe (99.99%) and Fe-16 mass% Cr plate were used for diffusion couples. The chemical composition of Fe-16 mass% Cr alloy is shown in Table 2. Figure 2 shows the schematic diagram of the diffusion couple and the experimental apparatus.

The diffusion couple was inserted into an electric furnace as shown in Fig. 2, and annealed at 1073 K for 691.2 ks in vacuum for experiment in dry environment. To simulate a humid environment, the diffusion couple was annealed under flowing Ar-20% H\(_2\) mixed gas. The gas flow rate was \(1.67 \times 10^{-6} \text{m}^3\text{s}^{-1}\). Zr sponge as an oxygen getter was

<table>
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<tr>
<th>Alloys</th>
<th>Fe Concentration (mass%)</th>
<th>Cr Concentration (mass%)</th>
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<tbody>
<tr>
<td>Fe-8Cr</td>
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<td>Fe-10Cr</td>
<td>90.2</td>
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<td>Fe-12Cr</td>
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<table>
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<tr>
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<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Al</th>
<th>P</th>
<th>S</th>
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<tbody>
<tr>
<td>Mass%</td>
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<td>0.1</td>
<td>0.12</td>
<td>0.006</td>
<td>0.032</td>
<td>0.006</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 Chemical composition of the Fe-Cr alloys.

Table 2 Chemical composition of Fe-16 mass% Cr alloy.
set on the bottom of the diffusion couples to avoid the oxidation of the samples. Two R-type thermocouples were placed on the top and bottom of the diffusion couple to monitor the temperature during the experiment. At the isothermal zone, the temperature was fluctuated around $C60^\circ K$. After the reaction, the diffusion couple was cut, polished and analyzed by SEM and EPMA. The concentration of Cr and Fe were quantitatively determined by point analysis of EPMA.

2.3 Internal oxidation in Fe-5 mass% Cr

Oxygen permeability in internal oxidation zone (IOZ) was measured by the means of internal oxidation of Fe-5 mass% Cr alloy. Table 3 shows the chemical composition of the alloy. Experimental procedures and conditions of the internal oxidation are exactly the same as described in 2.1. To evaluate the effect of dissolved hydrogen on the oxidation, the experiment was done in two different water vapor pressures. The apparatus was evacuated, filled with Ar-5% H$_2$ mixed gas of $1 \times 10^4$ Pa and $3 \times 10^4$ Pa respectively. At 1073 K, the measured total pressures in the apparatus were $1.3 \times 10^4$ Pa and $4 \times 10^2$ Pa. The water vapor pressures were calculated to be $1.1 \times 10^2$ Pa and $3.3 \times 10^2$ Pa respectively.

After oxidation, cross section of the sample was examined and the depth of IOZ was measured. The depth of IOZ was measured randomly on both side of the samples’ surface for at least 75 readings of each sample. Then, the mean value of the depth was determined.

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3. Results

3.1 Oxidation of Fe-Cr alloys

Figure 3 shows cross sections of Fe-8Cr, -10Cr and -12Cr in dry and humid environments. In dry environment, thin continuous oxide layer is observed on the Fe-8Cr alloy surface. Internal oxide precipitates beneath the continuous oxide layer. External scale is observed on the alloys with Cr concentration higher than 10 mass%. In these two alloys, no internal precipitated oxide is observed. However, in humid environment, only internal oxide precipitated is observed on Fe-10Cr. In Fe-12Cr alloy external oxide scale and internal precipitated oxide is observed.

Figure 4 shows various parts of cross section of Fe-8Cr and Fe-12Cr in dry and humid environments, respectively. The microstructures apparently show that internal oxidation and external oxidation occur simultaneously in one specimen, probably depending on the small difference of surface condition. Some parts of the samples show that internal oxide is formed beneath the continuous external scale. The thickness of continuous scale is about less than 2 $\mu m$ on both samples. Despite the difference in Cr concentration, both alloys exhibit almost an identical microstructure. These results indicated that the transition from internal oxidation to external oxidation occurred on Fe-8Cr in dry environment, while the transition took place on Fe-12Cr alloys in humid. Figure 5 summarizes the mode of oxide morphology of each sample in dry and humid conditions. In the higher Cr concentration, as such in Fe-17Cr alloy, the sample exhibits an external oxidation both in dry and humid conditions. While lower Cr concentration, as could be observed in Fe-5Cr alloy, gives completely internal oxidation.

3.2 Phase identification

Figure 6 shows the XRD patterns of the sample surfaces
oxidized in dry and humid conditions for 172.8 ks. The XRD patterns are not different both in dry and humid conditions. Fe-5Cr alloys show that only FeCr$_2$O$_4$ was formed. Alloys with Cr concentration from 8 to 12 mass% formed FeCr$_2$O$_4$ and Cr$_2$O$_3$. The peaks of Cr$_2$O$_3$ are less intense than of FeCr$_2$O$_4$. The results of Fe-17Cr show only Cr$_2$O$_3$ was formed. All samples show the peaks of $\alpha$-Fe, which means that the oxide scales are thin enough for x-ray to penetrate into alloy substrate.

Figure 7 presents the morphology of unpolished and polished (2 degree) surfaces of a Fe-12Cr alloy in humid environment. Unpolished surface shows that the oxide structures are undulating with some coarse oxide particles. From the elemental analysis, it is clear that Cr and Fe are enriched at the surface. Oxygen also was detected at this surface. On the contrary, surface that has been tilted and polished show that Cr and oxygen enriched in oxide scale. In some parts of the oxide, metallic Fe was observed in oxide close to the alloy due to uneven alloy/oxide interface. The intensity of Fe in the oxide decreases gradually from alloy/oxide interface toward the oxide scale. XRD results show that only Cr$_2$O$_3$ is detected at alloy/oxide interface.

### 3.3 Diffusion profile of Fe/Fe-16 mass% Cr

Figure 8 shows the Cr concentration profile of Fe/Fe-16 mass% Cr diffusion couples annealed at 1073 K for 691.2 ks in dry and humid conditions. The Cr concentration profiles in dry and humid environments do not exhibit significant difference in each other.
The interdiffusion coefficient of Cr was obtained from the data in Fig. 8 as a function of Cr concentration and shown in Fig. 9. The interdiffusion coefficients of Cr in dry and humid are scattered from $6 \times 10^{-16}$ to $10 \times 10^{-16}$ m$^2$s$^{-1}$. These values are very close to the value reported by Oikawa.$^{14}$ From these results, it is concluded that the effect of hydrogen on the diffusivity of Cr is negligible.

3.4 Morphology and thickness of IOZ of Fe-5Cr

Figure 10 shows typical optical microscope images of the internal oxide formed on Fe-5Cr alloys in dry condition and humid condition ($1.3 \times 10^4$ Pa and $4.0 \times 10^4$ Pa of Ar-5% H$_2$ gas mixture). In dry condition, the oxide precipitates in fine particles around 1 μm near the shallow sub-surface zone at the early stage of oxidation. As the oxidation proceeds, the oxide grows in spherical shape. In humid condition, some of the oxides grow in a preferential direction giving spike-like shape. The difference in morphology of precipitated oxides is clearly exhibited on samples oxidized at 1073 K for 432 ks in $1.3 \times 10^4$ Pa Ar-5% H$_2$ gas mixture. The IOZ containing spike-like oxide is thicker than the IOZ with spherical oxide. As oxidation time increases, i.e., at 432 ks, the difference in thickness becomes apparent between IOZs with spike-like and spherical oxides. However, almost similar thickness of IOZ was observed both in spike and sphere oxide on the sample that was exposed in $4.0 \times 10^4$ Pa Ar-5% H$_2$ for 432 ks.
Figure 11 shows the thickness of IOZ of Fe-5Cr as a function of the oxidation time. Thickness of IOZ that oxidized up to 172.8 ks in humid condition is thicker than that in dry condition. The growth of IOZ basically follows the parabolic rate law.

\[ x^2 = 2k_p t \quad (4) \]

where \( x \) is the thickness of IOZ, \( t \) is the oxidation time and \( k_p \) is the parabolic rate constant.

For the sample in dry condition, \( k_p \) is \( 1.75 \times 10^{-15} \text{ m}^2\text{s}^{-1} \).

In the humid conditions, growth of IOZ is enhanced. The parabolic rate constants are \( 2.70 \times 10^{-15} \text{ m}^2\text{s}^{-1} \) and \( 2.40 \times 10^{-15} \text{ m}^2\text{s}^{-1} \) in Ar-5% H\(_2\) gas mixture of \( 1.3 \times 10^4 \text{ Pa} \) and \( 4.1 \times 10^4 \text{ Pa} \), respectively.

### 4. Discussion

Internal oxidation behavior described in 3.1 and 3.2 indicated water vapor retarded the formation of the external scale of chromium oxide on Fe-Cr binary alloy. Hydrogen...
has known to easily dissolve in bulk α-Fe as summarized by many researchers.\textsuperscript{10–12,14} Hydrogen rapidly diffuses in the Fe after short exposure in hydrogen rich environment. According to the Wagner eq. (1), the possible effects of water vapor, i.e. dissolved hydrogen, may be the decrease of diffusion coefficient of Cr in the alloy and/or the increase of oxygen permeability in IOZ. The effect of hydrogen on the diffusivity of Cr was shown to be negligible in 3.3. The effect of hydrogen on the oxygen permeability was significant as shown in 3.4.

These data gives insight that interdiffusion experiment of Fe/Fe-16 mass% Cr diffusion couple in dry and humid condition was conducted in order to evaluate the effect of dissolved hydrogen on Cr diffusivity in Fe-Cr alloy.

The oxidation kinetics for growth of IOZ was parabolic, indicating that diffusion was the rate controlling process. This suggests that adsorption of oxygen on the surface, or surface reaction is not a limiting factor in the oxidation kinetics. Or in other word, the reaction between Fe and FeO is fast enough and assures the oxygen supply from the Fe/FeO buffer to the environment.

Wagner\textsuperscript{8)} has proposed theoretical expression for the kinetics of internal oxidation.

$$x^2 = \frac{2N_0^{(e)} D_O}{vN_Cr} t \quad (5)$$

where $N_{Cr}$ is the original concentration of Cr.

From eq. (4) and (5), it is well understood that the parabolic rate constant, $k_p$ is proportional to the oxygen permeability, $N_0^{(e)} D_O$. In this way, the permeability of oxygen in $\alpha$-Fe with or without hydrogen was determined. Figure 12 shows the oxygen permeability as a function of water vapor pressure. The oxygen permeability in humid is larger than that in dry as a factor of 1.4 and independent of water vapor pressure. Equation (1) states that Cr concentration is proportional to the square root of oxygen permeability. The diffusion experiment on Fe/Fe-16 mass% Cr showed that the diffusion coefficient of Cr in alloy is neither changed in dry nor in humid condition. Therefore, the ratio of Cr concentration required to form Cr$_2$O$_3$ scale in humid and dry conditions is given by the square root of the ratio oxygen permeability (eq. (6)). The resulting ratio is about 1.2.

Figure 13 summarizes the mode of oxidation in both dry and humid environment as a function of water vapor pressure and Cr concentration. Higher Cr concentration is required to form external oxide in humid compared with in dry environments.
Oxygen permeability, \( N_{O(4)}D_{O} \), is a product of mole fraction of oxygen in metal surface (or oxygen solubility) and diffusion coefficient of oxygen in alloy. An increase in oxygen permeability arises from increases in these two parameters. It is impossible to evaluate separately the contribution of the parameters in this study. However, the change of internal oxide’s shape of the Fe-5Cr alloy from sphere (in dry) to spike (in humid) strongly suggests that dissolved hydrogen enhances the transport of oxygen in IOZ.

In dry condition, many works have been done to investigate the enhancement of oxygen transport along the alloy/oxide precipitates interface in IOZ (Fe-Al alloy,15–17) Fe-Si alloy,18) Ni-Al alloy,19–22) Ni-Cr alloy.19–22) On the other hand, in this work it is clearly demonstrated that the presence of water vapor also changes the oxide shape from discrete spherical particles to spike-like precipitates. This is a clear evidence that the oxygen transport in IOZ was enhances by dissolved hydrogen along the metal/oxide precipitates interfaces.

5. Conclusion

The oxidation of Fe-Cr alloys was investigated in dry and humid environments at 1073 K under the oxygen pressure of \( 1.1 \times 10^{-14} \) Pa. The oxide scale formation at early stage is strongly influenced by the presence of humidity. The transition form internal to external oxidation in Fe-Cr alloys occurs at 8 mass% Cr and 12 mass% Cr in dry and humid environments, respectively. The oxygen permeability increases by factor of 1.4 in humid against in dry condition due to the change in morphology of internal oxides. The increase in oxygen permeability requires the more Cr content than in dry condition by the factor of 1.2 to form external scale of \( Cr_2O_3 \). Dissolved hydrogen enhances the transport of oxygen along metal/oxide precipitates interface.

REFERENCES