1. Introduction

It is necessary to raise the steam temperature of the fossil fuel power plants in order to improve the efficiency of the plants. For increasing the steam temperature, steam oxidation resistance at elevated temperatures is required for high Cr heat resistant ferritic steels, which are used as the main components of the plants because of their low thermal expansion coefficients.

It is well known phenomenologically that high temperature oxidation of steels is accelerated by the presence of water vapor in the ambient atmosphere. In particular, Nakagawa et al. reported that hydrogen affected the growth rate of the scale in oxidation at elevated temperatures. Using a diffusion system of (Fe, Cr)₃O₄/CoO, cation diffusivity was investigated at 750°C in argon atmosphere or in steam. As a result, the diffusivity of Fe ion in (Fe, Cr)₃O₄ became larger in steam than that in argon atmosphere, indicating that hydrogen (proton) promotes Fe ion outer diffusion from Fe–10Cr alloy. This is direct evidence that high temperature steam accelerates oxidation of Cr containing steels.

The amount of hydrogen dissolved into oxide layers on Fe–10Cr alloy after exposure to steam at 750°C was measured with thermal desorption spectroscopy (TDS). It was found that the dissolved hydrogen existed mainly in (Fe, Cr)₃O₄ spinel layer formed on the alloy surface. This result is related closely to the fact that oxidation of high Cr ferritic steels is accelerated remarkably by the existence of steam at elevated temperatures. Using a diffusion system of (Fe, Cr)₃O₄/CoO, cation diffusivity was investigated at 750°C in argon atmosphere or in steam. As a result, the diffusivity of Fe ion in (Fe, Cr)₃O₄ became larger in steam than that in argon atmosphere, indicating that hydrogen (proton) promotes Fe ion outer diffusion from Fe–10Cr alloy. This is direct evidence that high temperature steam accelerates oxidation of Cr containing steels.

KEY WORDS: ferritic steel; high chromium; steam-oxidation; hydrogen dissolution; iron–chromium spinel.

2. Experimental Procedure

2.1. Specimen

Fe–10mass%Cr alloy was used in this study. This alloy was melted in an arc furnace under a high purity argon atmosphere and formed into button shape ingot. This was annealed at 1000°C for 20 h and then cooled down to room temperature with the rate of 100°C/h. After the heat treatment, the specimens with the size of 5 mm × 5 mm × 30 mm were prepared for a series of experiments. Each specimen was polished on dry emery papers down to 600-grit and then cleaned in an ethanol using an ultrasonic cleaner.

2.2. High-temperature Oxidation Test in Steam

The steam oxidation test was carried out in the following way, and the detail is shown in elsewhere. Each specimen was first set in the furnace equipped with a chamber made of austenitic stainless steel. Then, the furnace was heated up to 200°C, while flowing argon gas in the chamber. During heating, the atmosphere in the chamber was exchanged from argon to steam at 200°C. Steam was generated from water containing oxygen at the level below 3 ppb. When the temperature in the furnace reached to 750°C, the counting of the oxidation time was started and the specimen was kept at 750°C for 100 h into superheated steam under atmosphere pressure. After this exposure to steam, the furnace was cooled down to 250°C, while keeping the steam atmosphere. The atmosphere in the chamber was exchanged from...
steam to argon at this temperature, and immediately the sample was taken out from the chamber. After this steam oxidation test, the cross-sections of the oxidized specimens were observed with a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM/EDX).

2.3. Thermal Desorption Analysis of Dissolved Hydrogen

After the steam oxidation tests, the amount of hydrogen dissolved in the specimen was analyzed using a thermal desorption spectrocope (TDS), equipped with a gas chromatograph. A high purity argon gas was used as the carrier gas in this experiment, but still traces of impurity gases, such as N₂ (<0.3 ppm), O₂ (<0.1 ppm), CO (<0.1 ppm), CO₂ (<0.1 ppm), total hydrocarbon (THC<0.1 ppm) and H₂ (<0.1 ppm), were contained inevitably in the carrier gas.

In order to identify the oxide layer where the hydrogen dissolved in, four specimens of Fe–10Cr binary alloy were prepared. The first one is as-oxidized after the steam oxidation, and the second one has the oxide layer removing mechanically the most outer oxide layer, Fe₂O₃, after the steam oxidation. The third one has only (Fe, Cr)₃O₄ spinel layer removing the outer oxide layers, Fe₂O₃ and Fe₃O₄ after the steam oxidation. The fourth one has no oxide layer by removing all oxide layers after the steam oxidation. The amount of hydrogen in these four specimens was analyzed using TDS in a similar way mentioned above.

2.4. Diffusion Experiment

In order to evaluate the effect of hydrogen (proton) on cation diffusivity in oxides formed on the alloy surface, the diffusion experiment using oxide formed by oxidation of metals was carried out. In this experiment, diffusion system of (Fe, Cr)₃O₄/CoO was selected, because Co can form Co₃O₄ spinel, and Co is quite similar to Fe with respect to the chemical character. This diffusion system was prepared in the following way.

Fe–10Cr binary alloy was oxidized in steam at 700°C for 100 h as mentioned in Sec. 2.2, and then the outer surface oxide was removed by dry polishing mechanically. As a result, (Fe, Cr)₃O₄ surface was obtained. In a similar way, CoO surface was obtained from the oxidation of Co–15Cr alloy in air at 900°C. These (Fe, Cr)₃O₄ surface and CoO surface were set into the diffusion couple with Mo holder as shown in Fig. 1. Here, Al₂O₃ fiber was sandwiched between the two oxides as the original marker and the interface between the alloy and Mo holder was separated by Al₂O₃ powders. Two diffusion couples of the same system, (Fe, Cr)₃O₄/CoO, were prepared. One was annealed in high purity argon atmosphere at 750°C for 100 h, and the other was annealed in steam at 750°C for 100 h in a similar way as mentioned in Sec. 2.2. After these two kinds of diffusion annealing, both couples were cut parallel to the diffusion direction and each section was examined with a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDX) in order to measure the concentration profile. The origin of the concentration profile is set at the position of the Al₂O₃ fiber.

3. Results and Discussion

3.1. Identification of the Layer Dissolving Hydrogen Produced by Steam

It has been found that the hydrogen (or proton) produced by high temperature steam dissolves mainly into oxide layers formed on steel surface during steam oxidation at elevated temperatures. In order to identify the layer where the hydrogen dissolves in, oxides during the steam oxidation tests were removed layer by layer and the thermal desorption analysis was carried out. The morphology of the cross section is shown in Fig. 2. Figure 2(a) shows the cross section of the specimen as-oxidized, and outer porous layer and inner dense layer are observed as reported previously.

Fig. 2 shows the cross section after removing Fe₂O₃ layer, and Fig. 2(c) shows the cross section after removing Fe₂O₃ and Fe₃O₄ after the steam oxidation. The fourth one has no oxide layer by removing all oxide layers after the steam oxidation. The amount of hydrogen in these four specimens was analyzed using TDS in a similar way mentioned above.

Fig. 1. Schematic illustration showing (Fe, Cr)₃O₄/CoO diffusion system.

Fig. 2. Cross section and surface of oxide layers on Fe–10Cr alloy after exposure to steam at 750°C for 100 h, (a). (b) Outer Fe₂O₃ layer is removed, (c) outer Fe₂O₃ and Fe₃O₄ layers are removed, and (d) all oxide layers are removed.
to (a)–(d) in Fig. 2. In Fig. 3, a large spectrum observed at about 200°C in each specimen is known to be caused by hydrogen trapped in oxide layers, whereas a small spectrum at about 350°C observed in (b) and (c) specimen is caused by hydrogen trapped by $M_23C_6$ carbide. The spectrum at 200°C was observed in specimens (a)–(c), but this disappeared in the specimen (d), in particular, the intensity and shape of spectra observed in the specimen (a)–(c) were exactly the same to each other. These facts indicate directly that hydrogen is trapped only in (Fe, Cr)$_3$O$_4$ spinel layer. In fact, the specimen (d) without any oxides shows no spectrum at about 200°C. Here, desorption rate increases over 350°C is attribute to the hydrogen produced by oxidation of alloy, because the surface of specimen (d) is the alloy.

3.2. Cation Diffusion in (Fe, Cr)$_3$O$_4$ Spinel

Figure 4 shows SEM image and the corresponding characteristic X-ray images showing the cross section of the diffusion system, (Fe, Cr)$_3$O$_4$/CoO, after diffusion annealing at 750°C for 100 h in high purity argon atmosphere. Al$_2$O$_3$ fibers as the marker are seen at the diffusion interface. Figure 5 shows similar images of (Fe, Cr)$_3$O$_4$/CoO diffusion system after diffusion annealing at 750°C for 100 h in steam. Comparing these two figures, the thickness of oxide layers in Fig. 5 is larger than that in Fig. 4, because the diffusion system of Fig. 5 is prepared by oxidation in steam. Besides the oxide layer thickness, there is no obvious difference in SEM image and the X-ray images between Fig. 4 and Fig. 5.

However, there is a large difference in concentration profiles in the two diffusion couples, and the results are shown in Figs. 6 and 7. In both figures, SEM images are the same as presented in Fig. 4 and Fig. 5, respectively, and the alumina fibers as the marker are also shown in SEM images in Figs. 6 and 7. The bottom figures in Figs. 6 and 7 show the concentration profiles taken along a line marked in the upper SEM images in Figs. 6 and 7. Comparing Fig. 6 to Fig. 7, it is found that the amount of Fe diffused from (Fe, Cr)$_3$O$_4$ layer to CoO layer is much larger in Fig. 7 than in Fig. 6, indicating that the amount of Fe ions supplied from Fe–10Cr metal through (Fe, Cr)$_3$O$_4$ layer is much larger in diffusion system annealed in steam. This is direct evidence that diffusivity of Fe in (Fe, Cr)$_3$O$_4$ becomes large in steam. In other words, diffusivity of Fe in (Fe, Cr)$_3$O$_4$ becomes large when (Fe, Cr)$_3$O$_4$ spinel contains hydrogen.
(proton). This is most probably the main reason why the existence of steam accelerates oxidation of high Cr ferritic steels.

The mechanism deduced from the above experimental results is shown schematically in Fig. 8. As Tveten et al. reported,7) dissolution of hydrogen (proton) into (Fe, Cr)\(_3\)O\(_4\) layer increases cation vacancies due to keeping charge valance between cations and anions, resulting in increasing the cation diffusivity. Here, diffusivity of Cr ion is much smaller than that of Fe ion in (Fe, Cr)\(_3\)O\(_4\). As a result, it is considered that dissolved hydrogen in (Fe, Cr)\(_3\)O\(_4\) layer promotes the outward diffusion of Fe ion from metal side to oxide layer through (Fe, Cr)\(_3\)O\(_4\) layer.

4. Conclusion

In order to elucidate the accelerated oxidation of high Cr ferritic steels in high temperature steam, hydrogen (proton) behaviour and cation diffusivity in oxides system were investigated. The obtained results are as follows.

1) Hydrogen dissociated from high temperature steam dissolved only in (Fe, Cr)\(_3\)O\(_4\) spinel layer on Fe–Cr alloy and did neither in Fe\(_2\)O\(_3\) layer nor in Fe\(_3\)O\(_4\) layer.

2) It is verified experimentally that Fe ion diffusivity in (Fe, Cr)\(_3\)O\(_4\) layer is promoted by the existence of hydrogen (proton) in it.

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