Vol. 4 №. 4 TRANSACTIONS OF NFsoc Dec. 1994

PROTECTION AND DAMAGE OF PREFORMED OXIDE SCALES OF Fe-25Cr-5Al AND -10Al ALLOYS DURING THEIR SUBSEQUENT SULFIDATION①

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ABSTRACT

The influence of preoxidation of Fe-25Cr-5Al and Fe-25Cr-10Al alloys on their subsequent sulfidation has been studied by a thermogravimetrical method. The oxidation-sulfidation procedure was decided according to the acoustic emission measurement results of the oxidizing-cooling processes. The transformation from oxidation to sulfidation at high temperatures was achieved. As a result, the outstanding cracking of the oxide scale was avoided. It is found that a complete alumina scale can impede effectively the occurrence and the development of sulfidation. Its protection, however, has a concern with the alloy composition. The microdefects of oxide scale are the places where sulfide nodules appeared and grew. They are also the main factors to decide whether the preformed oxide scale be still protective.

Key words: Fe-25Cr-5Al Fe-25Cr-10Al preoxidation sulfidation

1 INTRODUCTION

Generally, the alumina scale is of more effective protection than the chromia scale. The reasons are, first, the formation of alumina scale thinner than the chromia scale consumes less amount of the alloying element and has a little effect on the alloy composition; second, the Cr_2O_3 is easy to react with O_2 to form CrO_3 to evaporate at high temperatures, but Al_2O_3 is very stable; third, the electron jump energy in Al_2O_3 is very high (about 9.9 eV), thus Al_2O_3 is rather a mixed ionic-electronic conductor than being an electronic one like Cr_2O_3. In addition, the Al_2O_3 has a very high lattice energy, so it is of extreme low ion defect and electron defect concentration. From the oxidation protection point of view, thereby, the alumina scale is better than chromia scale.

The Al_2O_3 scale is also of a better protection than the Cr_2O_3 scale in the case of sulfidation. This has already been proved by some authors' studies[1]. However, most of those studies were carried out in the oxidizing sulfur-bearing environment. In this situation the oxide film was not only destroyed by sulfur, but also remedied by oxygen. Oxygen taking part in the reaction certainly would influence the action of sulfur. For the above reason a harsher environment of H_2S-H_2 mixed gas, i. e. the exclusive sulfidation condition, was exploited in order to highlight the sulfur effect. Moreover, although both the Fe-25Cr-5Al and -10Al alloys can form Al_2O_3 film in the oxidizing environment, the different aluminium contents will result in different purities of alumina, i. e. the different doping of other elements. Therefore, the effect of the Al_2O_3 preformed oxide scale is inevitably influ-

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① Supported by National Natural Science Foundation of China and Corrosion Science Laboratory; received Nov. 29, 1993

enced by the aluminium content of the substrate. The protection of an oxide film is decided by many factors. The basic ones are the integrity, the compactness, the ability of antithermoshock, the micro- and macro-defects, as well as the transport properties of the oxide film. The alloying element content will affect the protection of the oxide film through influencing the above properties of oxide. So in the present paper the study of the influence of preoxidation on the sulfidation of two alloys with different aluminium content, i. e. Fe-25Cr-5Al and Fe-25Cr-10Al has been conducted. The protection and failure mechanism of Al_2O_3 preoxidized film has been discussed according to the observation and analysis of the corrosion products by SEM, EDAX, EPMA and XRD.

2 EXPERIMENTAL

2. 1 *Experimental Apparatus*

The quartz spring thermobalance used in the test was almost the same as the one described in ref. [2]. In order to preoxidize the sample before sulfidation, another tube to supply a constant flow of oxygen to the quartz reaction chamber was attached. The flow of oxygen was controlled precisely by a steady pressure valve, a steady flow valve and a flow meter.

2. 2 *Preoxidation and Sulfidation*

After its surface treatment, the sample was suspended from the lower end of the spring and the reaction chamber sealed. The chamber was vacuumed by a rotary pump and then filled with pure O_2 to 10^5 Pa pressure. A constant flow being 20 mL/min was kept. After the temperature of the electric furnace went up to 1 000 ℃ and became stable, the furnace was lifted up to enable the sample being located in the centre of the steady temperature zone. Then the preoxidation began. The oxidation time were 10, 2 and 0. 5 h alternatively. When the preoxidation time was reached, the specimen was cooled with the furnace from 1 000 ℃ to 850 ℃. The cooling rate was 5 ℃/min, the choice of which was referred to ref. [3]. Afterwards, the O_2 in the reaction chamber was exhausted, the H_2S-H_2 mixed gas with a sulfur pressure of 0. 57 Pa was filled into the reaction chamber at high temperature. After the gas flow was stable (about 5 min), the dependence of the elongation of the spring on time began to be recorded. When the sulfidation weight-gain exceeded 5 mg/cm^2, closed the gases, lowered the furnace and stopped the reaction.

3 RESULTS

3. 1 *Reaction Kinetics*

Fig. 1 shows the preoxidation-sulfidation kinetics curves of Fe-25Cr-5Al and -10Al alloys. To show the effect of preoxidation, the sulfidation kinetics curves of bare Fe-25Cr-5Al and -10Al were also given in the same diagram. By comparision with the results in ref. [4] it can be found that the Al_2O_3 preformed oxide scales formed on Fe-25Cr-5Al and -10Al were of a much better protection than the Cr_2O_3 scale formed on the Fe-25Cr alloy. What is different from the sulfidation is that the weight-gain of Fe-25Cr-5Al was lower than that of Fe-25Cr-10Al after their preoxidation. This shows that the protection of the Al_2O_3 formed on the Fe-25Cr-5Al was better than that on the Fe-25Cr-10Al. Not any weight change for the Fe-25Cr-5Al

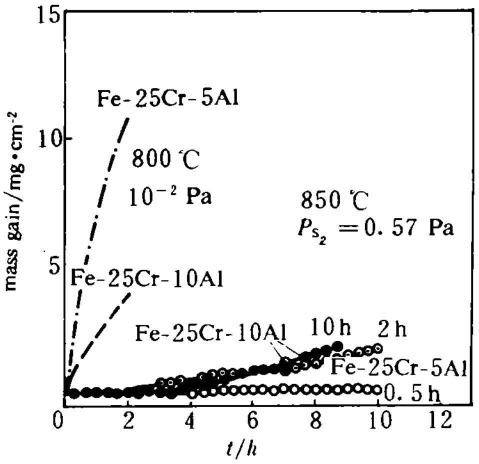

Fig. 1 **Sulfidation kinetics of Fe-25Cr-5Al and -10Al alloys at 850 ℃ and P_{S_2} = 0. 57 Pa in H_2S-H_2 mixed gas after different preoxidation at 1 000 ℃**

after its three kinds of preoxidation appeared in the period of 10 h sulfidation. However, the weight of Fe-25Cr-10Al preoxidized for 2 h and 10 h increased slowly after only 3 h sulfidation, but the weight-gain of the sample preoxidized for 0.5 h was extremely low.

3.2 *Morphologies, Structure and Composition of Corrosion Products*

Fig. 2 shows the surface morphologies of the oxide scales after 10 h preoxidation of the two alloys. The difference of aluminium content resulted in a remarkable difference in the oxide scale morphologies. The oxide scale of Fe-25Cr-5Al was thicker and flater, but the oxide scale of Fe-25Cr-10Al was very thin and a netted ridge structure appeared. Their weight-gains after 10 h oxidation were 0.18 and 0.09 mg/cm^2, respectively. The analysis of XRD demonstrates the main oxide on both alloys was α-Al_2O_3, which is the only stable aluminium oxide at high temperature. But the analysis of EDAX shows that there exists iron and chromium in addition to aluminium in the oxide. The atomic percentages of the three metal elements in the oxide scales are 53.71% Al, 20.54% Cr, 25.75% Fe for Fe-25Cr-5Al and 79.29% Al, 6.56% Cr, 14.15% Fe for Fe-25Cr-10Al. The composition is of little difference at different areas.

It can be concluded from the above results that the α-Al_2O_3 was doped by iron and chromium, whether a spinel oxide formed or not is not able to be sure.

No sulfide was found on the surface of Fe-25Cr-5Al preoxidized for the three kinds of periods of time, oxide scales maintained basically the initial state after sulfidation. The typical sulfide morphologies on the surface of Fe-25Cr-10Al is shown in Fig. 3. Sulfides in the shape of chrysanthemum distributed unevenly on the oxide scale. The sulfide shapes were different, but basically in the shape of flake or match. Fig. 3(b) and 3(c) show the high magnification morphologies of these two kinds of sulfides. The sulfide ball in Fig. 3(c) was just beginning to break through the oxide scale. It is indicated by the EDAX analysis that the sulfide crystal in the shape of match was mainly composed of sulfur, chromium and iron, the aluminium content was extremely low. The chromium content was high in the flake shape sulfide. However, the contents of chromium and aluminium were high in the equiaxial sulfide grains around. In a word, the nearer the position to the ball centre was, the higher the aluminium content became.

Fig. 3(d) shows the distribution of sulfide balls on Fe-25Cr-10Al preoxidized for 10 h after sulfidation. It can be concluded that sulfides located mostly along the oxide ridges. This indicates the oxide ridges were the weak parts of the oxide scale and the place at which sulfides could easily form. As contrasted with the above, the oxide scale of Fe-25Cr-10Al was more even after a shorter period of preoxidation and was of no ridges. The number of the sulfide ball was not very much on the whole

Fig. 2 Surface morphologies of preoxidized scales on Fe-25Cr-5Al(a) and Fe-25Cr-10Al(b) alloys after furnace cooling

sample surface. This is completely consistent with the kinetics results.

Fig. 4 shows the sulfide cross-sections of Fe-25Cr-10Al. The interface between sulfides and the base was lower than the initial surface. This was evidently resulted from the outwards diffusion of metal ions. It can also be found by a careful observation that an uneven internal sulfidation occured in the alloy substrate under the sulfide balls and developed mostly along grain boundaries. The internal sulfidation zone was predominantly composed of the sulfide of aluminium by analysis of EPMA.

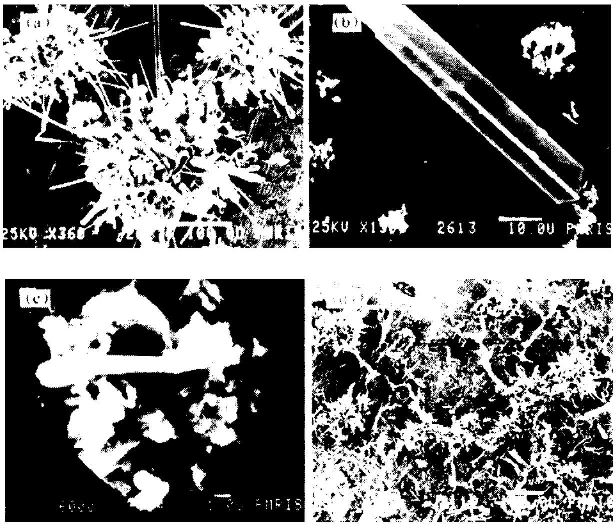

Fig. 3 Surface morphologies of Fe-25Cr-10Al sulfidized for 10h
(a), (b), (c)—preoxidized for 0.5h; (d)—preoxidized for 10h

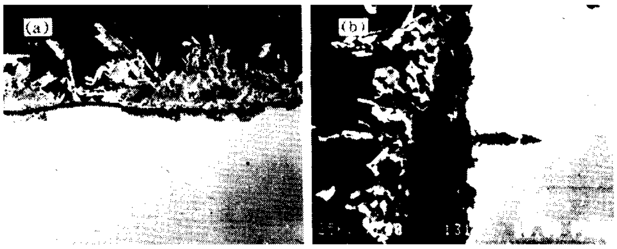

Fig. 4 Cross-section of sulfide formed on preoxidized Fe-25Cr-10Al alloy in H_2S-H_2 mixed gas at 850 °C and $P_{S_2} = 0.5$ Pa for 10h

Chromium distributed uniformly in every layer of the sulfide scale, but iron enriched in the outer layer.

4 DISCUSSION

It can be concluded from the above result that the protection of Al_2O_3 is much better than that of Cr_2O_3[4]. Although the Al_2O_3 scale is broken by sulfides, the sulfidation rate of the aluminium bearing alloy is also very slow. This is not only because the growth rate of Al_2S_3 is rather low[2], but also the formation and the growth of sulfides occur not on the whole surface of oxide scale, but at some local areas only.

The oxide scale on Fe-25Cr-5Al is very stable under the very harsh sulfidation condition in the present study. No sulfides are found on the sample surface after the sulfidation for more than 10 h. Mari *et al*[5] has found that no sulfide could be observed on the surface of Fe-25Cr-5Al sulfidized in the H_2S-H_2 gas mixture with a 1.5 Pa sulfur pressure at 900 ℃ for 100h after oxidation at 1 000 ℃ for only 30min. However, it is different from this that sulfides appear on the oxide scale of Fe-25Cr-10Al, and the shorter the preoxidation time, the longer the protection time. It can be determined that the effect of the body diffusion of sulfur in the Al_2O_3 scale is negligible by the analysis of the distribution of sulfides on the oxide scale surface, and the effect of micro-defects for the oxide scale is very outstanding. The oxide ridges appear along the grain boundaries or the scratch traces by the abrasion of the alloy substrate. Wood *et al*[6] have put forward two models about the formation of this kind of ridge.

The appearance of the oxide ridges is harmful to the protection of Al_2O_3 scale. Especially the cracking of the ridges during cooling will lead to the direct contact between the sulfur-containing gas passing through the oxide scale fissures and the alloy base. Thus sulfides form and grow in these places. This can be inferred from the distribution of sulfides along ridges in Fig. 3(d). In order to explain the harmful effect of the ridges on the oxide scale, a model is put forward in Fig. 5. Firstly, sulfur passes through crevices in the ridges and contact with the alloy base. The sulfide nodules form on the base surface. Because the affinity of aluminium with sulfur is higher than that of chromium or iron with sulfur, Al_2S_3 forms preferentially, certainly with the doping of chromium and iron. The doping of chromium and iron increases the cation defect concentration of Al_2S_3. Chromium and iron diffuse outwards through Al_2S_3 to combine with sulfur on the sulfide surface. Although the defect structure and transport properties of Al_2S_3 are not clear, one of the common features is that the mutual-solubility is very high between different sulfides. Along with the progress of the reaction, metal ions diffuse outwards and sulfur inwards through the formed sulfide phase continuously. Under most of the sulfide balls appears the internal sulfidation along grain boundaries. Since the sulfur pressure is

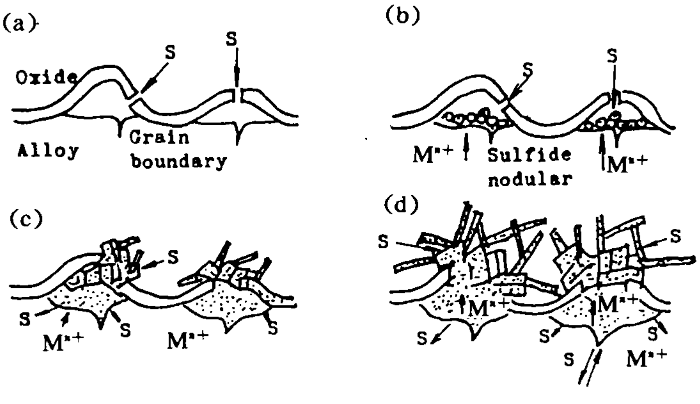

Fig. 5 A progressive development model of sulfide through Al_2O_3 scale on preoxidized Fe-25Cr-10Al alloy at high temperature

very low, about being the decomposition pressure of the sulfide, in the interface between the sulfide and the alloy base, and deffects in the grain boundaries are much more than in the inner part of the grains. In addition the alloying elements are easy to segregate to grain boundaries, so the metal in grain boundaries is easy to be sulfidized preferentially. The sulfidation along grain boundaries destroys the combination among the grains and has a strong influence on the mechanical properties of metallic materials.

The analysis of EDAX indicates that the chromium content is rather high in the alumina scale on Fe-25Cr-5Al. After a 10 h preoxidation, the oxide scale on Fe-25Cr-5Al is rather flat and no oxide ridges appear, this may be the result of chromium doping. The AE(acoustic emission) measurements in the former paper of the authors[3] show that the cracking of alumina scale on Fe-25Cr-10Al is more serious than on Fe-25Cr-5Al, i. e. the tendency to form miro-crevice of the former's oxide scale is larger than that of the later's. Because the destruction of the Al_2O_3 scale concentrates mainly in the micro-defects i. e. the oxide ridges, to decrease or to eliminate these defects will certainly improve the protection of alumina scale remarkably. The doping of chromium to Al_2O_3 and its influence on the micro-defect of Al_2O_3 need to be studied in more detail further.

5 CONCLUSIONS

(1) An integrated alumina scale can hinder effectively the formation of sulfides. Even Fe-25Cr-5Al was preoxidized in the pure O_2 only for 30 min, no sulfides can be found after its sulfidation for 10h in the H_2S-H_2 gas mixture with $P_{S_2} = 0.57$ Pa at 850 ℃. Sulfide balls appear on Fe-25Cr-10Al preoxidized for the three kinds of time. The weight-gain incubation of sulfidation of Fe-25Cr-10Al has no relationship with the period of preoxidation time.

(2) The Al_2O_3 scale on Fe-25Cr-5Al is very flat and has large amount of chromium doping in it; but the neted oxide ridges formed on the oxide scale of Fe-25Cr-10Al along grain boundaries of scratch traces of the alloy base after the 10h preoxidation, in which the content of chromium is very low.

(3) Sulfide balls distribute predominantly along the oxide ridges. The micro-defects are the places where sulfides form and grow. The body diffusion of sulfur in Al_2O_3 is not evident and not the main factor to determine the destruction of the preoxidized scale.

(4) Sulfides form preferentially on the grain boudaries of the alloy base. In most cases the internal sulfidation occurs under sulfide balls.

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