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Dependence of High-Temperature Steam Oxidation Resistance on the Stability of the Chromium Sulfide in High-Chromium Heat-Resistant Steels

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Abstract

The presence of sulfur at an impurity level in heat resistant steels could improve remarkably the steam oxidation resistance. As is well known, sulfur tends to form sulfides, in particular, chromium sulfides when the steel contains chromium. Therefore, there are two possibilities of sulfur states in the steel. One is in atomic sulfur state as a solid solution, and the other is in sulfide state as a precipitate. However, it still remains unclear which sulfur state contributes largely to the improvement of the steam oxidation resistance of the steels. In order to elucidate the sulfur state operated more effectively in improving the oxidation resistance, the steam oxidation resistance was investigated with high chromium ferritic steels, Fe-10mass%Cr-0.08mass%C-(0~0.015)mass%S, with controlling the sulfur states in them by proper heat treatments. From a series of experiments, it was found that the sulfide state played a more important role in improving the steam oxidation resistance than the atomic sulfur state. Furthermore, this sulfur effect worked significantly in the steam oxidation test performed at the temperatures above 873K which corresponded to the temperature for the chromium sulfide to dissolve and instead for the chromium oxide to form in the steels. This result indicates that the beneficial effect of sulfur in improving the steam oxidation resistance is related closely to the sulfide stability against the oxide in the steels.

1. Introduction

The steam temperature has been increasing in order to raise the efficiency of power generation in advanced energy plants. For the heat resistant steels used in such plants, high-temperature steam oxidation resistance is very important as well as creep strength. According to our previous report^(1,2), the presence of sulfur at an impurity level in both the high chromium ferritic and the austenitic steels could improve remarkably the steam oxidation resistance. However, the steam oxidation resistance of the low chromium ferritic steels could not be improved by the sulfur addition. This fact may imply that the beneficial sulfur effect on the steam oxidation resistance was closely related to the chromium content in the steels.

As is well known, sulfur tends to segregate strongly into any interfaces such as specimen surface, grain boundaries and/or oxide/alloy boundaries. Thus, sulfides were easily formed in the steels at high temperatures. In particular, chromium sulfides were formed in chromium-containing steels because of the strong affinity of sulfur for chromium. Therefore, the sulfur states in high chromium steels are classified mainly into two cases. One is the atomic sulfur state in a solid solution, and the other is the precipitated sulfur state

in chromium sulfides. However, it is not clear which sulfur state works more effectively in improving the steam oxidation resistance. The purpose of the present study is to elucidate the effective sulfur state in high chromium ferritic steels and its role in improving the high-temperature steam oxidation resistance.

2. Experimental Procedure

2.1 Selection of sulfur content

The most important technical points in this study were to control the sulfur content in preparing the specimens and then to control the sulfur state by proper heat treatments. Namely, two kinds of high chromium ferritic steels were prepared; one is the sulfur-free steel and the other is the sulfur-doped steel. Their chemical compositions are listed in Table 1. On the basis of the Fe-S binary phase diagram⁽³⁾, the sulfur content in the sulfur-doped steel was determined so that sulfur made a solid solution with iron at 1473K, but it precipitated as sulfides or segregated in grain boundaries when tempered at 873K. As listed in Table 2, four kinds of heat treatments were carried out by varying the tempering time to promote the precipitation or the segregation of sulfur in the steels. According to the phase diagram, the maximum solubility limit of sulfur in iron at 1473K is 310 ppm in mass% units. Furthermore, from thermodynamic calculations⁽⁴⁾, the solubility limit of sulfur was estimated to be about 270 ppm in a Fe-10%Cr alloy at 1473K. The sulfur content in the sulfur-doped steel was 150 ppm as shown in Table 1, and hence a complete solid solution of sulfur could be present in the steel at 1473K. Also, such a solid solution state was obtained even at room temperature by the water-quenching from 1473K, so that sulfur atoms in the as-quenched specimen were soluble in the matrix or in the martensite phase. On the other hand, when the quenched specimen underwent subsequently the temper treatment as shown in Table 2, sulfur would form sulfides or segregate in the grain boundary, because the solubility limit of sulfur was estimated to be null at 873K. Furthermore, to exclude the effect of the matrix structures on the steam oxidation resistance, the martensitic phase should be maintained in the specimen even after tempering. So, the tempering temperature was set at 873K, a temperature low enough to prevent the microstructural evolution from the martensite phase to the ferrite phase.

Table 1 Chemical compositions of steels used in this study, (mass%).

Steel	C	Cr	S	Fe
sulfur-free steel	0.081	10.06	0.001	Bal.
sulfur-doped steel	0.079	10.05	0.015	Bal.

Table 2 Heat-treatment conditions for controlling the sulfur state in the steels.

No	heat-treatment conditions	sulfur state
1	quench 1473K, 1.8ks	solid solution
2	quench 1473K, 1.8ks + temper 873K, 1.8ks	sulfide and/or grain boundary segregation
3	quench 1473K, 1.8ks + temper 873K, 7.2ks	sulfide and/or grain boundary segregation
4	quench 1473K, 1.8ks + temper 873K, 18ks	sulfide and/or grain boundary segregation

2.2 Specimen preparation

The sulfur-free steel was first prepared in a vacuum induction furnace. On the other hand, the sulfur-doped steels were prepared by remelting the sulfur-free steel together with a proper amount of sulfur in an arc furnace under a high purity argon gas atmosphere. Then, these sulfur-free and sulfur-doped steels were hot-worked at 1423K. These steels were cut into the specimens with the size of 10mmx50mmx5mm and then underwent the proper heat treatment

for controlling the sulfur states in the steel following the ways shown in Table 2. The solution treatment was performed at 1473K for 1.8ks with the hot-worked steel and then followed by water-quenching. This steel was used as the specimen contained atomic sulfur in a solid solution. After quenching, it was cut into three pieces and each was tempered at 873K for three kinds of times, 1.8ks, 7.2ks or 18ks, followed by air-cooling. These steels were used as the specimens contained sulfides as the precipitates. Besides these steels, the enough precipitated ones were also prepared. After hot-working at 1423K as mentioned above, they were normalized at 1323K for 1.8ks and tempered at 1043K for 5.4ks. Each of the specimens were polished with the emery papers down to #2000 followed by the buff polishing with alumina powders down to 1 μ m, and finally cleaned in an acetone solution using an ultrasonic instrument.

2.3 Microstructure observation

Prior to the steam oxidation test, the microstructures and the precipitates existing in the specimen were observed using an optical microscope (OM) and a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM/EDS). For the OM observation, the specimens were etched in the Vilella's reagent of a 50% glycerin-33% hydrochloric acid-17% nitric acid aqueous solution. For the SEM/EDS observation, electropolishing was carried out in an electrolytic solution of 90% acetic acid and 10% perchloric acid.

2.4 Steam oxidation test

A schematic drawing of the system for steam oxidation test is shown in Fig. 1. The time and the temperature for the steam oxidation test were set as shown in Table 3. Every specimen was first set into a furnace equipped with a chamber made of an austenitic stainless steel, and then water was bubbled by argon gas for reducing the amount of dissolved oxygen in water under 3 ppb. Subsequently, argon gas was flowed into the furnace during heating. Then the atmosphere in the furnace was exchanged from argon to steam at 473K. The steam oxidation test was started at the time when the furnace was heated up to each oxidation test temperature. After a set time was passed, the furnace was cooled down, while purging the steam from the chamber with the argon gas. To evaluate the steam oxidation resistance, the mass gain was measured with each specimen after the steam oxidation test using a precision balance with the accuracy of 0.1 mg or better. Also, the specimen surface was observed by the SEM/EDS.

2.5 DTA and TG measurement

In order to investigate the sulfide stability against the oxide formation, a differential thermal analysis (DTA) with a thermal gravimetry (TG) was carried out in air using powders of iron sulfide and chromium sulfide prepared by Kojundo chemical lab Co., Ltd. The powder

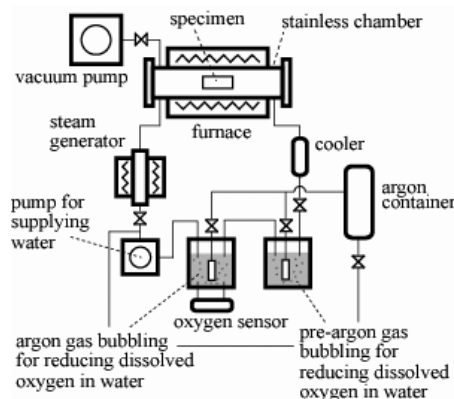


Fig. 1 Schematic illustration showing the system for steam oxidation test.

Table 3 Condition for the steam oxidation test performed in this study.

Temperature, T/K	Time, t/ks
923	28.8
773	720
823	720
873	720
923	720
973	720
1023	720

specimen was heated up from room temperature to 1473K at a constant rate of 0.17K/sec (10K/min).

3. Results and Discussion

3.1 Microstructures in steels before steam oxidation test

For the sulfur-free steel, typical microstructures are shown in Fig. 2 (a) for the quenched specimen, and (b) and (c) for the tempered specimens. Every specimen contained only the martensite phase. This is also the case in the sulfur-doped steel.

Figure 3 (a) shows the SEM image taken from the surface of the sulfur-doped steel tempered at 873K for 18ks. Figure 3 (b) shows the EDS spectrum taken from a precipitate indicated by an arrow in the image (a). It was found from the EDS analysis that the precipitate contained a large amount of sulfur and chromium as shown in Fig. 3 (b), so this precipitate was probably a

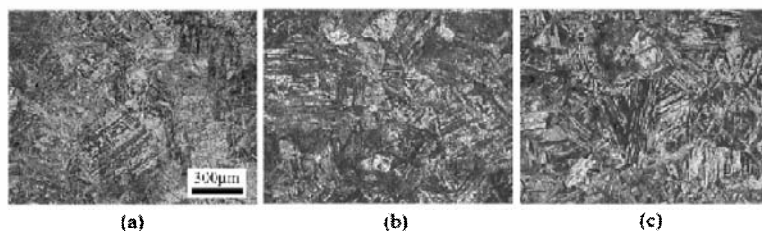


Fig. 2 Microstructures of the sulfur-free steel, (a) in as-quenched state and in tempered state at 873K for (b) 1.8ks and (c) 18ks

chromium sulfide. On the other hand, such precipitates were not observed in the as-quenched specimen of the sulfur-doped steel.

In addition, the microstructural difference was examined among the as-quenched and the tempered specimens of the sulfur-free steel. Figure 4 shows typical SEM images showing the martensitic lath/blocks and carbides in these specimens. Using an image analyzing method, the area fraction of carbides and the average martensitic lath/block width were measured, and the results are shown in Fig. 5 (a) and (b), respectively. From Fig. 5 (a), it was found that the amount of carbides increased monotonously with increasing tempering time. On the other hand, the average martensitic lath/block width increased until 7.2ks and then almost saturated at a certain value around 0.8µm as shown in Fig. 5 (b). Similar tendency was also obtained from the sulfur-doped steel.

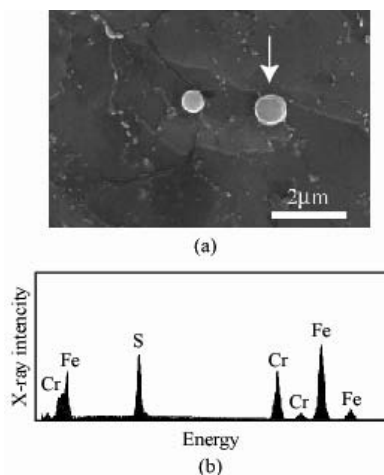


Fig. 3 (a) SEM image of the surface of the S-doped steel tempered at 873K for 18ks and (b) the EDS spectrum taken from a precipitate indicated by an arrow in the image (a).

3.2 Dependence of steam oxidation resistance on sulfur states in steels

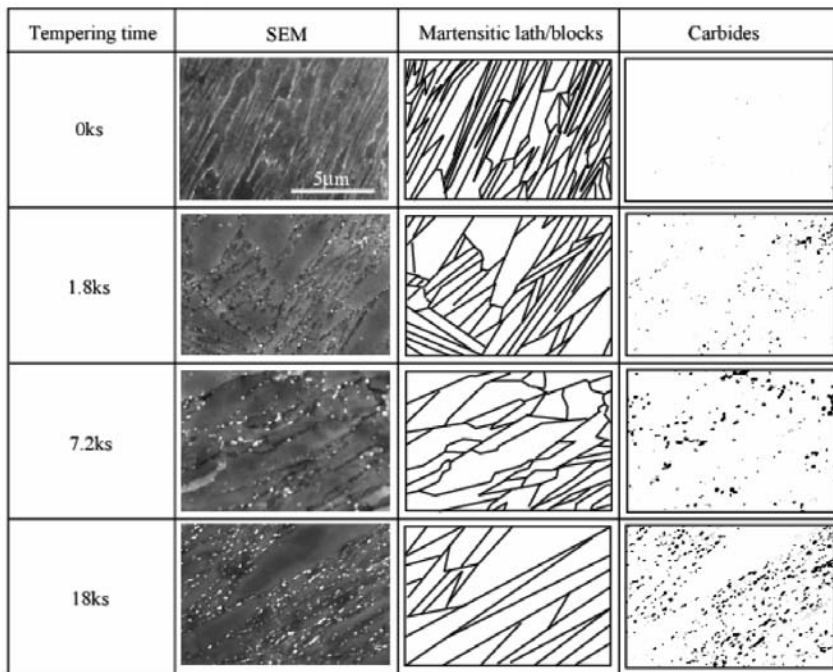


Fig. 4 Images used for the quantification of average martensitic block width and carbides area fraction in the S-free steel tempered at 873K for 0, 1.8, 7.2 and 18ks respectively.

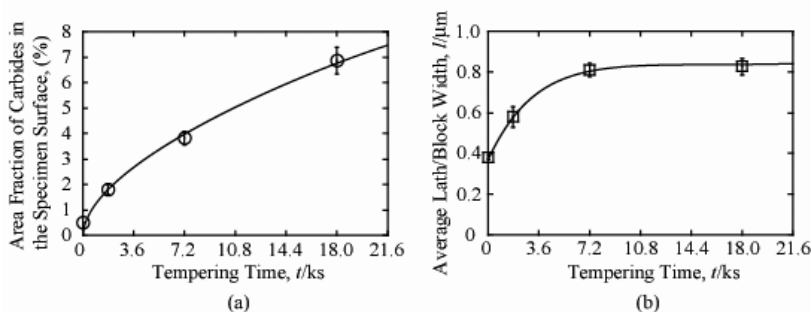


Fig. 5 Changes in (a) area fraction of carbides and (b) average martensitic lath/block width in the S-free steel with tempering time.

The results of mass gains measured after the steam oxidation tests at 923K for 28.8ks are shown in Fig. 6 for both the sulfur-free and the sulfur-doped steels. The mass gains of the as-quenched specimens were nearly similar between the sulfur-free and the sulfur-doped steels. However, there was a clear dependence of the mass gain of the specimens on both the tempering time and the sulfur content in the steels. Namely, the mass gains of the sulfur-doped steel decreased with increasing tempering time, whereas those of the sulfur-free steel increased slightly with increasing tempering time. Figure 7 shows the SEM images taken from the surfaces of the sulfur-free steel and the sulfur-doped steel, both exposed to the steam atmosphere at 923K for 28.8ks. The morphology changed with the sulfur content and also with the tempering time. For example, as shown in Fig. 7 (a), (b) and (c), the surfaces of the sulfur-free steels were covered thoroughly with oxides irrespective of the tempering time. On the other hand, for the sulfur-doped steel shown in Fig. 7 (d), the surface of the as-quenched specimen was covered with oxides in the whole area, as was similar to the surface of the sulfur-free steel. However, only the nodular-like oxides were observed on the surface of the

tempered sulfur-doped steel shown in Fig. 7 (e) and (f). In particular, the formation of such nodular-like oxides was rather limited in the sulfur-doped steel tempered for 18ks as shown in Fig. 7 (f). These morphological changes were consistent with the result that the mass gain of the sulfur-doped steel decreased with increasing the tempering time as shown in Fig. 6.

3.3 Factors affecting steam oxidation resistance of steels

The steam oxidation resistance of the steels used in this study might depend on three factors as follows:

- Grain size including the lath/block size.
- Carbide precipitation.
- Sulfur state.

They were dependent on the tempering time. According to the microstructural observations on the carbides and the martensitic lath/blocks before the steam oxidation test, the amount of carbides increased monotonously with increasing tempering time as shown in Fig. 5 (a). On the other hand, as shown in Fig. 5 (b), the average width of the martensitic lath/blocks became nearly constant when the tempering time exceeded 7.2ks. For the sulfur-free steels, the change of mass-gain with the tempering time shown in Fig. 6 was similar to the change in the area fraction of carbides shown in Fig. 5 (a). In other words, the mass gain of the sulfur-free steels increased monotonously with increasing tempering time as the area fraction of carbides did. It has been reported that the formation of chromium-rich carbides lowers the effective chromium content in the matrix, resulting in the deterioration of the oxidation resistance of steels⁽⁵⁾. Thus, the steam oxidation resistance of the sulfur-free steels might be affected more strongly by the amount of carbide precipitates than the coarsening of martensitic lath/blocks.

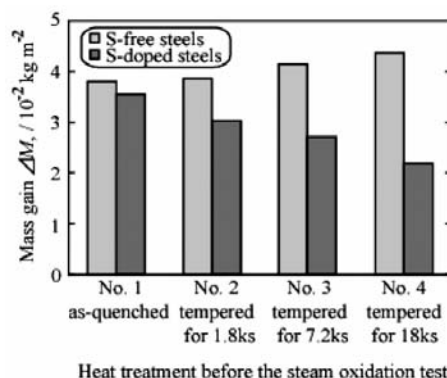


Fig. 6 Mass gains measured after the steam oxidation at 923K for 28.8ks for the S-free and S-doped steels, No. 1, 2, 3 and 4, each heat treated in the way shown in Table 2.

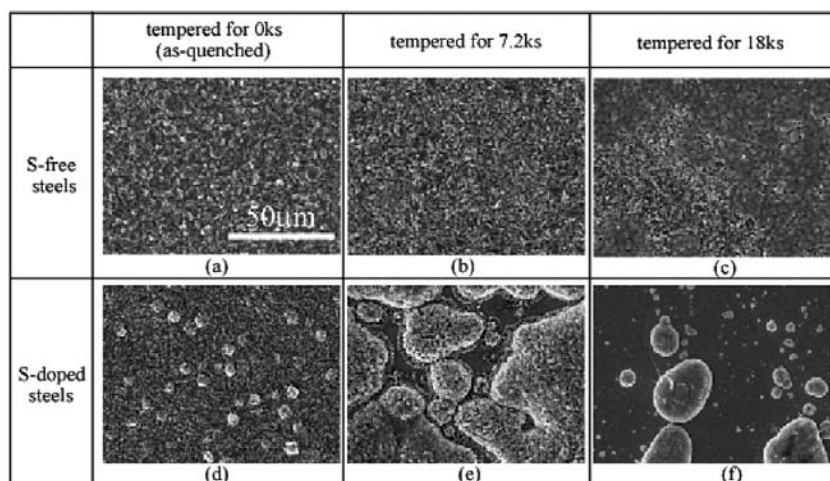


Fig. 7 SEM images taken from the surface of the S-free steels tempered at 873K (a) for 0ks, (b) for 7.2ks and (c) for 18ks, and of the S-doped steels tempered at 873K (d) for 0ks, (e) for 7.2ks and (f) for 18ks after exposing to steam atmosphere at 923K for 28.8ks.

The sulfur-doped steels resembled the sulfur-free steels in the microstructural evolution of

the carbides and martensitic lath/blocks during tempering. Despite this resemblance, the mass gains of the sulfur-doped steels changed in an opposite way to those of the sulfur-free steels as shown in Fig. 6. This difference between the sulfur-free and the sulfur-doped steels was attributable to the difference in the sulfur content between them. As shown in Fig. 3, a chromium sulfide precipitated in the tempered specimen, but it was not observed in the as-quenched specimen. This result implied that sulfide precipitation progressed during tempering. Therefore, it is considered that the atomic sulfur in a solid solution did not work so effectively but the presence of chromium sulfide in the steels operated effectively in improving the steam oxidation resistance.

3.4 Dependence of the sulfur effect on the steam oxidation temperature

Figure 8 shows the mass gains of the sulfur-free and sulfur-doped steel measured after exposing to the steam atmosphere at 773, 823, 873, 923, 973 and 1023K for 720ks. This figure indicates that the dependence of the sulfur effect in improving the steam oxidation resistance of the steels on the temperature of the steam oxidation test. It was found that the mass gains of the sulfur-free steel were almost same with that of the sulfur-doped steel at 773K and 823K. However, the mass gains of the sulfur-doped steels were smaller than those of the sulfur-free steels at the temperature above 873K. This result implies that the beneficial sulfur effect on the improvement of the steam oxidation resistance appeared at the temperature above 873K.

Figure 9 shows the result of TG-DTA measurement performed under air atmosphere using iron sulfide and chromium sulfide powders in the range from room temperature to 1473K. From this figure, it was found that the iron sulfide started to react chemically with air at about 773K. On the other hand, chromium sulfide started to react at about 873K. After the measurement, it was confirmed by X-ray diffraction that the reaction products was Fe_2O_3 and Cr_2O_3 respectively. The temperature, 873K, was consistent with that appearing the sulfur effect in improving the steam oxidation resistance of the steels as shown in Fig. 8. Therefore, the chromium sulfide may relate to the protective chromium-rich oxide formation at the temperature above 873K.

4. Conclusion

In order to elucidate the effective sulfur state in the steels and its role in improving the steam oxidation resistance, the steam oxidation behavior was investigated using the high chromium ferritic steels with varying the sulfur content and the heat treatment. It was found that the

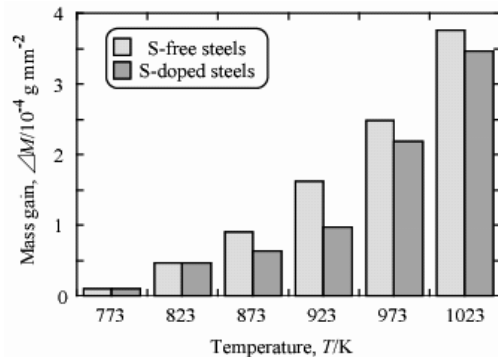


Fig. 8 Dependence of the mass gains taken from the S-free and the S-doped steels on the steam oxidation temperature between 773K and 1023K.

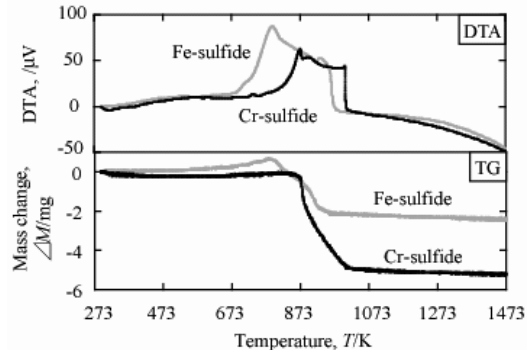


Fig. 9 TG-DTA curves obtained from Fe- and Cr-sulfide.

steam oxidation resistance was improved when sulfur made chromium sulfide, but never improved when sulfur existed in a solid solution. However, chromium sulfide could not exist stably in the oxide at the temperature above 873K. In an oxygen-containing atmosphere, chromium sulfide reacted with oxygen and then chromium oxide was formed as a reaction product. Consequently, it is suggested that this reaction leads to promote the chromium-rich oxide, resulting in the better oxidation resistance of the sulfur-doped steels than that of the sulfur-free steels.

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