

SULFIDATION KINETICS OF FeCr AND FeCrY ALLOYS

M. F. Pillis and L. V. Ramanathan*

Instituto de Pesquisas Energéticas e Nucleares, C.P. 11049 Cidade Universitária,
CEP 05422-970 São Paulo, Brazil

Abstract

The sulfidation behavior of Fe₂₀Cr and Fe₂₀Cr_{0.7}Y alloys in H₂–H₂S atmospheres at 700 and 800°C was determined by thermogravimetry. Isothermal measurements were carried out and the sulfidation kinetics were evaluated from the mass gain vs. time curves. The reaction products were examined in a scanning electron microscope and the compositions of micro-regions were determined using energy dispersive spectroscopy and X-ray diffraction. Yttrium addition increased the sulfidation resistance of the FeCr alloy.

Keywords: rare earths, sulfidation, thermogravimetry

Introduction

Alloys used in high-temperature applications are usually Fe, Ni or Co based and contain other elements in sufficient quantities to promote the formation of protective oxides of chromia, alumina or (at times) silica [1]. Besides these, other elements are added to these alloys to improve the protective properties of the surface oxides and they include reactive elements such as Zr, Hf, Y etc. [1–13] Many industrial atmospheres contain sulfur and, in general, the sulfidation rates of most commercial alloys are many orders of magnitude higher than their oxidation rates [14]. Consequently, alloys developed for use in oxidising atmospheres do not perform well in sulfur-bearing atmospheres. This paper deals with the effect of yttrium addition on the high-temperature sulfidation behavior of Fe₂₀Cr alloy.

Experimental

FeCr and FeCrY alloys with compositions as shown in Table 1 were produced in a vacuum induction furnace. The alloy ingots were forged at 980°C to result in a 60% reduction in the cross-section. Specimens with an area of 0.4 cm² were cut, ground to 220 mesh, degreased in acetone and dried. The specimens were isothermally sulfid-

* Author for correspondence: E-mail: mfpillis@net.ipen.br

ised in a Shimadzu TGA-50H vertical thermobalance at 700 and 800°C in a stream of $H_2-2\%H_2S$. The specimens were first heated to the test temperature in inert argon atmosphere. This gas was also used as the purge gas within the thermobalance. At the test temperature, $H_2-2\% H_2S$ gas was introduced. Mass gain vs. time curves were obtained. The spalled reaction product was retained in the pan of the balance. Thus the overall mass gain included that of the spalled reaction product. The linear rate constants were obtained by regression of the mass gain curves. To determine the parabolic rate constants a plot of the square of mass gain per unit area vs. time was first made followed by the regression of the steady state region. The best fit was found to be for parabolic kinetics. The sulfidised specimens were examined in a scanning electron microscope and micro-regions on the surfaces were analysed using energy dispersive spectroscopy and by X-ray diffraction.

Table 1 Chemical composition of the alloys

Alloy	Elements		
	Fe	Cr	Y
FeCr	80.26	19.74	–
FeCrY	79.26	20.05	0.69

Results and discussion

The mass gain vs. time curves for the two alloys, sulfidised at 700°C and 800°C, are shown in Fig. 1. It can be observed that the addition of Y to Fe20Cr alloy altered significantly the sulfidation kinetics. At 700°C, the alloys without and with Y showed parabolic behavior, whereas at 800°C both the alloys exhibited linear kinetics. The parabolic and linear sulfidation constants at the two temperatures are shown in Table 2.

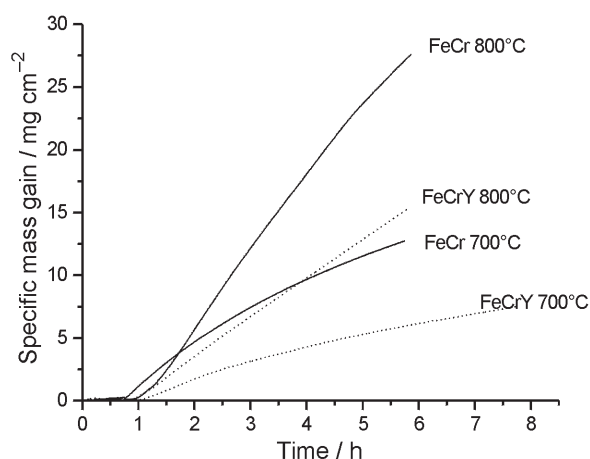


Fig. 1 Mass gain vs. time curves of FeCr and FeCrY alloys, sulfidised at 700 and 800°C

Table 2 Parabolic and linear sulfidation constants of the alloys

Alloy	Test temperature/°C	$K_p/g^2 \text{ cm}^{-4} \text{ s}^{-1}$	$K_l/g \text{ cm}^{-2} \text{ s}^{-1}$
Fe20Cr	700	$1.20 \cdot 10^{-8}$	–
	800	–	$1.62 \cdot 10^{-6}$
Fe20Cr0.7Y	700	$3.25 \cdot 10^{-9}$	–
	800	–	$8.69 \cdot 10^{-7}$

Figure 2a shows the surface of FeCr alloy before sulfidising and reveals the ferrite grains. Figure 2b is a micrograph of a region on the surface of the sulfidised specimen where the sulfide has detached but remained on the substrate.

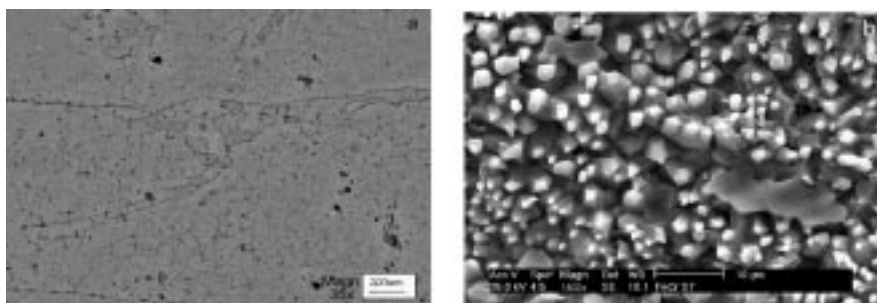
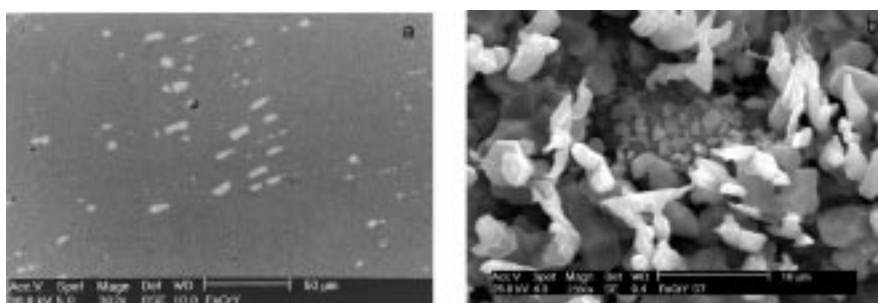
**Fig. 2** Surface of FeCr alloy: a – before sulfidising; b – after sulfidising at 800°C (N=2000)

Figure 3a shows the surface of FeCrY alloy before sulfidising. The light regions were identified by EDS as intermetallic Fe–Y. Figure 3b shows a region on the surface of sulfidised FeCrY alloy. The arrow indicates a region where the morphology is quite distinct and it revealed the presence of Y. This region probably corresponds to the light regions shown in Fig. 3a.

**Fig. 3** Surface of FeCrY alloy: a – before sulfidising (N=420); b – after sulfidising at 800°C (N=3200)

The reaction product layer on the two alloys spalled easily at 700 and 800°C. A number of cracks, both intergranular and transgranular were observed on the sulfide

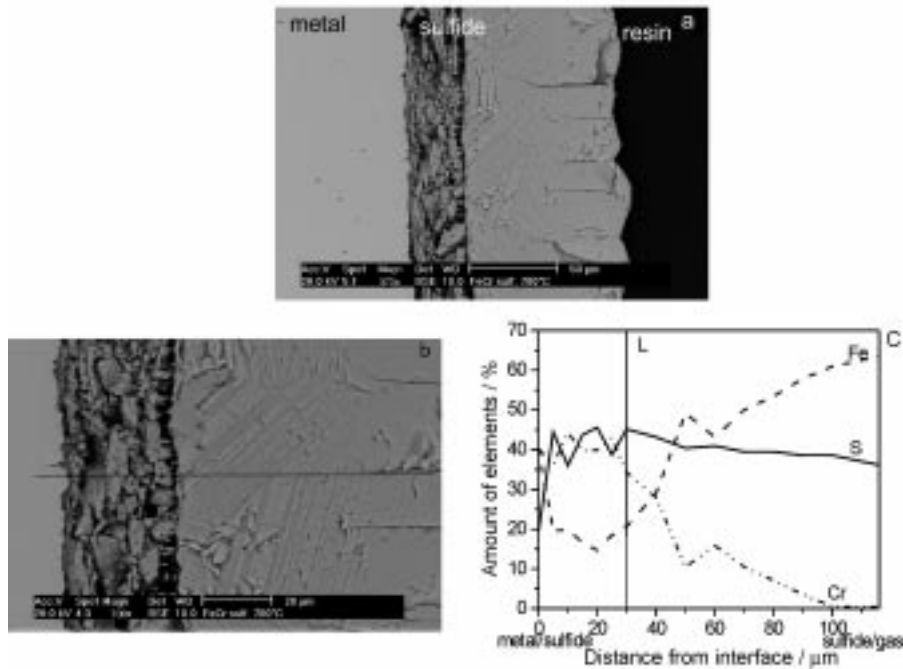


Fig. 4 a – Cross-section of FeCr alloy sulfidised at 700°C (N=500); b – same as in (a) at a higher magnification (N=1000); c – composition profile through (b)

formed on the alloy surfaces. The sulfide grain size on the Y-containing alloy was smaller than that on the Y-free alloy.

Figure 4a shows a cross-section of alloy Fe20Cr sulfidised at 700°C. The sulfidised layer is made up of two sub-layers. Figure 4b is a magnified version of Fig. 4a. The composition profile across the sulfide layer, determined by EDS analysis, is shown in Fig. 4c. The inner layer, close to the metal/sulfide interface is richer in chromium and contains some iron. The external sub-layer is made up of only iron and sulfur. Line 'L' in Fig. 4c delineates the two sub-layers. The average thickness of the sulfide layer is 120 μm. The metal/sulfide interface on this alloy is planar. The external sub-layer is made up of dark and light lamellas. EDS analysis of these lamellas revealed that the dark ones were richer in chromium. There were no significant variations in sulfur content between the dark and light lamellas. Large cracks were observed on the outer sulfide layer. The diffractogram of the external layer formed on the FeCr alloy sulfidised for 5 h at 700°C indicated the presence of only $Fe_{1-x}S$. During specimen handling, the reaction product spalled exposing a layer of adherent sulfide. X-ray diffraction analysis of this exposed and adherent sulfide indicated the presence of $Fe_{1-x}S$, Fe_7S_8 and Cr_2S_3 .

Figure 5a shows a cross-section of alloy Fe20Cr0.7Y sulfidised at 700°C. Figure 5b is a magnified version of Fig. 5a. A chemical composition profile within the sulfide layer as determined by EDS analysis is shown in Fig. 5c. Again, line 'L' indicates the separa-

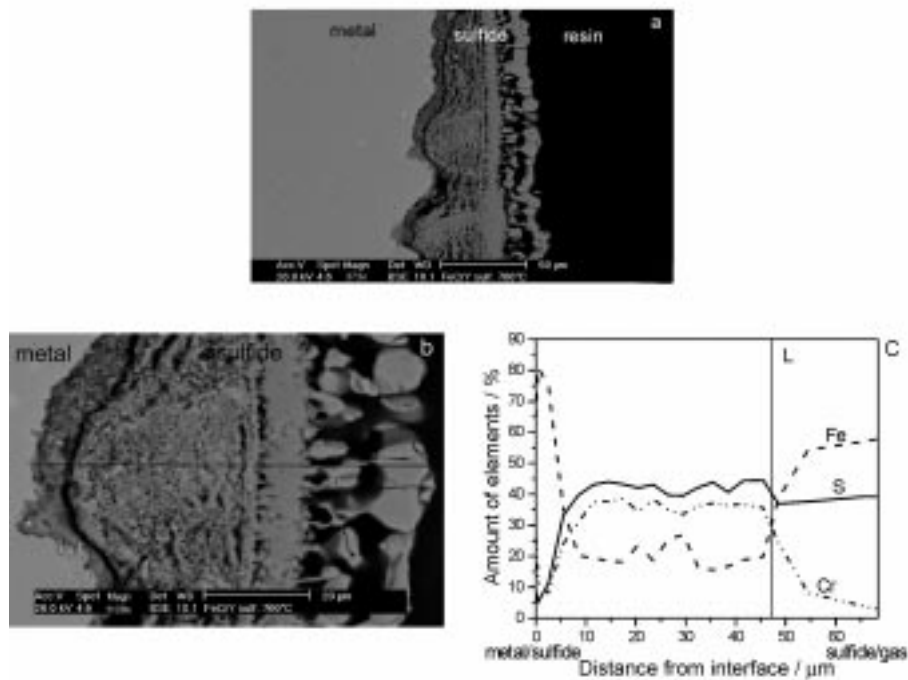


Fig. 5 a – Cross-section of FeCrY alloy sulfidised at 700°C; b – at a higher magnification (N=1500); c – composition profile through (b)

tion between the inner and outer layers of sulfide. The average total thickness of the sulfide layer on this alloy is about 75 μm , which is considerably less than that formed on alloy Fe20Cr. The sulfide layer intrudes into the alloy in different regions, which is distinctive of this alloy compared to the sulfide layer on alloy Fe20Cr, where the interface was planar. The light regions seen in the interior of the sulfide layer were found to be rich in Y. These light spots were not found in the external sulfide layer. X-ray diffraction analysis of the surface of the specimen sulfidised for 5 h at 700°C and after spalling of the external layer revealed Fe_{1-x}S , Cr_2S_3 and Y_2S_3 .

Figure 6 shows the cross-section of alloy Fe20Cr0.7Y sulfidised at 700°C for 2 h. This figure shows a region where the sulfide layer has not spalled. The light-grey regions within the alloy were identified by EDS analysis as a Fe–Y phase. This phase can also be seen in the sulfide layer, up to a certain depth. In the outer regions of the sulfide layer, EDS analysis indicated the presence of only Fe–S (probably Fe_{1-x}S), and no light-grey spots were observed. Based on these observations, it can be stated that in the initial stages, sulfidation took place predominantly by cation diffusion and formed the outer sulfide layers. Subsequently it occurred by anionic diffusion with the sulfidised front moving into the alloy. In this case, Fe–Y phase acted as a ‘marker’ indicating the direction of growth of the sulfide layer.

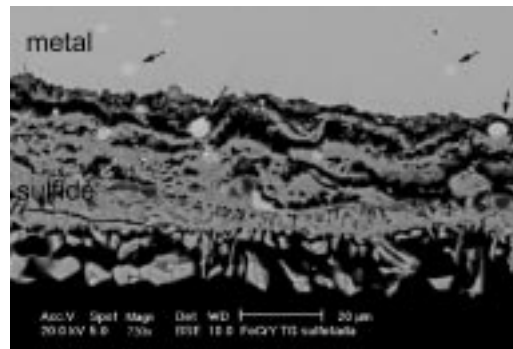


Fig. 6 Cross-section of FeCrY alloy sulfidised at 700°C for 2 h (N=1000)

Conclusions

- The addition of Y increased the sulfidation resistance of Fe20Cr alloy.
- The alloys Fe20Cr and Fe20Cr0.7Y exhibited parabolic sulfidation constants at 700°C and linear sulfidation constants at 800°C in H₂-2% H₂S atmospheres.
- The grain size of the sulfide formed on Fe20Cr was larger than that formed on the Y-containing alloy.

References

- 1 P. Y. Hou and J. Stringer, *Mat. Sci. Eng.*, 87 (1987) 295.
- 2 T. N. Rhys-Jones, H. J. Grabke and H. Kudielka, *Corr. Sci.*, 27 (1987) 49.
- 3 D. P. Moon, *Mat. Sci. Tech.*, 5 (1989) 754.
- 4 A. M. Huntz, *Mat. Sci. Eng.*, 87 (1987) 251.
- 5 C. M. Cotell, G. J. Yurek, R. J. Hussey, D. F. Mitchell and M. J. Graham, *Oxid. Metals*, 34 (1990) 173.
- 6 J. K. Tien and F. S. Pettit, *Metall. Trans.*, 3 (1972) 1587.
- 7 C. S. Giggins, B. H. Kear, F. S. Pettit and J. K. Tien, *Metall. Trans.*, 5 (1974) 1685.
- 8 T. N. Rhys-Jones and H. J. Grabke, *Mat. Sci. Tech.*, 4 (1988) 446.
- 9 D. P. Whittle and J. Stringer, *J. Philos. Trans. R. Soc. London*, A295 (1980) 309.
- 10 I. M. Allam, D. P. Whittle and J. Stringer, *Oxid. Metals*, 12 (1978) 35.
- 11 B. Pieraggi and R. A. Rapp, *J. Electrochem. Soc.*, 43 (1995) 4015.
- 12 R. J. Hussey, P. Papaiacovou, J. Shen, D. F. Mitchell and M. J. Graham, *Mat. Sci. Eng.*, A120 (1989) 147.
- 13 J. G. Smeggil, *Mat. Sci. Eng.*, 87 (1987) 261.
- 14 K. N. Strafford and P. K. Datta, *Corr. Sci.*, 35 (1993) 1053.