Correlation of High-temperature Steam Oxidation with Hydrogen Dissolution in Pure Iron and Ternary High-chromium Ferritic Steel

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The high-temperature oxidation in both air and steam was examined experimentally with pure iron and a Fe–10Cr–0.08C (mass%) ternary ferritic steel. In case of pure iron, the thickness of the oxide scale formed in steam at 923 K for 360 ks was comparable to that of the scale formed in air. On the other hand, in case of the ternary ferritic steel, the oxide scale formed was much thicker in steam than in air. Thus, the oxidation rate was nearly independent of the air and the steam atmosphere for pure iron, but was dependent for the ternary ferritic steel. In the present study, this difference was investigated from a viewpoint of the hydrogen dissolution in the oxide scale during the steam oxidation. The amount of dissolved hydrogen was measured using a thermal desorption spectroscopy (TDS). It was found that the amount of the dissolved hydrogen was much larger in the ternary ferritic steel than in pure iron. Also, it was shown that the hydrogen dissolution in the ternary ferritic steel was related to the presence of (Fe,Cr)3O4 in the oxide scale. The defect structure in this chromium-rich oxide was modified by hydrogen dissolution, so that the ionic diffusion could be enhanced in it, resulting in the more accelerated oxidation rate in steam.

KEY WORDS: high-temperature oxidation; air; steam; hydrogen dissolution; pure iron; high chromium ferritic steel.

1. Introduction

In fossil-fuel fired power plants, heat resistant steels are utilized as the materials for boiler components. There is a recent trend that the steam temperature increases in order to raise the efficiency of the power plant. However, this trend leads to the accelerated formation of the oxide scale on the heat resistant steel. As a result, exfoliation from thick and/or unadhesive oxide scales shortens the component lifetime and induces the other troubles such as the erosion of steam turbine.1,2) Therefore, the steam oxidation resistance at high temperatures is one of the most important properties for such heat resistant steels.

There are some publications dealing with the effect of water vapor on the high-temperature oxidation of pure iron3,4) and iron-chromium alloys5–7) but the mechanism still remains unknown.5) It is known that the high-temperature oxidation of these materials is often accelerated by the presence of water vapor in the ambient atmosphere. For example, Kvernes et al.5) showed that the oxidation rate of Fe–13mass%Cr alloys increased with increasing content of water vapor in the oxygen gas atmosphere. Ikeda et al.6) also reported that the oxidation rate of Fe–5–20 mass%Cr alloys increased drastically in the presence of water vapor in the oxygen gas. On the other hand, it is known that the oxidation rate of pure iron is independent of the content of water vapor in oxygen gas or in air.3,4) Thus, the presence of chromium in the iron-based alloys is related to the acceleration of the oxidation rate as long as the atmosphere contains water vapor.

Recently, it has been reported that hydrogen dissolves into the specimen during steam oxidation and affects the growth rate of the oxide scale.9–11) For example, Nakagawa et al. showed that hydrogen permeated through a tube of the 2–12 mass% Cr steel in the direction from the inside in steam to the outside in air, and then the accelerated oxidation was seen at the outside surface in air at 873 K.9,10) Furthermore, they reported that there was a strong resemblance in the structure, morphology and thickness of the oxide scale formed on between the air-side surface and the steam-side surface. In other words, hydrogen induced “steam-like oxidation” occurred even at the air-side surface of the steel. Yang et al.12) reported similar experimental results using a 16–18 mass% chromium ferritic steel (SUS430). Thus, hydrogen indeed plays an important role in the oxidation.

According to our previous studies, the steam oxidation resistance was improved significantly by sulfur doping into high-chromium ferritic steels11,13–15) and austenitic steels as well.14) It was found that a total amount of the dissolved hy-
drogen during the steam oxidation was much smaller in the sulfur-doped steel than in the sulfur-free steel.\textsuperscript{11} Therefore, the hydrogen dissolution is probably one of the important factors to affect the steam oxidation resistance of the steels.

In the present study, high-temperature oxidation was conducted in both air and steam. The measured oxidation resistance in both the atmospheres was discussed in terms of the amount of the dissolved hydrogen in pure iron and a high-chromium ferritic steel.

2. Experimental Procedure

2.1. Specimen Preparation

Pure Fe of 99.99\% and Fe–10.06Cr–0.081C (mass\%) ternary steel were used in this study. The pure iron was melted in an arc furnace under a high purity argon atmosphere. Then, it was cold-rolled and annealed at 1 273 K for 72 ks. The ternary steel was melted in a vacuum induction furnace. It was hot-worked at 1 423 K, then normalized at 1 323 K for 1.8 ks and tempered at 1 043 K for 5.4 ks. These materials were cut into the specimens with the size of 5×5×50 mm. Each specimen was polished with emery papers up to #600 and cleaned in an acetone solution by using an ultrasonic instrument.

2.2. High-temperature Oxidation Test in Air and in Steam

The air oxidation test was carried out in a muffle furnace. Each specimen was put into the furnace at 473 K and heated up to 923 K. It was kept in air at 923 K for 360 ks and then cooled down to 523 K. Subsequently, it was pulled out from the furnace and cooled down to room temperature in air.

The steam oxidation test was carried out in the system shown in Fig. 1. Each specimen was first set in the furnace equipped with a chamber made of austenitic stainless steel. Then, the furnace was heated up to 923 K, while flowing argon gas in the chamber. Subsequently, the atmosphere in the chamber was exchanged from argon to steam at 473 K. Steam was generated from water containing oxygen at the level below 3 ppb. When the temperature in the furnace reached to 923 K, the counting of the oxidation time was started and the specimen was kept at 923 K for 360 ks in the superheated steam under a pressure of 1×10\(^5\) Pa. After this exposure to steam, the furnace was cooled down to either 723 K or 623 K or 523 K, while keeping the steam atmosphere in the chamber. After cooling down to each temperature, the atmosphere in the chamber was exchanged from steam to argon, and only argon gas was flowed in the chamber during the subsequent cooling down to room temperature.

The cross-sections of the oxidized specimens were observed with a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM/EDS). Also, the oxides in the surface scale were identified by the X-ray diffraction (XRD) using a filtered Fe-K\(\alpha\) radiation. This analysis was carried out in the depth direction from the gas-side to the alloy-side of the oxide scale by polishing the surface mechanically.

2.3. Thermal Desorption Analysis of Dissolved Hydrogen

The amount of hydrogen dissolved in the specimen was analyzed using a thermal desorption spectrooscope (TDS) equipped with a gas chromatograph. Prior to each measurement, the gas chromatograph was calibrated with an argon gas containing 29.8 ppm hydrogen gas in order to quantify the hydrogen content in a carrier gas. A high purity argon gas (99.9999\%) was used as the carrier gas in this experiment, but still traces of impurity gases, such as \(N_2\) (<0.3 ppm), \(O_2\) (<0.1 ppm), \(CO\) (<0.1 ppm), \(CO_2\) (<0.1 ppm), THC (<0.1 ppm) and \(H_2\) (<0.1 ppm), were contained inevitably in the carrier gas.

While flowing of this carrier gas at a constant rate, \(R_{\text{gas}}=3.3\times10^{-7}\) m\(^3\)/s (20 mL/min), the specimen was heated up from room temperature to 1 173 K with the rate of 5.6×10\(^{-2}\) K/s (200 K/h). During heating, the hydrogen content in the carrier gas, \(X_{\text{H}_2}\) (vol. ppm), was measured at every 300 s (5min) interval. The hydrogen desorption rate, \(R_{\text{des}}\) (mass ppm/s), was obtained from the following equation,\textsuperscript{11}

\[
R_{\text{des}} = \frac{R_{\text{diss}} X_{\text{H}_2}}{V_{\text{ideal}}} \left(\frac{M_{\text{H}_2}}{M_{\text{sp}}}ight)
\]

where \(M_{\text{H}_2}\) (kg/mol) is the molecular mass of hydrogen and \(M_{\text{sp}}\) (kg) is the mass of specimen. This analysis is based on the ideal gas volume, \(V_{\text{ideal}}=2.24\times10^{-2}\) m\(^3\)/mol, at the standard temperature and pressure. Then, the total hydrogen content in the specimen, \(X_{\text{total}}\) (mass ppm), was related to \(R_{\text{diss}}\) as follows,

\[
X_{\text{total}} = \int R_{\text{des}} dt
\]

where \(t\) (s) is the measurement time.

In order to confirm no presence of the dissolved hydrogen in the specimen before the steam oxidation test, the hydrogen content was measured in an as-prepared steel. Also, the hydrogen desorption profile of the hydrogen-charged
specimen was measured in order to obtain the peak temperature at which hydrogen desorption takes place from the steel itself. For this experiment, hydrogen was charged electrochemically at a constant current density of $1.0 \times 10^2 \text{A/m}^2$ for 432 ks (5 d) in a $1.0 \times 10^{-2} \text{mol/m}^3$ $(0.10 \text{mol/L})$ NaOH aqueous solution containing 4.2 mol/m$^3$ $(1.0 \text{g/L})$ Na$_2$S·9H$_2$O as a hydrogen recombination poison.16)

3. Results and Discussion

3.1. Oxidation Rate of Pure Iron and Ternary High-chromium Ferritic Steel in Air and in Steam

Figure 2 shows the SEM images taken from the cross-section of the oxide scale formed on pure iron and Fe–10.06Cr–0.081C (mass%) ternary steel, both exposed to either air or steam at 923 K for 360 ks. In case of pure iron, there was a similarity in the total thickness of the oxide scale, irrespective of the air and the steam atmosphere. From the XRD analysis, it was found that the oxide scale formed in both the atmospheres was composed of three layers, i.e., Fe$_2$O$_3$ layer, Fe$_3$O$_4$ layer and the thickest FeO layer, as shown in Figs. 2(a) and 2(b).

In contrast to pure iron, the ternary high-chromium ferritic steel exhibited the atmosphere-dependent oxidation. As shown in Figs. 2(c) and 2(d), the total thickness of the oxide scale was much thinner in air than in steam. The oxide scale formed in air was too thin to be identified by the XRD and the EDS analysis, whereas the thick scale formed in steam was composed of the iron-rich layer and the chromium-rich layer. Figure 3 shows a series of X-ray diffraction patterns obtained from the high-chromium ferritic steel exposed to steam at 923 K for 360 ks. This analysis was carried out with polishing the oxide scale in the depth direction from gas side to alloy side.

The weak peaks from FeO appeared together with the strong peaks from Fe$_2$O$_3$ or (Fe,Cr)$_2$O$_4$. Finally, the polished surface reached to the steel substrate and the peaks from $\alpha$-Fe appeared. From the XRD analysis and the SEM/EDS observation, it was found that the outer iron-rich layer consisted of the two layers; a dense Fe$_3$O$_4$ layer and a porous Fe$_2$O$_4$ layer. Although a small amount of FeO was present, the inner chromium-rich layer consisted mainly of (Fe,Cr)$_2$O$_4$, which contained about 23 at% chromium to be substituted for iron ion. These results indicated that the presence of either FeO or (Fe,Cr)$_2$O$_4$ was a principal difference in the oxide-scale structure between pure iron and the ternary steel.

3.2. Hydrogen Desorption Profile Obtained From As-prepared Steel

Before starting the steam oxidation test, the amount of dissolved hydrogen was measured first in an as-prepared steel. The hydrogen desorption profile is shown in Fig. 4.
No hydrogen desorption was observed at the temperatures below about 700 K. But, the hydrogen desorption rate increased largely with increasing temperature over 700 K. However, such a large amount of hydrogen detected over 700 K is of no interest in this study for the following reason. In the hydrogen-detecting system with a gas chromatography, impurity gases must influence inevitably the hydrogen desorption profile at high temperatures. This is because, some chemical reactions take place between the steel and the impurity gases at such high temperatures, and then a large amount of hydrogen gas was formed as shown in Fig. 4. Therefore, hereafter our main concern was focused on the hydrogen to be detected at the temperature lower than 700 K.

3.3. Change in Hydrogen Desorption Profile of Steel by Exchanging Atmosphere from Steam to Argon Gas During Cooling

Figure 5 shows the hydrogen desorption profiles obtained from three steel specimens. These specimens were exposed to steam at 923 K for 360 ks, and cooled down to 723 K, 623 K and 523 K respectively, while keeping the steam atmosphere in the chamber. When the temperature reached to each temperature, the atmosphere was exchanged from steam to argon gas. Thus, every specimen was exposed to steam in the same manner and only the difference was in the exchange temperature from steam to argon gas. The peak of the hydrogen desorption profile was observed at about 600 K in all the specimens irrespective of the exchange temperature. This result indicates that the stable sites of hydrogen dissolved in the specimen are not dependent on the exchange temperature.

However, as shown in Fig. 5, the maximum hydrogen desorption rate decreased with increasing exchange temperature. This reason is explained as follows. Any steam was no longer present in the atmosphere at the temperatures below the exchange temperature. When the exchange temperatures of 623 K and 723 K were higher than the peak temperature of 600 K, a part of hydrogen dissolved in the specimens might diffuse out in the course of the cooling process from the exchange temperature to the peak temperature. Therefore, the amount of hydrogen remaining in the specimen decreased with increasing exchange temperature. As a result, the lower hydrogen desorption rate was observed in the specimens with the higher exchange temperature. However, the exchange temperature of 523 K was lower than the peak temperature of 600 K. In this case, a larger amount of hydrogen dissolved during the steam oxidation test at 923 K for 360 ks could remain in the specimen. So, the procedure of setting the exchange temperature at 523 K will permit us to obtain a nearly precise amount of hydrogen dissolved in the specimen during the steam oxidation test.

3.4. Hydrogen Desorption Profiles Obtained from Steels Covered with and without Oxide Scale

Figure 6 shows the hydrogen desorption profiles obtained from the high-chromium ferritic steel with and without exposing to steam.

No hydrogen desorption was observed at the temperatures below about 700 K. But, the hydrogen desorption rate increased largely with increasing temperature over 700 K. However, such a large amount of hydrogen detected over 700 K is of no interest in this study for the following reason. In the hydrogen-detecting system with a gas chromatography, impurity gases must influence inevitably the hydrogen desorption profile at high temperatures. This is because, some chemical reactions take place between the steel and the impurity gases at such high temperatures, and then a large amount of hydrogen gas was formed as shown in Fig. 4. Therefore, hereafter our main concern was focused on the hydrogen to be detected at the temperature lower than 700 K.
growth rate, it is the most important layer to determine the diffusivity of cations and/or anions in the oxide in some ways. For example, Tveten et al.\textsuperscript{20} reported a role of the dissolved hydrogen in the oxide scale on the oxidation mechanism of pure chromium. They showed that the number of chromium-ion vacancies increased with increasing hydrogen concentration in the chromia (Cr\textsubscript{2}O\textsubscript{3}) scale in order to hold charge neutrality in it. This caused the enhancement of outward diffusion of chromium ion in Cr\textsubscript{2}O\textsubscript{3}.

(Fe,Cr)\textsubscript{3}O\textsubscript{4} may be treated on the analogy of this Cr\textsubscript{2}O\textsubscript{3}. In the oxide, Fe\textsubscript{3}O\textsubscript{4}, with the spinel-type structure, Frenkel-type defects, which are pairs of cation vacancy and cation interstitial, are dominant at high temperatures, and then the diffusion coefficient of the cation, $D_C$ (m\textsuperscript{2}s\textsuperscript{-1}), changes depending on the oxygen activity, $a_{O_2}$, as follows:\textsuperscript{22–24}

$$D_C = D_0 a_{O_2}^{2/3} + D_1 a_{O_2}^{-2/3} \quad \text{.........................}(3)$$

where $D_V$ (m\textsuperscript{2}s\textsuperscript{-1}) and $D_I$ (m\textsuperscript{2}s\textsuperscript{-1}) are the partial diffusion coefficients of iron ion via the vacancy and the interstitial, respectively. Also, $a_{O_2}$ is equal to a fractional ratio of the oxygen partial pressure, $P_{O_2}$ (Pa), to the total pressure, $P_{\text{total}} = 1.013 \times 10^5$ Pa (1 atm), i.e., $a_{O_2} = P_{O_2}/P_{\text{total}}$. Here, $D_0$ and $D_1$ are described as the following equations,

$$D_V = D_0^V \exp \left( - \frac{E_V}{RT} \right) \quad \text{.........................}(4)$$

$$D_I = D_0^I \exp \left( - \frac{E_I}{RT} \right) \quad \text{.........................}(5)$$

where $D_0^V$ (m\textsuperscript{2}s\textsuperscript{-1}) and $D_0^I$ (m\textsuperscript{2}s\textsuperscript{-1}) are the frequency factors, $E_V$ (J/mol) and $E_I$ (J/mol) are the activation energy for the cation diffusion due to the vacancy and the interstitial, respectively. Also, $R$ and $T$ have the usual meanings.

Dieckmann et al.\textsuperscript{22,23} showed that the cation diffusivity in Fe\textsubscript{3}O\textsubscript{4} at the temperature of 1 173 to 1 673 K was dominated by the iron-ion vacancy in the range of high oxygen activity, but by the iron-ion interstitial in the range of low oxygen activity. Also, Töpfer et al.\textsuperscript{25} showed that the defect concentration and the diffusion coefficient of cations, iron ion and chromium ion, depended on the composition, $x$, in (Fe\textsubscript{1–}$x$Cr\textsubscript{$x$})\textsubscript{3}O\textsubscript{4} ($x$=0, 0.1, 0.2, 0.3 and 0.4) at 1 473 K. The diffusion coefficients of iron ion and chromium ion changed with the oxygen activity in a similar manner. However, the value of the diffusion coefficient of chromium ion was about three orders of magnitude smaller than that of iron ion. Furthermore, the concentration of the cation vacancy was almost independent of the chromium content, $x$, whereas the concentration of the cation interstitial decreased with $x$, resulting in the small diffusion coefficient of cations in (Fe\textsubscript{1–}$x$Cr\textsubscript{$x$})\textsubscript{3}O\textsubscript{4} in the range of low oxygen activity. Then, $D_I$ for iron ion and chromium ion decreased linearly with increasing chromium content, $x$, and it was about two orders of magnitude lower in (Fe\textsubscript{0.8}Cr\textsubscript{0.2})\textsubscript{3}O\textsubscript{4} than in Fe\textsubscript{3}O\textsubscript{4}.

3.6. Defect Structures in (Fe,Cr)\textsubscript{3}O\textsubscript{4} and Cation Diffusivity

Since the (Fe,Cr)\textsubscript{3}O\textsubscript{4} layer determines the overall scale-growth rate,\textsuperscript{18} it is the most important layer to determine the oxidation resistance of the ternary steel. In addition, a relatively large amount of hydrogen was probably dissolved in this layer during the steam oxidation. According to the literature,\textsuperscript{19–21} the dissolved hydrogen may modify the defect concentration in metal oxides, which may change the diffusivity of cations and/or anions in the oxide in some ways.
Fig. 8. Diffusion coefficients of iron ion and chromium ion in the spinel-type oxide layer in case when cation interstitial dominates the cation diffusivity in the (Fe,Cr)₃O₄ layer.

...um of the interfaces among the oxide layers, we calculated the oxygen activities at the layer boundaries using the thermodynamic data of each oxide. Here, (Fe,Cr)₃O₄ was a solid solution between Fe₃O₄ and FeCr₂O₄, and contained about 23 at% of chromium ion to be substituted for iron ion as mentioned in the Sec. 3.1. In this level of chromium-ion content, the lower limit of the oxygen activity in the spinel phase is not varied drastically by mixing FeCr₂O₄ with Fe₃O₄. Therefore, the value obtained from the equilibrium of FeO/Fe₃O₄ was employed as the oxygen activity at the layer boundary of (Fe,Cr)₃O₄/FeO in this study.

Figure 8 shows the oxygen-activity dependence of the diffusion coefficient of cations in the spinel-type oxide layer. In case when (Fe,Cr)₃O₄ was assumed to be formed in the interstitial-dominant range of the low oxygen activity, the diffusivity of iron ion decreased by one order of magnitude due to the chromium ion in (Fe,Cr)₃O₄. In other words, the (Fe,Cr)₃O₄ layer is more oxidation resistant than the Fe₃O₄ layer. This trend will increase with increasing chromium content in the spinel layer. However, the diffusivity of chromium ion was about three orders of magnitude lower than that of iron ion as mentioned in the preceding Sec. 3.6. In case when hydrogen is dissolved in the spinel-type oxide, the cation interstitial may decrease in order to hold the charge neutrality in it. In this way, the dissolved hydrogen probably works to decrease the diffusivity of chromium ion, resulting in the attendant decrease of the chromium content in the spinel layer. The decrease of the chromium content leads to the increase of the cation-interstitial concentration in (Fe,Cr)₃O₄. As the diffusivity of iron ion may depend more strongly on the chromium content than the dissolved hydrogen, the decrease of the chromium content could increase apparently the iron-ion diffusion in the spinel layer. As a result, the chromium content was further suppressed to be low in (Fe,Cr)₃O₄ in the presence of hydrogen. This is a role of the dissolved hydrogen in deteriorating the oxidation resistance of the ternary steel in steam. On the other hand, such a hydrogen effect will not be dominant in air, resulting in a remarkable atmosphere dependence on the oxidation resistance of the ternary steel, as shown in Figs. 2(c) and 2(d).

In contrast, the amount of the dissolved hydrogen was smaller in pure iron than in the ternary steel. In addition, the nonstoichiometry in FeO is quite large intrinsically. Therefore, the influence of the dissolved hydrogen on the defect-dependent property is probably smaller in FeO than in (Fe,Cr)₃O₄, resulting in the similar oxidation rate of pure iron tested in between air and steam.

4. Conclusion

Employing a thermal desorption spectroscopy (TDS), the amount of hydrogen dissolved in both pure iron and the ternary high-chromium ferritic steel was measured after the steam oxidation test at 923 K. It was found that the amount of the dissolved hydrogen was much larger in the ternary steel than in pure iron. Especially, hydrogen was likely to dissolve preferentially in (Fe,Cr)₃O₄. On the other hand, the strong dependence of the oxidation rate on the atmosphere, air or steam, was observed only in the ternary steel. It was concluded that the hydrogen dissolved in the (Fe,Cr)₃O₄ layer during the steam oxidation caused the more accelerated rate of oxidation in steam than in air.

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