Oxidation of Metals, Vol. 12, No. 6, 1978

Microcrack Generation and Its Healing in the Oxide Scale Formed on Fe–Cr Alloys

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Received December 20, 1977

Fe-base alloys containing 5, 10, and 20 wt. % Cr were oxidized in a stream of O_2 *at 750 and 900°C up to 264 hr. A "sulfur decoration" method was applied to detect the cracks generated in the scale during oxidation. This method revealed frequent crack generation and its healing in the scale. In the case of low-Cr alloys, the cracks are filled up with newly formed Fe-rich oxide but may be regenerated during further oxidation. Cracks are generated in the scale on an Fe–20Cr alloy also, although this alloy is not so severely attacked because of rapid healing.*

KEY WORDS: Fe–Cr alloys; high-temperature oxidation; scale cracking; sulfidation; healing.

INTRODUCTION

The resistance of alloys to high-temperature oxidation depends to a large extent on the diffusivity of ionic species in the scale formed on the alloys. In practice, however, the alloys are often attacked severely because of crack generation in the scale and its spallation from the surface. Although the mechanism of crack generation has been discussed by many authors,[1,2] no consistent explanation has been given. In fact, the current experimental methods alone cannot give sufficient information on this phenomenon, e.g., when, where, and how cracks are generated. A sudden increase in oxidation rate strongly suggests that cracks have formed in a scale, but the position and extent of the cracks remain entirely unknown. Although optical and electron

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scanning microscopy can detect microcracks very well, they are not capable of distinguishing the cracks generated during oxidation from those generated in the course of cooling. Brückman *et al.*[3] and Barnes *et al.*[4] showed the direct penetration of gaseous oxygen to the oxide–metal interface on Fe–Cr alloys by successive oxidation by O^{16} and O^{18}. These studies proved clearly the existence of short-circuit paths such as cracks, but the location remained unknown. In addition, they required a special experimental technique of activation analysis.

We successfully detected cracks generated during oxidation by the "sulfur-decoration" method.[5] This method consists of sulfidizing the specimen by H_2S gas for 30–60 sec at the end of an oxidation run and measuring the distribution of S in the scale by an electron probe microanalyzer (EPMA). If there is no crack in the scale, only the surface will be sulfidized, and if any cracks formed, sulfidation will take place along the cracks. EPMA depicts the sulfur distribution, which corresponds to the position of cracks in the scale. In the present study this method was applied to follow the generation and healing of the cracks during oxidation of Fe–Cr alloys containing 5–20% Cr.

EXPERIMENTAL

Sample Preparation. Electrolytic Fe and Cr were weighed and melted. The alloys were hot- and cold-rolled, annealed and cut into coupons about 1 × 1 × 0.1 cm. The coupons were polished through 3/0 grit emery paper, washed with alcohol and distilled water, and dried rapidly. Their compositions are given in Table I.

Oxidation. Drilled specimens, hung with a quartz bar on a boat, were inserted into a furnace heated at a given temperature (750 or 900°C) and oxidized for 5–264 hr in a stream of O_2 passed through silica gel at a flow rate of 200 cm^3/min under atmospheric pressure.

Sulfidation. At the end of an oxidation run, O_2 was replaced by Ar without removing the specimens in the furnace. Then H_2S gas was passed through the reaction tube for 30–60 sec.

Detection of cracks. The specimens were mounted in resin and polished with diamond paste. The sulfur distribution was examined by EPMA.

Table I. Composition of Fe–Cr Alloys, wt.%

Alloy	Fe	Cr	C	Si	Ni	S	Al
Fe–5Cr	Bal.	4.86	0.005	0.002	0.005	0.010	0.003
Fe–10Cr	Bal.	9.50	0.003	0.003	0.004	0.010	0.005
Fe–20Cr	Bal.	19.20	0.005	0.003	0.005	0.010	0.003

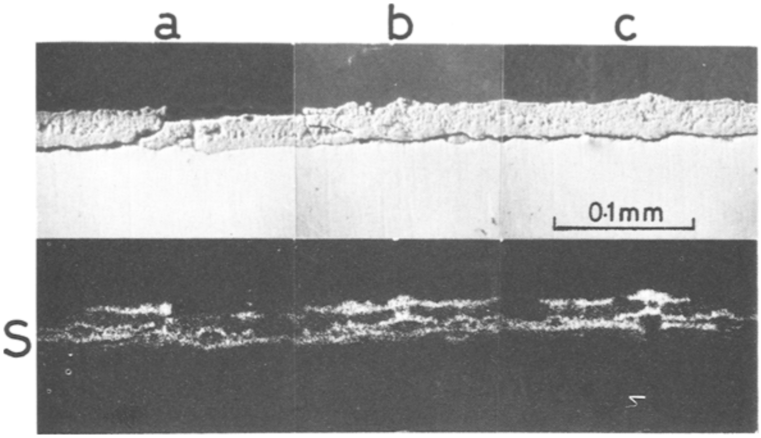

Fig. 1. Distribution of S in the scale on Fe–5Cr oxidized in O_2 at 750°C for 5 hr.

RESULTS AND DISCUSSION

Fe–5Cr

Figures 1–4 represent the results obtained on an Fe–5Cr alloy oxidized in a stream of O_2 at 750°C for 5–264 hr. The scale formed under these conditions was composed essentially of iron oxides, although the inner part was enriched considerably with Cr. Figure 1, which shows the cross section of the alloy oxidized for 5 hr, illustrates the considerable penetration of S

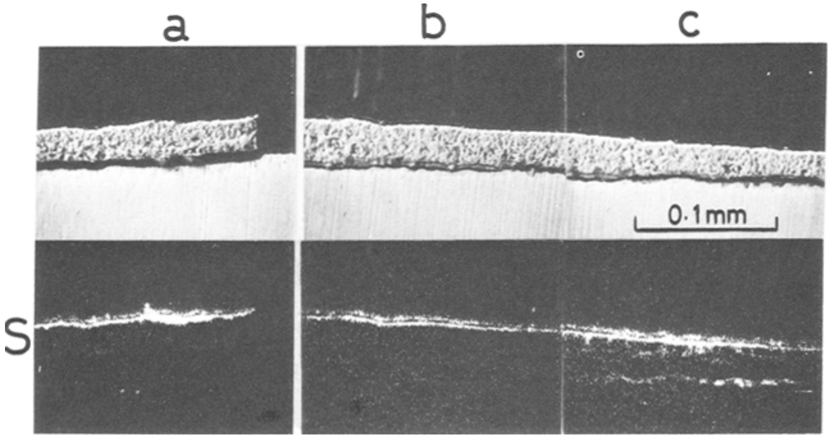

Fig. 2. Distribution of S in the scale on Fe–5Cr oxidized in O_2 at 750°C for 25 hr.

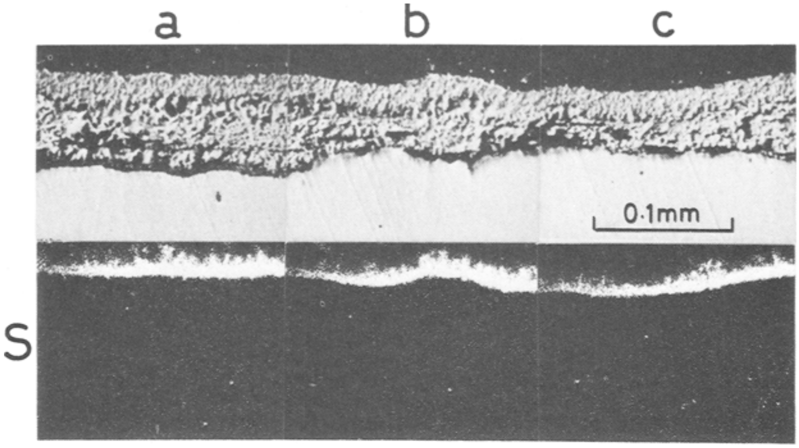

Fig. 3. Distribution of S in the scale on Fe–5Cr oxidized in O_2 at 750°C for 75 hr.

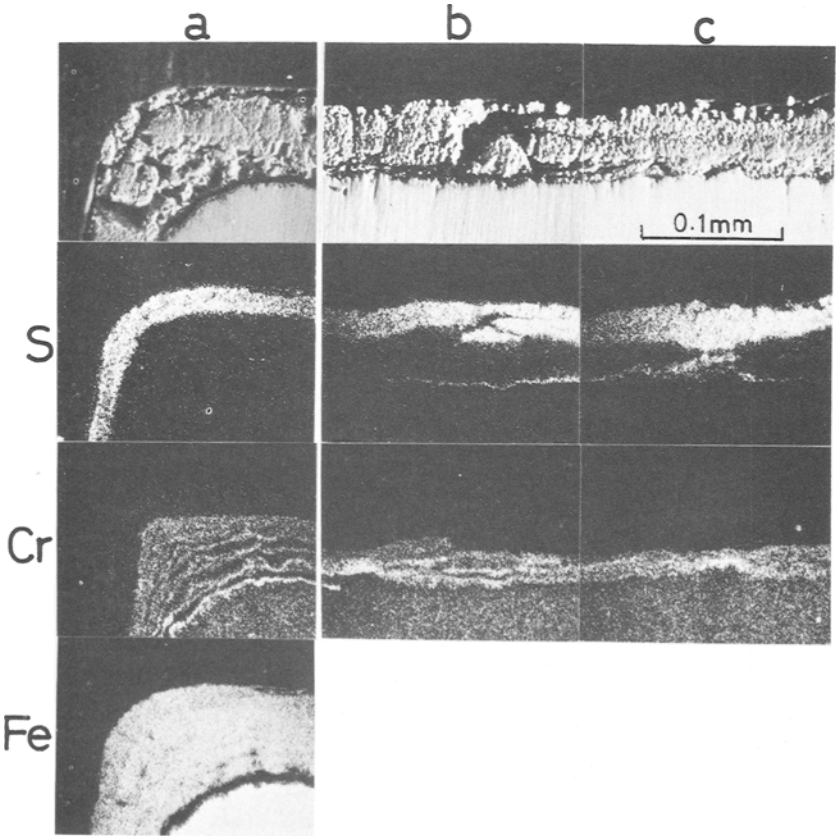

Fig. 4. Distribution of S in the scale on Fe–5Cr oxidized in O_2 at 750°C for 264 hr.

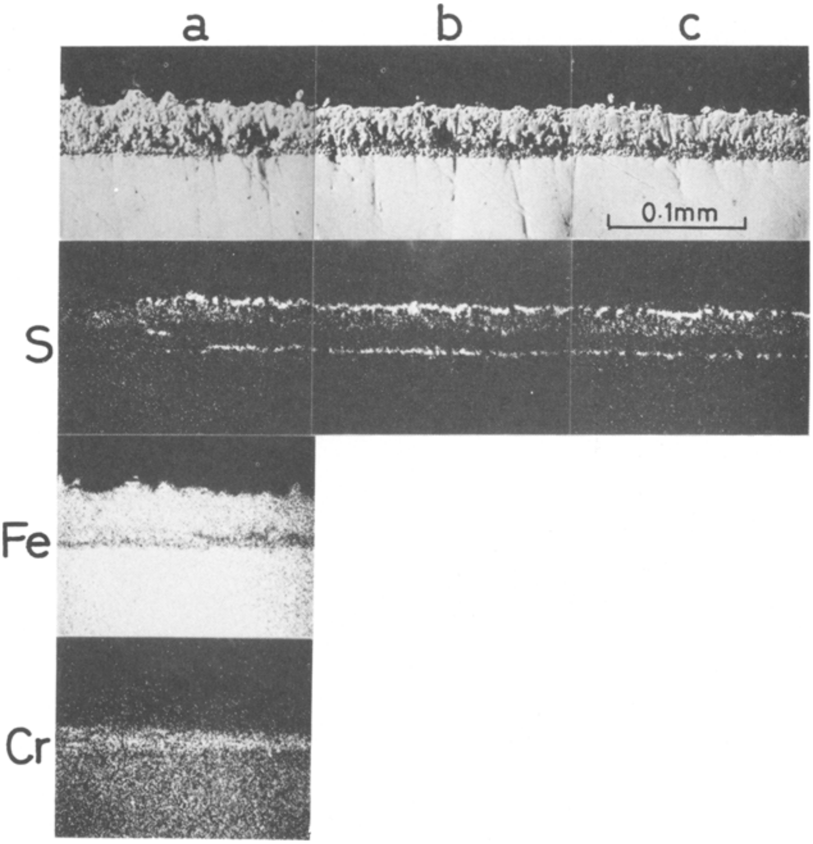

Fig. 5. Distribution of S in the scale on Fe–5Cr oxidized in O_2 at 900°C for 25 hr.

along the scale–alloy interface. This means that the O_2 gas penetrated as far as the scale–alloy interface during the oxidation and accordingly that this scale was little protective. The electronic image of Fig. 1c shows no cracks in the scale, but the corresponding X-ray image of S proves the existence of extensive cracks. Thus a comparison of the electronic image and the distribution of S shows that microcracks in the scale can not be detected by microscopic observation only.

Figure 2 shows the cross section of the 5% Cr alloy oxidized for 25 hr. A slight penetration of sulfur to the scale–alloy interface was noted. The scale on this specimen, however, must have been more cracked in an earlier period of oxidation as shown in Fig. 1. Most of those cracks seem to have been filled up with the oxide produced during further oxidation. It is noted

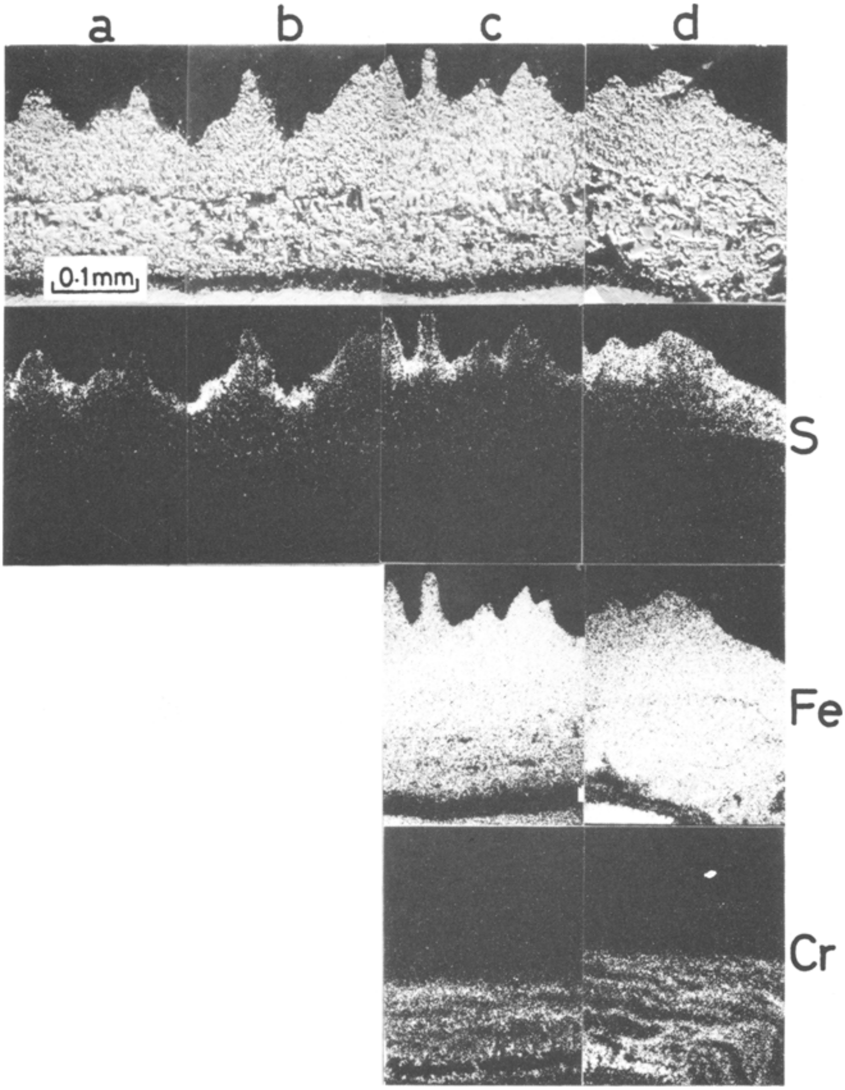

Fig. 6. Distribution of S in the scale on Fe–5Cr oxidized in O_2 at 900°C for 75 hr.

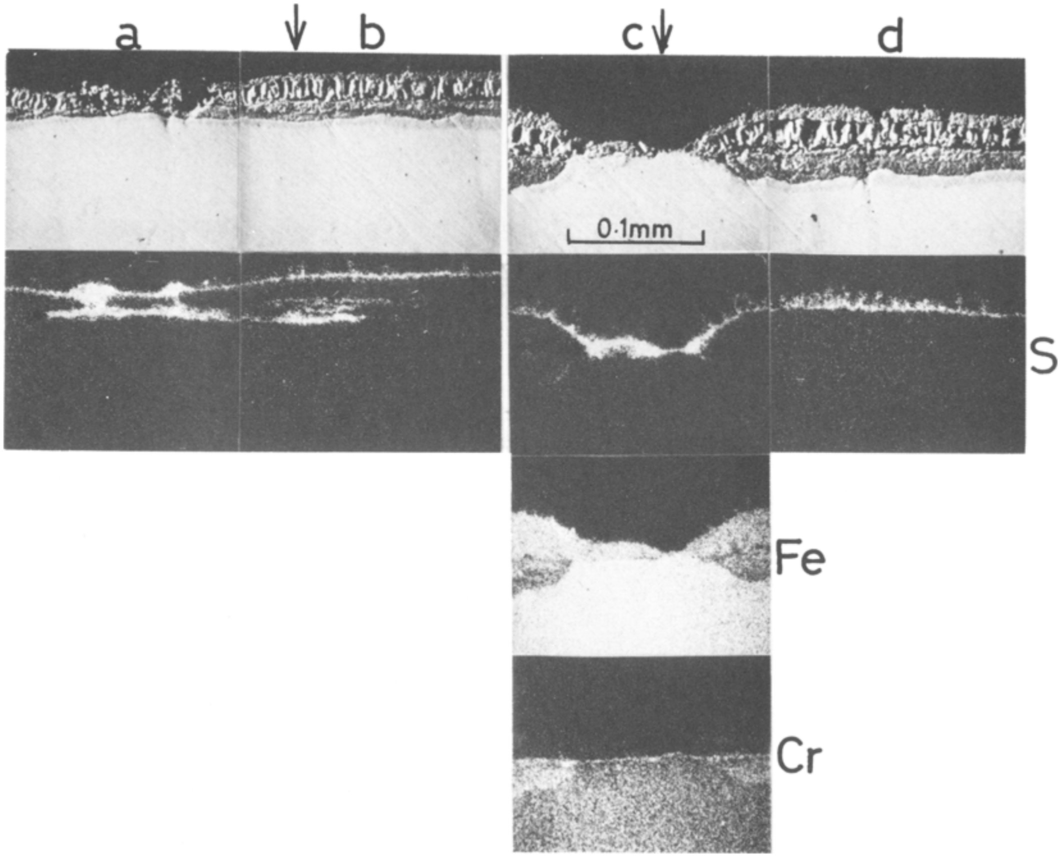

Fig. 7. Distribution of S in the scale on Fe–10Cr oxidized in O_2 at 750°C for 25 hr.

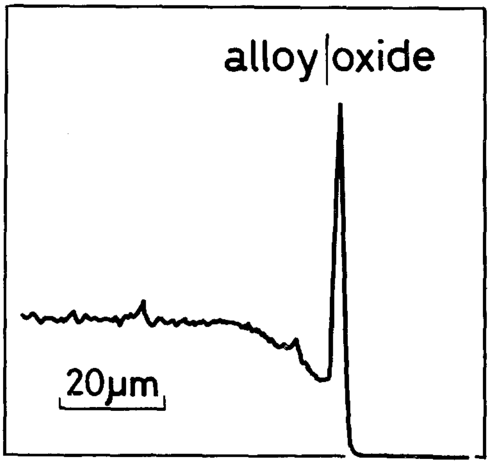

Fig. 8. Cr distribution in Fe–10Cr oxidized in O_2 at 750°C for 25 hr. The formation of a Cr-rich scale caused severe Cr depletion in the substrate. The scanned position is marked with an arrow in Fig. 7c.

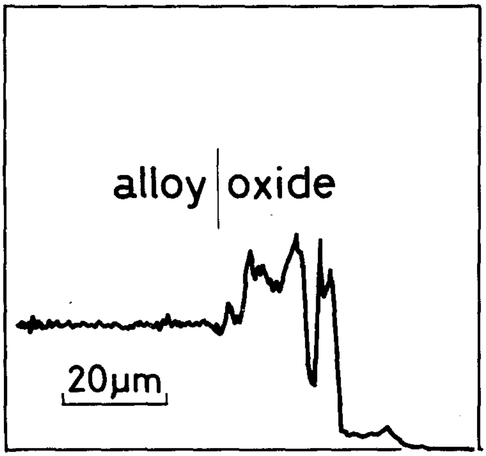

Fig. 9. Cr distribution in Fe–10Cr oxidized in O_2 at 750°C for 25 hr. The penetration of O_2 through cracks consumed a Cr-depleted zone to form an inward-grown oxide. The scanned position is marked with an arrow in Fig. 7b.

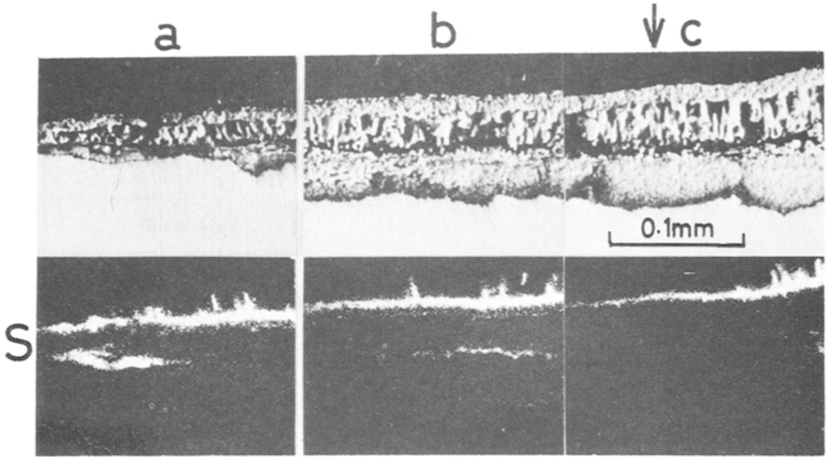

Fig. 10. Distribution of S in the scale on Fe–10Cr oxidized in O_2 at 750°C for 75 hr.

that penetration of sulfur is not observed in Fig. 2a even though part of the scale spalled. This means that this spallation did not occur during oxidation but in the course of cooling. Thus the sulfur-decoration method can distinguish the cracking and spallation in the course of cooling from those during oxidation.

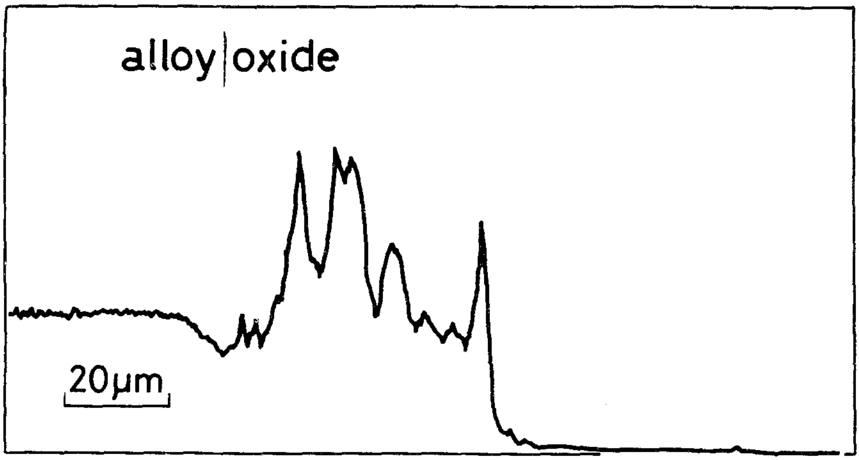

Fig. 11. Cr distribution in Fe–10Cr oxidized in O_2 at 750°C for 75 hr. The filling up of a crack regenerated a Cr-depleted zone. The scanned position is marked with an arrow in Fig. 10c.

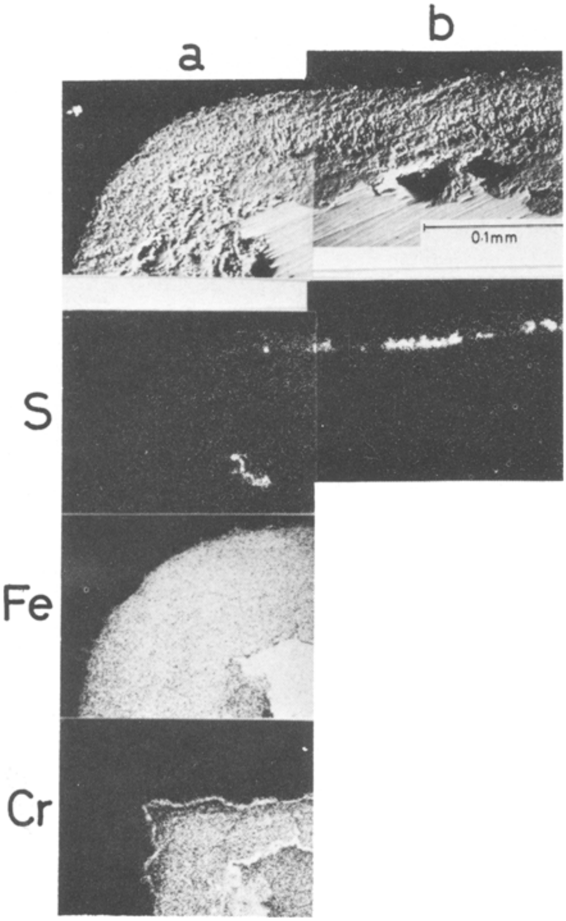

Fig. 12. Distribution of S in the scale on Fe–10Cr oxidized in O_2 at 750°C for 264 hr.

Figure 3 shows the alloy oxidized for 75 hr. There is very little sulfur penetration; the sulfur is confined to the exterior. This means that the cracks were filled up with a newly formed oxide. Three other photographs, not shown in the paper, also revealed no penetration of sulfur. Further oxidation (264 hr), however, generated cracks again (Fig. 4).

Thus we can see clearly that the cracking of scale and its healing repeat during the oxidation of the 5%Cr alloy. This repetition is also seen from several Cr-enriched layers in the scale (X-ray image of Cr in Fig. 4). Figure 4 reveals the uniform penetration of S to about 20 μ in depth over the whole surface of the scale. This S-penetrated layer probably consists of Fe_3O_4 and Fe_2O_3 which are more fragile and thus more cracked than FeO.

Figures 5 and 6 show the results of oxidation of 5% Cr alloy at 900°C. The penetration of sulfur is observed in an early period of oxidation (Fig. 5) and further oxidation must have filled up the cracks (Fig. 6). This is the same feature as seen when oxidized at 750°C, except that the outer layer of the scale was more prone to cracking.

Fe–10Cr

Figures 7–12 show the result of the oxidation of the Fe–10Cr alloy at 750°C in a stream of O_2. Figure 7 represents the cross section of this alloy oxidized for 25 hr. The scale represented in Fig. 7c consists of very thin, intermediate, and very thick parts. A very thin layer enriched with Cr is observed at the original alloy surface (Fig. 7c). This indicates that the Fe–10Cr alloy is covered with a rather protective Cr-enriched scale in the early period of oxidation. The Cr-enriched oxide layer, however, will not be formed again if cracking takes place in this layer, for selective oxidation of Cr results in Cr depletion at the interface (Fig. 8). Thus the alloy continues to be attacked severely once cracks are generated. The distribution of S at each part of the scale in Fig. 7 shows clearly the typical sequence of oxidation: the crack generation (Fig. 7c, the part of intermediate thickness), the O_2 penetration through cracks (Fig. 7a), and the subsequent development of thick scale (Fig. 7b).

Because the O_2 penetration through cracks causes rapid inward growth of oxide, the Cr-depleted zone is consumed (Fig. 9). The oxide which grew inward contains a lot of Fe and is less protective than the initial Cr-enriched oxide. Thus the outward scale growth by cation diffusion is also appreciable. The scale on the Fe–10Cr alloy therefore, consists of two layers: the outer layer which grows outward by cation diffusion (without stress generation) and is composed mainly of Fe oxide, and the inner layer which grows inward by O_2 penetration (accompanied by internal stress generation) and which contains a considerable amount of Cr. Consequently, the scale tends to be cracked along the interface of these two layers. This crack is detected by the penetration of sulfur (Fig. 7b). Such lateral cracking is also seen in Fig. 1.

These cracks, however, are filled up with an oxide formed thereafter. The sulfur penetration is not observed in Fig. 7d, although this part of the scale also must have been cracked in the early stages.

Figure 10 shows a specimen oxidized for 75 hr. It has features similar to those of the 25 hr-oxidized specimen, that is, (a) the crack generation, (b) the lateral cracking along the interface, and (c) the filling up of the crack. The reappearance of the Cr-depleted zone is observed at the interface on which a

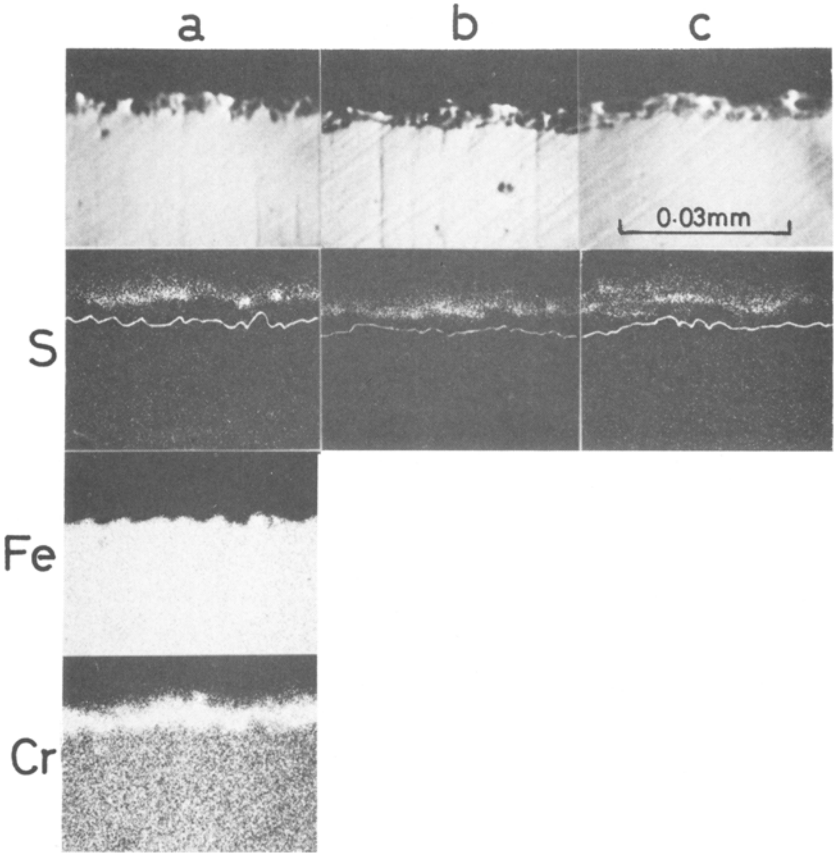

Fig. 13. Distribution of S in the scale on Fe–20Cr oxidized in O_2 at 900°C for 25 hr.

thick and crack-free scale has grown (Fig. 11). The oxygen potential at this interface must be comparatively low, and consequently Cr may have been selectively oxidized.

The result of the oxidation for 264 hr is represented in Fig. 12. Cracks seem to have been filled up generally. But it is expected that further oxidation will generate cracks again.

The following is a summary of the oxidation of the Fe–10Cr alloy. To begin with, this alloy is covered with a protective scale enriched with Cr. The selective oxidation of Cr leaves a Cr-depleted zone just below the scale (Fig. 8), and sufficient Cr for healing is not available at the scale–alloy interface when cracks are generated in the scale. Thus the penetration of O_2 through these cracks causes rapid oxidation, and the Cr-depleted zone is consumed

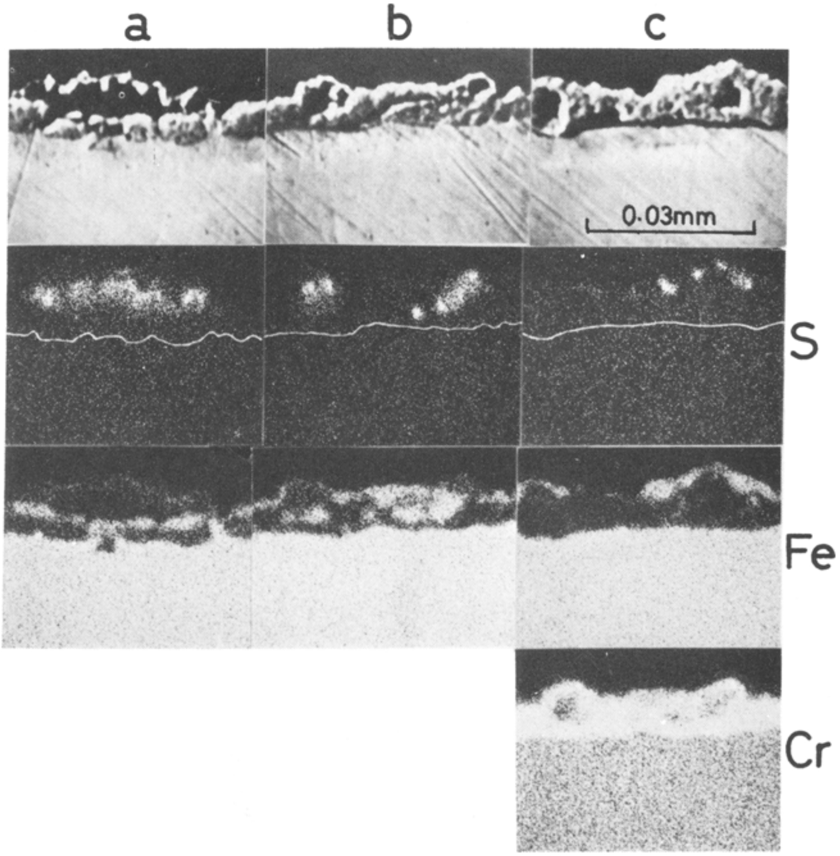

Fig. 14. Distribution of S in the scale on Fe–20Cr oxidized in O_2 at 900°C for 75 hr.

to form an Fe rich oxide. However, when the cracks are filled up with the newly formed oxide, the oxygen potential at the scale–alloy interface is lowered, and the selective oxidation of Cr is resumed. But the complete reformation of Cr-enriched scale is impossible in Fe–10Cr because of regeneration of cracks in the scale. Therefore the total scale thickness of this alloy depends on the endurance of the initial protective scale.

Fe–20Cr

The results on Fe–20Cr oxidized in O_2 at 900°C for 25–200 hr are shown in Figs. 13–15. The oxide scale consists mainly of a single layer of Cr_2O_3 in contrast with Fe–5 and –10Cr alloys. Figure 13 shows the result of

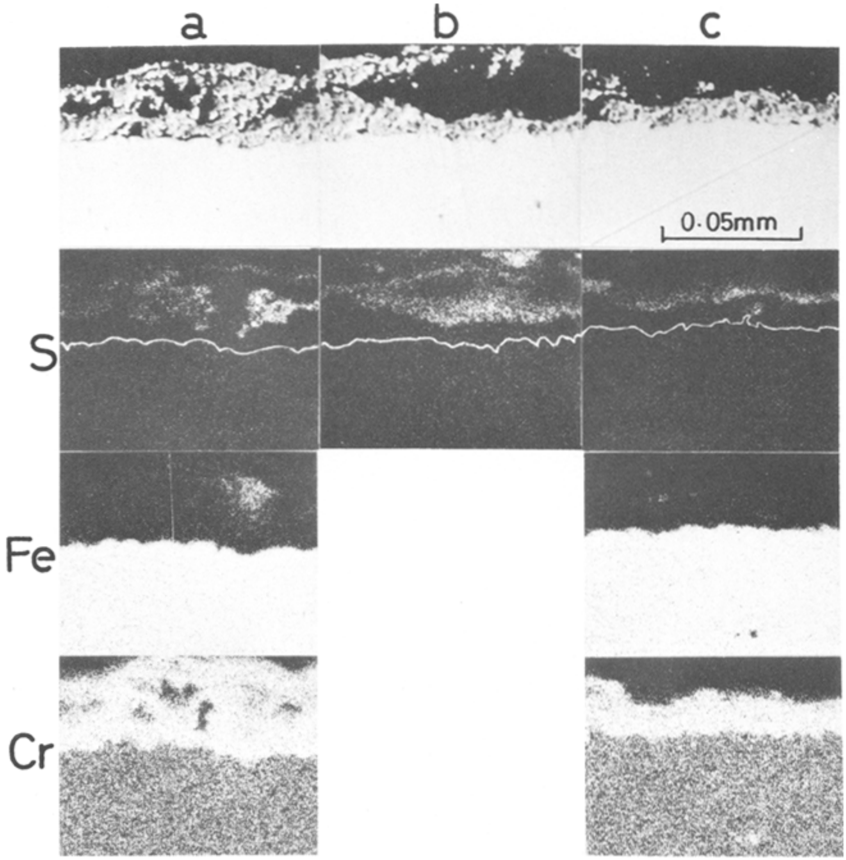

Fig. 15. Distribution of S in the scale on Fe–20Cr oxidized in O_2 at 900°C for 200 hr.

oxidation for 25 hr. The location of the interface between the scale and the alloy is sketched in the photos as a fine white line. Although most of the sulfur remains at the surface, a slight penetration is observed in Fig. 13c, but the sulfur does not reach the scale–alloy interface. This indicates that the scale on 20Cr alloy is not completely protective, but that the alloy resists severe oxidation because of the rapid healing.

Figure 14 shows the result of 75 hr oxidation. One can see some penetration of sulfur (Fig. 14a, b) and appreciable oxidation of Fe, but the penetration does not reach the interface. This also indicates that cracks had formed and subsequently healed.

Figure 15 shows the result of 200 hr oxidation. The penetration of sulfur is increasingly severe with increasing oxidation time. Even at the

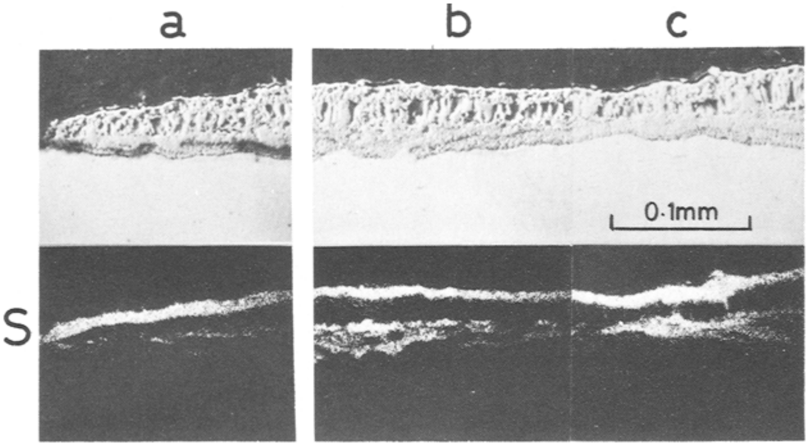

Fig. 16. Distribution of S in the scale on Fe–10Cr oxidized in O_2 at 750°C for 25 hr, quenched to room temperature, and reheated to 750°C for a few minutes.

thinnest part of the scale sulfur penetration was observed (Fig. 14c). However, all the cracks healed sooner.

As seen from Figs. 13–15, the cracks are sometimes generated in the scale on the Fe–20Cr alloy also. However, these cracks are readily healed by virtue of rapid Cr diffusion from the interior to the surface region of the alloy, as discussed in an earlier paper.[6]

Influence of Thermal Shock

The Fe–10Cr alloy was oxidized in O_2 at 750°C for 25 hr. After being quenched to room temperature, it was reheated to 750°C and exposed to H_2S. The result is shown in Fig. 16. The penetration of sulfur is greater in this sample (Fig. 16) than in the sample without thermal shock (Fig. 7), particularly the penetration along the interface between the outward-grown, outer layer and the inward-grown, inner layer. Thus it is concluded that thermal shock promotes crack generation in the scale.

CONCLUSIONS

The following conclusions were reached concerning the oxidation of Fe–Cr alloys containing 5, 10, and 20 wt.% Cr in a stream of dry O_2 at 750 and 900°C for 5–264 hr.

1. Cracks generated in the scale during high-temperature oxidation are successfully detected by the "sulfur-decoration" method.

2. The Fe–Cr alloys exhibited alternating crack generation in the scale and subsequent healing in the following sequence.

Fe–5Cr

1. There are many cracks in the scale in the early period which allow O_2 penetration.
2. These cracks are filled up with newly formed oxide.
3. Further oxidation generates cracks again.

Fe–10Cr

1. Initially, the surface is covered with a protective scale.
2. Once a crack is generated, it is not healed because the Cr in the substrate is depleted near the scale–metal interface.
3. This crack is later filled up with an Fe-rich oxide, but a new crack is generated at another part of the scale.
4. This alloy is eventually covered with a thick scale.

Fe–20Cr

1. The surface is covered with a protective scale.
2. Cracks are sometimes generated in the scale.
3. The cracks are readily healed.

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