

# Oxidation Behavior of Fe-25Cr Alloy under Mechanical Loading in Atmosphere Containing SO<sub>2</sub> at High Temperature

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Fe-25Cr alloy was pre-treated in Ar or N<sub>2</sub>-0.1%SO<sub>2</sub> at 973K, and then external stresses were applied in the N<sub>2</sub>-0.1%SO<sub>2</sub> at 973K. By the pre-treatment, 1 μm thickness scale which consist of a mixture of oxides and sulfides of Cr and/or Fe were formed. With applying stress of 15MPa there was little strain for 36ks, although the scale grew somewhat and an Fe oxide formed at the metal/scale interface. At high stresses, 25 and 30MPa, the scale cracked due to plastic strain between 0.9% and 3.5%, and corrosion progressed very rapidly. In case of the Ar pre-treatment a thin Cr<sub>2</sub>O<sub>3</sub> with 0.1 μm formed on the Fe-25Cr. With applying stress the scale cracked, but corrosion was limited within the cracks. The thin Cr<sub>2</sub>O<sub>3</sub> scale seems to be very effective on corrosion resistance of the Fe-25Cr under external loading, and it was also resistive against the creep deformation.

**Keywords** : Fe-25Cr, SO<sub>2</sub>, external stress, crack formation, oxidation and sulfidation

## 1. Introduction

Materials used at high temperature applications have been often suffered not only from high temperature corrosion, but also by external loadings such as creep and fatigues. Degradation of materials could be progressed synergistically under co-operation of these two factors, and it gives great influence on the service life of the components.<sup>1)</sup> Such things of mechanical fracture of oxide scale, oxidation rate, and material strength under external loading are important to investigate in this co-operated condition. Up to now several reports have dealt with understanding from fundamental and/or phenomenological aspects, such as the effect of surface scale on the strength of materials,<sup>2,3)</sup> effect of mechanical-properties and fracture behavior of oxide scales,<sup>1,4)</sup> the influence of mechanical load on oxidation rate.<sup>5)</sup>

It was generally accepted from investigations<sup>6-9)</sup> on corrosion of several heat resistance steels in gas mixtures bearing S, O, and C at temperatures between 873 and 1073K that a protective oxide scale was cracked at strain reached to 1 to 2%, accompanied with an internal sulfidation. The material strength was also decreased with the progress of internal sulfidation. However, there are still unanswered questions on effect of external loading on

corrosion behavior of iron-based alloys in the mixed oxidant atmospheres containing sulfur.

In the present investigation, the Fe-25Cr was tested in the N<sub>2</sub>-0.1%SO<sub>2</sub> at 973K under various levels of external load in order to inquire into understanding synergetic degradation of the Fe-25Cr. For comparison purpose an Ar gas atmosphere was also used.

## 2. Experimental

An Fe-25Cr alloy used in this study was commercially available, and it has a following nominal composition (mass %): 24.94Cr, 0.04Si, 0.09Mn, 0.03Al, 0.02Ni, 0.001P, 0.002S, 0.006C, and Fe remainder. Grain sizes of the alloy ranged between 250 and 1400 μm. Figure 1 shows a specimen shape. Its dimensions are a gage length of 30mm and a diameter of 6mm, which were fabricated from a 10mm diameter rod stock using a conventional lathe. The gage section of specimens was polished using silicon carbide papers from 150 to 1200 grit, followed by surface finishing with a 3 μm diamond paste.

Figure 2 shows a schematic representation of an apparatus used for this study. A multi-functional testing machine (SERVO-PULSER, Shimadzu Co.) equipped with an environmental quartz chamber and an electric furnace.

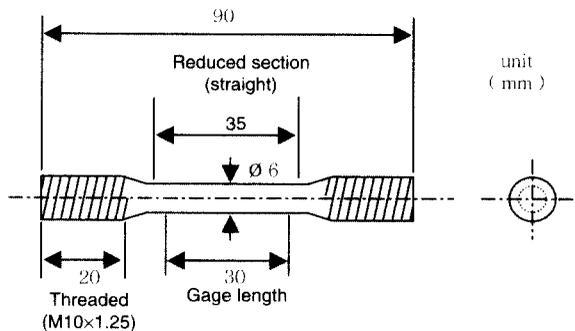


Fig. 1. Specimen for tensile tests at high temperature

Test gases were introduced into a reaction chamber after passing through a narrow helical quartz tube, as shown in Figure 2. Because of difficulty to measure directly elongation of the gage section of the specimen, strain of the gage section was measured at room temperature after testing. Change in strain with time was calculated from the time-displacement chart of a cross-head of the test machine. The values of strain contain 20% error, which seems to occur at the initial stage of testing.

All experiments were carried out at a temperature of 973K. Test gases used in this study are an Ar gas with purity (99.9995 pct purity, O<sub>2</sub> is less than 0.2 ppm) and N<sub>2</sub>-0.1vol.%SO<sub>2</sub>. Partial pressures of O<sub>2</sub> and S<sub>2</sub> in the N<sub>2</sub>-0.1%SO<sub>2</sub> at 973K are  $2.8 \times 10^{-8}$  and  $8.5 \times 10^{-8}$  Pa, respectively. As shown in Figure 3, in which an oxide-sulfides stability diagram is given for Cr and Fe at 973K, both oxides of Cr and Fe are stable phases to be formed in the atmosphere.

After setting a specimen in the test apparatus, a reaction chamber was evacuated and then an Ar gas was introduced, and this process was repeated for several times. After the final evacuation, the test gas was filled in the chamber and continued to pass at a constant rate of  $3.3 \text{ ml s}^{-1}$  during the tensile test. Specimen was heated up to 973K for 3.6ks and then kept there for 7.2ks to stabilize temperature. The process for 10.8ks is called as a pre-treatment in this study. A mechanical load was applied to a specimen in a rate of  $0.73 \text{ MPa/s}$ , after the pre-treatment. At an end of the test the furnace was power-off, and the specimen was cooled under a corrosion gas stream down to 673K.

The morphologies of surfaces and cross-sections of tested specimens were observed by SEM and sometimes with BEI (Back scattered electron image). In case of a thin oxide film, a specimen was prepared by FIB (Focused Ion Beam; JEOL Co.) to observe a microstructure by using TEM. In some cases, a surface scale was peeled off using an adhesion tape and a bottom side of the scale was observed. Compositions of each element in the scale were

Fig. 2. Schematic diagram of the test apparatus

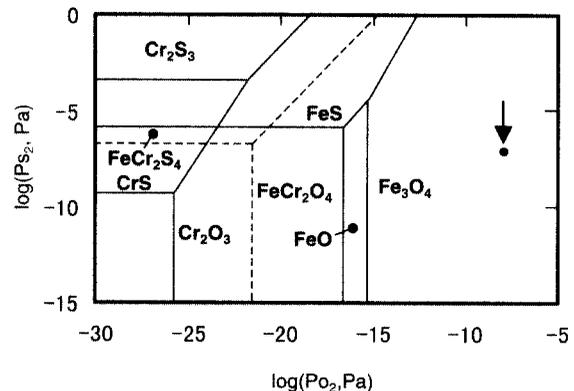


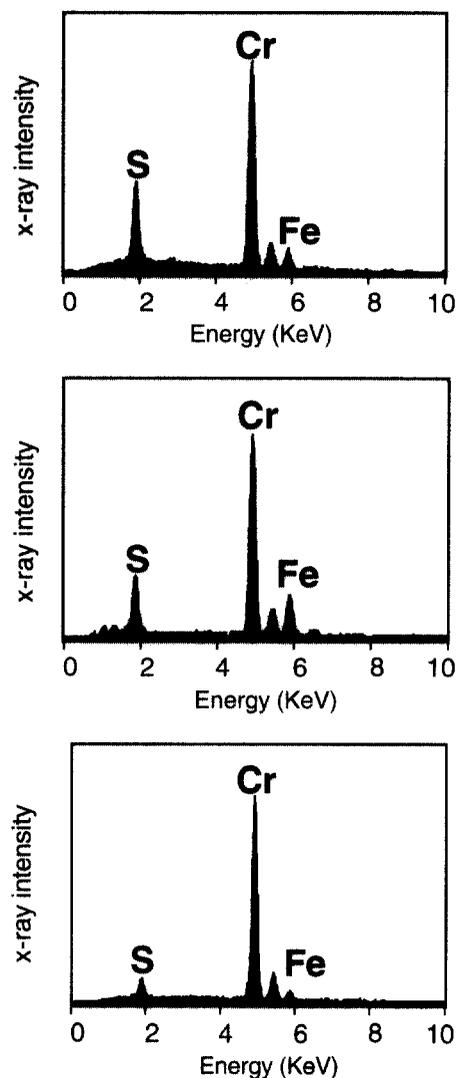
Fig. 3. Phase stability diagram for Cr-O-S and Fe-O-S systems at 973K

analyzed by using EDS, WDS and XRD.

### 3. Results And Discussion

#### 3.1 Corrosion of the Fe-25Cr in the N<sub>2</sub>-0.1%SO<sub>2</sub> at 973K

Without external loading the corroded Fe-25Cr was observed at different stages on surface morphologies of the scale and X-ray intensities of each element were measured. The results obtained are shown in Figure 4 (a), (b), and (c). As shown in Figure 4(a), narrow leaf-like products ( $1 \sim 2 \mu \text{ m}$  length and about  $0.3 \mu \text{ m}$  width) formed on the surface of a specimen during heating up to 973K for 3.6ks. These corrosion products consist of both Cr-sulfides and Cr-oxides. However, with increasing time at 973K the Cr-sulfides gradually disappeared and the scale became relatively flat, consisting mainly of Cr<sub>2</sub>O<sub>3</sub>. It was found that Cr-sulfides formed at an initial stage of the corrosion. However, it is not a thermodynamically stable phase as shown in Figure 3, so that it could be



**Fig. 4.** Surfaces of the Fe-25Cr after test in the  $N_2$ -0.1% $SO_2$  at 973K (a) during heat-up from room temperature to 973K for 3.6ks, (b) after the pre-treatment, (c)corrosion for 36ks after the pre-treatment

**Fig. 5.** Scales on the Fe-25Cr after testing in the  $N_2$ -0.1% $SO_2$  at 973K

(left: cross-section, right: bottom side of a scale). (a) after the pre-treatment (b) corrosion for 36ks after the pre-treatment.

considered that Cr-sulfides formed due to direct reaction between Cr and  $SO_2$  gas under a non-equilibrium condition.

Cross-sections and bottom side of scales of the above specimens are examined as shown in Figure 5. Figure 5

(a) is a specimen after the pre-treatment, and Figure 5 (b) is a specimen corroded for 36ks after the pre-treatment. The thickness of the scale was about  $1\mu m$  and the interface between the scale and the metallic substrate was relatively flat. There is little growth of the scale with

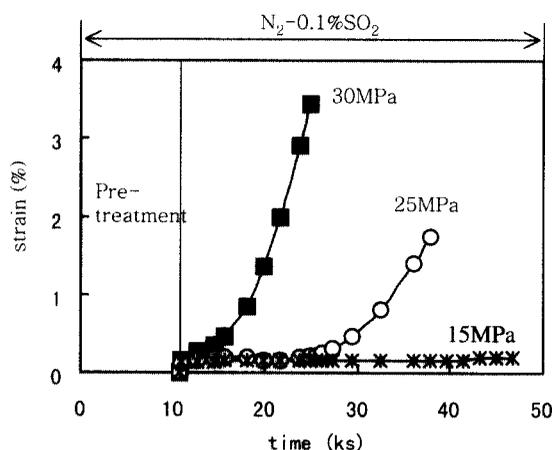
increasing time.

### 3.2 Corrosion behavior of the Fe-25Cr under mechanical load

Different levels of external stress were applied for the Fe-25Cr after the pre-treatment in the N<sub>2</sub>-0.1%SO<sub>2</sub> at 973K. Strain-time curves obtained under 15 ~ 30MPa are shown in Figure 6. There was little deformation (less than 0.1%) under 15MPa for 36ks. With increasing stresses, the strain reached to 1.8% at 25MPa for 27ks and 3.5% at 30MPa for 14.1ks.

Figure 7 shows a cross-section and morphologies of top and bottom surfaces of the scale formed on the Fe-25Cr under 15MPa for 36ks at 973K. It was found that the scale grew thicker and a top surface became rough when compared with those of unstressed specimen in Figure 4(c) and Figure 5. There are two features on the bottom side of the scale, as shown in Figure 8, where (a) is for a flat surface and (b) for corrosion products. The relative X-ray intensities among each element for the flat surface were almost coincided with those in Figure 4(c). On the contrary, X-ray intensity of Fe increased for the corrosion products. It was shown that the newly formed product at the metal/scale interface was almost Fe-oxides.

Figure 9 shows surface morphologies of the Fe-25Cr strained between 0.9% and 3.5% under stresses of 25 and



**Fig. 6.** Strain vs. time curves for the Fe-25Cr in the N<sub>2</sub>-0.1%SO<sub>2</sub> at 973K under stresses of 15, 25, and 30MPa.

30MPa. As shown in Figure 9(a), the scale cracked perpendicular to the tensile axis, and it was found that strain about 0.9% was enough to cause mechanical fracture of a surface scale.

A cross-section and X-ray mappings of each element for the Fe-25Cr strained up to 1.8% under 25MPa are shown in Figure 10. The scale consisted of a multi-layer structure, oxides and sulfides of Cr and/or Fe, and there are nodules on the top surface, which correspond to the cracks in Figure 9. The nodule consisted of Fe-sulfide

**Fig. 7.** Scales on the Fe-25Cr in the N<sub>2</sub>-0.1%SO<sub>2</sub> at 973K for 36ks under a stress of 15MPa, after the pre-treatment (a) cross-section, (b) scale surface of a scale, (c) bottom side of the scale

**Fig. 8.** EDS analyses on a bottom side of the scale formed on the Fe-25Cr in the N<sub>2</sub>-0.1%SO<sub>2</sub> at 973K for 36ks under 15MPa (local area of Figure 7 (c)) (a) a flat area, (b) a corrosion products area

**Fig. 9.** Surfaces of the Fe-25Cr deformed in the  $N_2$ -0.1%SO<sub>2</sub> at 973K under various mechanical loads (a) 0.9% strain under 25MPa for 35ks (b) 1.8% strain under 25MPa for 27ks, (c) 3.5% strain under 30MPa for 14.1ks

**Fig. 10.** X-ray mappings of Fe,Cr,O and S on a scale of the Fe-25Cr in the  $N_2$ -0.1%SO<sub>2</sub> at 973K for 27ks under a stress of 25MPa. A strain was 1.8%

(FeS) surrounded by Fe-oxide (Fe<sub>2</sub>O<sub>3</sub>).

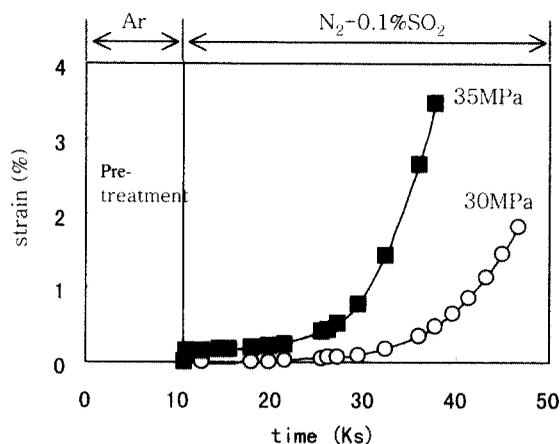
### 3.3 Pre-treatment in Ar

Pre-treatment in Ar at 973K formed an about 100 nm thickness Cr<sub>2</sub>O<sub>3</sub> layer on the Fe-25Cr, as shown in Figure 11. After the Ar pre-treatment, the  $N_2$ -0.1%SO<sub>2</sub> was introduced, and then mechanical loads were applied to the specimen. Strain to time curves under stresses of 30 and 35MPa are shown in Figure 12. It was found that deformation rates were significantly lower than those of the specimens with the  $N_2$ -0.1% SO<sub>2</sub> pre-treatment, when compared with the curves in Figure 6.

Figure 13 shows a surface and a fractured cross-section of a specimen with 3.7% strain under 35MPa with the Ar pre-treatment. Patterns of cracks array in the scale are more regular than that of specimens with the  $N_2$ -0.1%SO<sub>2</sub> pre-treatment. As shown in Figure 9, corrosion was limited at the cracked sites, and there is almost no further

**Fig. 11.** A Cr<sub>2</sub>O<sub>3</sub> layer formed on the Fe-25Cr after the Ar pre-treatment at 973K

corrosion. Accordingly, a thin Cr<sub>2</sub>O<sub>3</sub> layer formed during the Ar-pretreatment has excellent corrosion resistance in the  $N_2$ -0.1%SO<sub>2</sub> at 973K. This seems to be due to a good adhesion of the Cr<sub>2</sub>O<sub>3</sub> scale to the alloy substrate. This property of the scale also reduced the creep rates of the



**Fig. 12.** Stress vs. time curves for the Fe-25Cr in the N<sub>2</sub>-0.1%SO<sub>2</sub> at 973K under stresses of 30 and 35MPa. The pre-treatment was carried out in Ar

alloy. Meanwhile, the scale formed in the N<sub>2</sub>-0.1%SO<sub>2</sub> pre-treatment has lack of adhesion on the substrate and fractured at lower strain. Higher creep rates and rapid corrosion progressed might be caused by these scale properties.

#### 4. Conclusions

1) In case of the N<sub>2</sub>-0.1%SO<sub>2</sub> pre-treatment without external loading, the scale (1 μm) grew with a mixture of oxides and sulfides of Cr and/or Fe, and oxides became rich in the scale with time. With applying a stress of 15MPa the scale remained unchanged, except that Fe oxides tended to form at the metal/scale interface. In higher stresses than 20MPa, the scale cracked and corrosion progressed very rapidly. The 0.9% strain was enough to cause the cracks and rapid corrosion progress.

2) In case of the Ar pre-treatment without external loading, an about 100 nm Cr<sub>2</sub>O<sub>3</sub> formed on the Fe-25Cr. With applying stress the scale cracked, but corrosion was limited within the cracks. The thin Cr<sub>2</sub>O<sub>3</sub> scale was very effective on corrosion resistance of the Fe-25Cr under the creep deformation, and it was also resistive against the creep deformation.

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**Fig. 13.** Surface and fractured morphologies of the scale formed on the Fe-25Cr in the N<sub>2</sub>-0.1%SO<sub>2</sub> at 973K under 35MPa. Strain was 3.7% after testing for 27.6Ks. The pre-treatment was carried out in Ar. (a) Specimen surface, (b) fractured cross-section