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Effect of Pre-oxidation on High Temperature Sulfidation Behavior of FeCr and FeCrAl Alloys

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Abstract: High temperature corrosion of structural alloys in sulfur bearing environments is many orders of magnitude higher than in oxidizing environments. Efforts to increase sulfidation resistance of these alloys include addition of alloying elements. Aluminum additions to iron-chromium alloys bring about increase in sulfidation resistance. This paper reports the effect of pre-oxidation on the sulfidation behavior of Fe-20Cr and Fe-20Cr-5Al alloys in H_2-2%H_2S environment at 800° C. The surfaces of sulfidized specimens were also examined. Pre-oxidation of the two alloys results in an incubation period during subsequent sulfidation. After this incubation period, the Fe-20Cr alloy showed sulfidation behavior similar to that when the alloy was not pre-oxidized. The incubation period during sulfidation of the Fe-20Cr-5Al alloy was significantly longer, over 45 hours, compared to 2 hours for the Al free alloy. Based on the microscopic and gravimetric data a mechanism for sulfidation of these alloys with pre-oxidation has been proposed.

Keywords: Sulfidation, iron-chromium alloy, iron-chromium-aluminium alloy; pre-oxidation.

1. Introduction

The resistance of structural alloys to rapid degradation in aggressive environments at elevated temperatures usually depends on the ability of the alloys to form and maintain a protective reaction product scale. In most oxidizing environments, Cr_2O_3 is the predominant constituent of the scale on chromium containing iron based alloys. These have been the main alloys used in elevated temperature applications and in regions of coal gasification and petrochemical processes. The gas environments in these processes are, in general, complex multi-component mixtures that contain sulfur bearing gases (H_2S and SO_2) in addition to oxidants (CO_2/CO and H_2O/H_2). High temperature corrosion of various metals and alloys in sulfur bearing environments is many orders of magnitude higher than their oxidation rates [1-4]. This difference is mainly attributed to the nature of the sulfide scale, which is non-adherent and highly porous, whereas the oxide scale is compact and adherent to the substrate [5-8].

Despite significant efforts during the last 15 years, the sulfidation mechanism is still not adequately explained. The very large number of transition metal sulfides compared to the corresponding oxides makes sulfidation studies more complicated. Sulfides are thermodynamically less stable, fuse at lower temperatures and reveal significant shifts in stoichiometry, compared to the corresponding oxides [6].

A number of studies describe the behavior of Fe-Cr alloys in H_2S-H_2 mixtures [9-11]. In all cases, Cr additions were reported to be beneficial. The nature of the products formed on the alloy surface depended on the Cr content. With less than 40% Cr, the scale was duplex, and consisted of $Fe_{1-x}S$ in its external part and a mixture of $Fe_{1-x}S$-$FeCr_2S_4$ in its internal part. Addition of 3-5 wt% Al to Fe-17Cr alloys increased sulfidation resistance in H_2S environments with sulfur partial pressure (Ps_2) of $6x10^{-2}$ torr [12]. Further increase in Al content, in iron aluminides, increased sulfidation resistance even more at 800°C,

9260

International Symposium High temperature corrosion in Energy Related Systems, 2002, Angra dos Reis, RJ and this was attributed to the formation of α-Al_2O_3 scale. Addition of Cr as a ternary element to iron aluminides decreased sulfidation resistance.

In the light of the above contributions with respect to the effect of Al addition to Fe-Cr alloys on sulfidation behavior, in this investigation the effect of the pre-oxidation on the sulfidation behavior of Fe-20Cr and Fe-20Cr-5Al alloys in H_2-H_2S environments at 800° C, has been studied. The sulfide scales have been characterized and a mechanism for sulfide scale growth has been proposed.

2. Methods and Materials

Iron-chromium (FeCr) and Iron-chromium-aluminum (FeCrAl) alloy ingots with compositions as shown in Table I were prepared in a vacuum induction furnace. The ingots were hot forged at 980° C, specimens cut to size and ground to 220 mesh. The specimens were pre-oxidized in oxygen for 4h at 1000°C and then exposed to flowing H_2-2%H_2S in a thermobalance at 800°C. Heating to and cooling of the specimens from the test temperature was carried out in an argon atmosphere. The sulfur partial pressures during these tests were 10^{-8} atm. Sulfidation kinetics of the alloys were determined from the mass gain versus time curves.

Table I: Chemical composition of the two alloys

Alloys	Elements		
	Cr	Al	Fe
FeCr	19.74	-	balance
FeCrAl	18.44	4.95	balance

The surfaces of specimens were examined in a scanning electron microscope and the composition of the reaction products determined using energy dispersive analysis (EDS) and X-ray diffraction analysis.

3. Results and discussion

Pre-oxidation of the alloys

The two alloys were isothermally oxidized for 4h at 1000°C as these parameters correspond to a steady state region in the parabolic oxidation mass gain versus time curve of these alloys. Fig. 1 reveals the surfaces of the alloys oxidized for 4h at 1000°C. The oxides on the surface of FeCr alloy were found to be Cr_2O_3 and $FeCr_2O_4$ and that on the surface of FeCrAl alloy to be α-Al_2O_3, θ-Al_2O_3, Cr_2O_3 and $FeCr_2O_4$, as shown in the diffractograms in Fig.2.

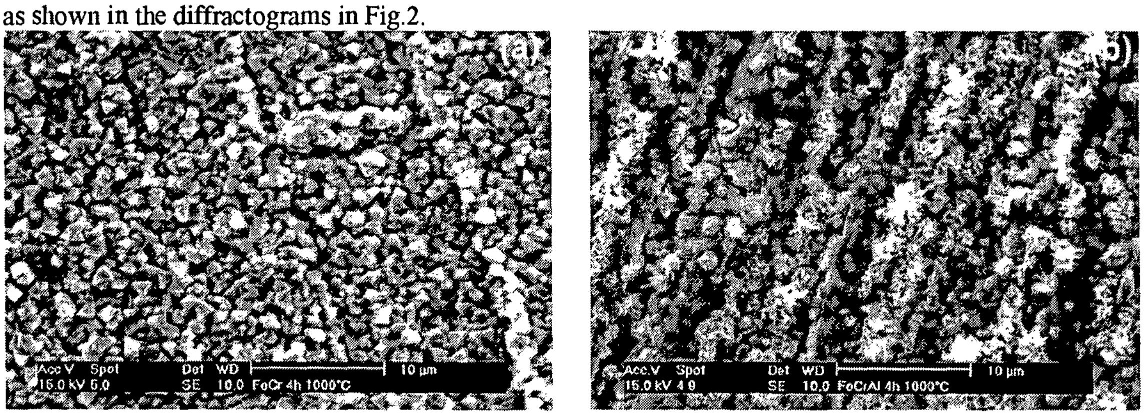
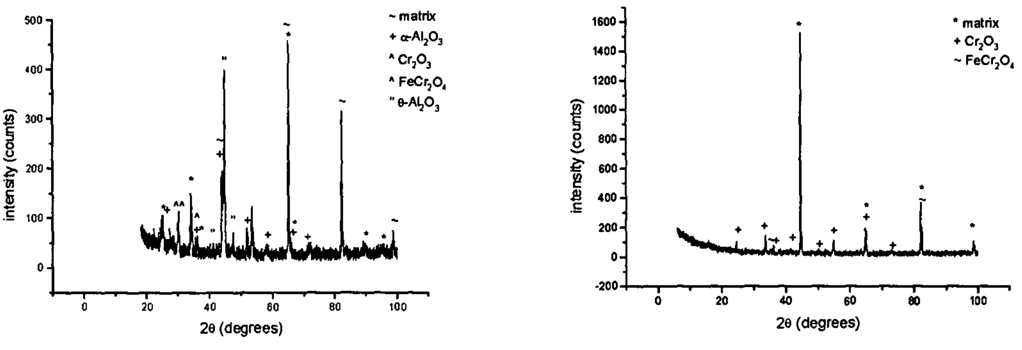


Fig. 1: Surfaces of alloys oxidized at 1000°C for 4 hours. (a) FeCr; (b) FeCrAl.



(a) (b)

Fig. 2: X-ray diffractograms of alloys oxidized at 1000°C for 4 hours. (a) FeCr, (b) FeCrAl.

Sulfidation of pre-oxidized alloys

The isothermal sulfidation curves of the two alloys pre-oxidized for 4h at 1000°C and sulfidized at 800°C are shown in Fig. 3. To enable comparison, the figure also shows the sulfidation curves of the two alloys that were not pre-oxidized [13, 14]. The mass gain and sulfidation rate of the pre-oxidized FeCr alloy reveals a rate transition after about 2 h. During this period, the oxide on the alloy surface protects the alloy in the sulfidizing environment. After this initial 'incubation period', the sulfidation rate of the alloy increases. The pre-oxidized FeCrAl alloys exhibits parabolic sulfidation kinetics and the oxide layer formed during pre-oxidation protects the alloy for at least 45 h at 800°C in the sulfidizing environment. The α-Al_2O_3 layer formed on the FeCrAl alloy during pre-oxidation is more compact and contains fewer defects compared to Cr_2O_3 formed on FeCr during pre-oxidation. This results in lower diffusion rates of species across the oxide layer. Thus, the incubation period for sulfidation is significantly longer.

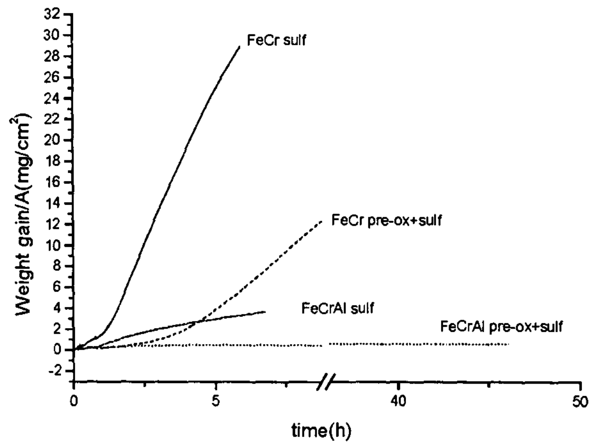


Fig. 3: Sulfidation curves of pre-oxidized FeCr e FeCrAl alloys at 800°C.

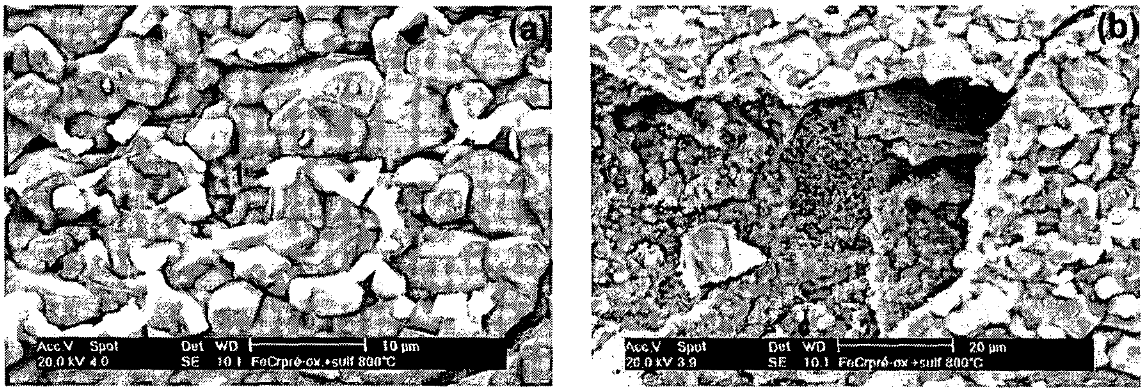
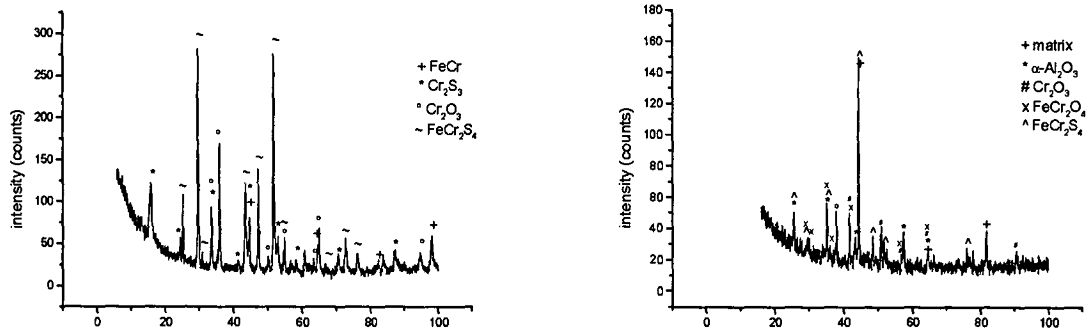


Fig. 4: Surfaces of pre-oxidized FeCr alloy sulfidized at 800°C in a thermobalance. (a) unspalled region; (b) spalled region.

The surface of FeCr alloy pre-oxidized and sulfidized at 800°C is shown in Fig. 4a. EDS analysis at region 1 in this figure revealed S and O. The outer layer was found to be rich in Cr and Fe. Fig. 4b shows a region on the same specimen where the sulfide layer had spalled. EDS measurements at various regions on this specimen revealed that the S and Fe contents decreased in the direction of the sulfide/alloy interface. This reveals that S does not diffuse easily through the oxide layer and that the sulfides formed preferentially at the gas interface. The Cr content increased towards the interface with the alloy. The x-ray diffractogram in Fig. 5a reveals the various phases present on the surface of the pre-oxidized and sulfidized FeCr alloy. Besides the Cr_2S_3 and $FeCr_2S_4$, chromia formed during the pre-oxidation stage was also detected.



(a)

(b)

Fig. 5: X-ray diffractograms of alloys pre-oxidized for 4h at 1000°C and sulfidized at 800°C in the thermobalance. (a) FeCr; (b) FeCrAl.

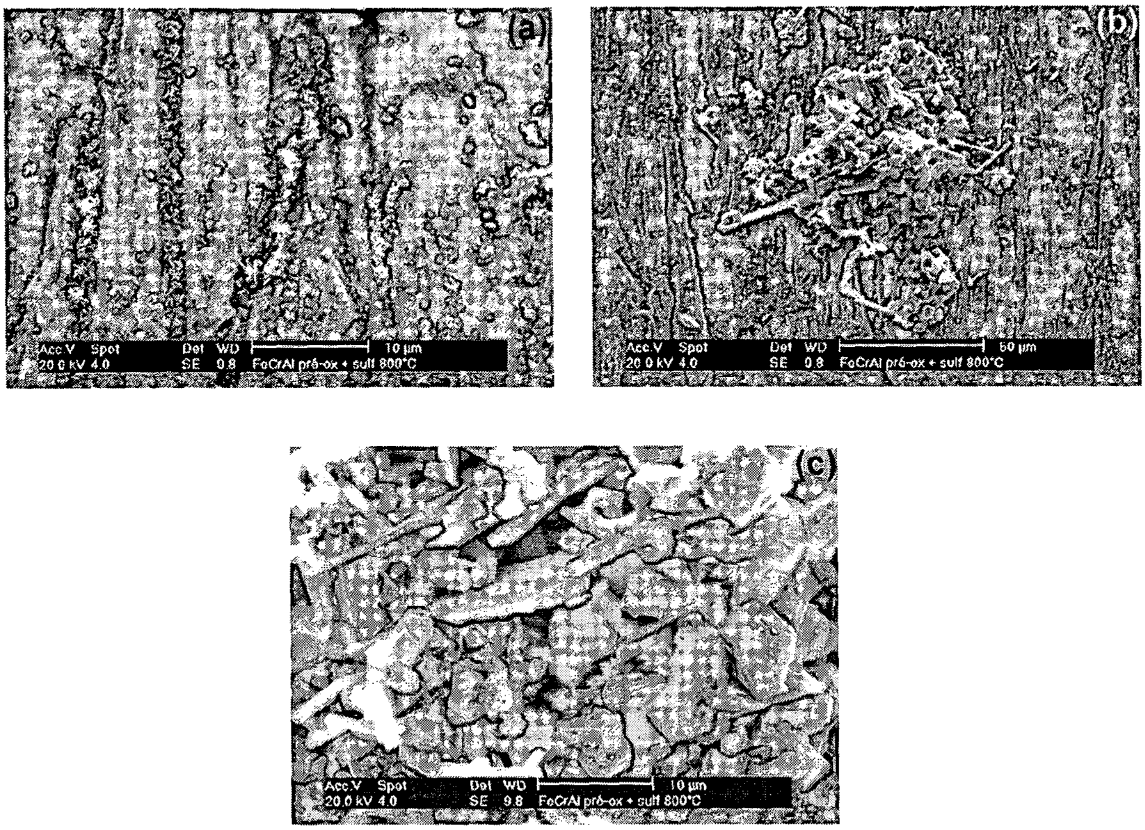


Fig. 6: Surface of FeCrAl alloy pre-oxidized and sulfidized at 800°C in a thermobalance. (a), (b) and (c) are different regions of the same specimen.

The surface of FeCrAl alloy pre-oxidized for 4h at 1000°C and sulfidized at 800°C for 45 h is shown in Fig. 6a. EDS data from a different region of this specimen, shown in Fig. 6b, revealed high Al content and oxygen in region 1, (the back ground). On some regions of the specimen nodule formation was observed (region 2). EDS analysis of a region within this nodule (shown in Fig. 6c) revealed the presence of Fe, Cr, S and some Al. Some sulfide nuclei can be seen at various points on the surface of the specimen shown in fig. 6a. An x-ray diffractogram of the surface of this alloy is shown in Fig. 5b. Besides $FeCr_2S_4$, the oxides α-Al_2O_3, Cr_2O_3 e $FeCr_2O_4$, formed during pre-oxidation were detected. These observations are coherent with the model proposed by Stott et al. [15]. Sulfide formation occurred at specific regions and not all over the surface, as observed on the surface of the alloy that was not pre-oxidized. On the basis of this it can be stated that the pre-oxidized alloy would not be resistant to the sulfidizing environment for very long times. Nevertheless, pre-oxidation of Al containing FeCr alloy extends the life of components made from this alloy and exposed to sulfidizing environments.

Growth sequence of sulfides on pre-oxidized FeCr and FeCrAl alloys

A schematic representation of sulfide layer growth on FeCr alloys pre-oxidized at 1000°C for 4h and sulfidized at 800°C is shown in Fig.7. On the pre-oxidized FeCr alloy, during sulfidation, Fe^{2+}, Fe^{3+} and Cr^{3+} diffuse through the oxide layer as shown in Fig 7a and sulfides nucleate at the oxide/gas interface (Fig. 7b). With time at temperature, S diffuses through the oxide layer and encounters the cations diffusing outward, to form sulfides within the oxide layer (Fig. 7c). With continued exposure to the sulfidizing environment, more S diffuses through the oxide layer and sulfide growth takes place at the oxide/metal interface as shown in Fig. 7d and at this stage the incubation period comes to an end.

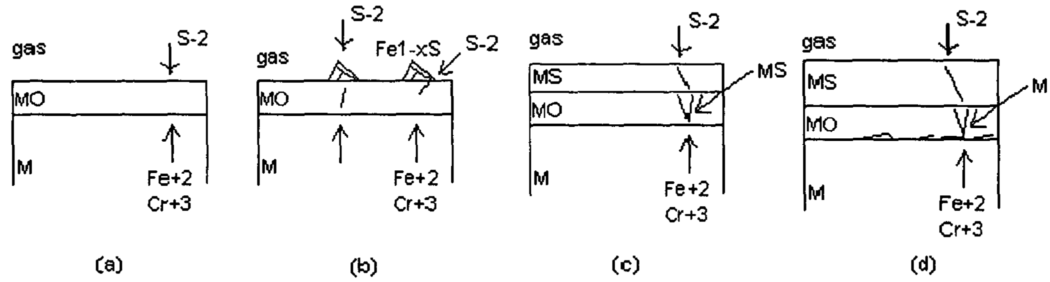


Fig. 7: Schematic diagram showing sulfide layer growth on pre-oxidized FeCr alloy during sulfidation at 800°C. (a) diffusion of S^{2-}, Fe^{2+}, Fe^{3+} e Cr^{3+} in oxide layer; (b) nucleation of sulfides at oxide/gas interface; (c) formation of sulfides in oxide layer; (d) growth of sulfides takes place near oxide/alloy interface and ends "incubation period".

Sulfidation of the pre-oxidized FeCrAl alloy can be considered to follow a sequence quite similar to that presented in Fig. 7 for FeCr alloy. For extended periods of exposure the aluminium oxide layer formed on the alloy surface remains unattacked. With time at temperature, S ions penetrate the alumina layer, reach the alloy surface and react with Fe and Cr to form their sulfides. These sulfides push outwards and protrude through the alumina, rather than spread laterally along the oxide/alloy interface. After extended exposure to the sulfidizing environment at 800°C, significantly longer than that carried out in this investigation, the number of sulfide protrusions could increase until breakdown of protection given by the alumina to the alloy.

4. Conclusions

- The FeCr alloy pre-oxidized for 4h at 1000°C showed an incubation period of about 2 h during subsequent sulfidation at 800°C. After this incubation period, the sulfidation behavior was similar to that of the alloy that had not been pre-oxidized. Sulfide growth occured at the oxide/gas interface.
- Pre-oxidation of the FeCrAl alloy at 1000°C for 4h significantly increased its resistance to sulfidation. An incubation period of at least 45 hours in a sulfidizing environment at 800°C has been observed.
- The overall improvement in sulfidation behavior indicates that serious consideration can be given towards the use of pre-oxidized alumina forming alloys for applications where extended exposures at low to medium S partial pressures are foreseen.

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