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Microstructural Characterization of Reaction Products on Iron Based Alloys Exposed to H_2/H_2S Atmospheres at High Temperatures

Marina F. Pillis*, Lalgudi V. Ramanathan

Comissão Nacional de Energia Nuclear
Instituto de Pesquisas Energéticas e Nucleares
Cidade Universitária, C.P. 11049, 05422-970 São Paulo - SP, Brazil

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Thermogravimetric measurements in H_2/H_2S environments for up to five hours were carried out to determine the sulphidizing behavior of Fe-20Cr and Fe-20Cr-0.7Y alloys. These measurements helped to determine the mechanism of sulphidization in the early stages. The reaction products were characterized using a scanning electron microscope coupled to an energy dispersive analyzer and by X-ray diffraction analysis. The addition of yttrium influenced the morphology of the sulphide layer and the reaction kinetics.

Keywords: *sulphidation, reactive elements*

1. Introduction

In many industries, metallic materials are exposed at high temperatures to sulphur containing environments. The corrosion of these metals under these conditions is severe compared to corrosion in atmospheres containing only oxygen. It is well known that not only in highly sulphidizing atmospheres but also in combustion chambers containing small quantities, or even traces of sulphur, high temperature alloys normally resistant to corrosion (through the formation of chromia or alumina), degrade rapidly[1]. Many of the standard alloys when exposed to air at high temperatures remain almost unattacked as they form a protective surface layer of Al_2O_3 or Cr_2O_3. In contrast, in the presence of sulphur, a non-protective layer forms on the surface of these alloys. This layer is heterogeneous and quite thick. The sulphide layer exhibits poor protective properties compared to the oxide layer, due to the highly defective crystal lattice of the sulphides. Besides this, even with high concentrations of chromium and aluminium in the alloy, heterogeneous surface layers form, containing sulphides of all the alloying elements[2].

The addition of aluminium or chromium to iron reduces the sulphidation rate. However, this rate is controlled by various physico-chemical properties of the reaction products such as ionic defect structure and stoichiometry. Thus the search for alloys that would form sulphides at low growth rates was the focus of this investigation.

In spite of the significant efforts during the last few years, the sulphidation mechanism is still not well explained compared to oxidation. The very large number of transition metal sulphides compared to the corresponding oxides makes sulphidation studies more complicated. Sulphides are thermodynamically less stable, fuse at lower temperatures and reveal significant shifts in stoichiometry compared to the corresponding oxides[2]. In general, it has been observed that the sulphidation rates of commercial alloys is many orders of magnitude higher than the oxidation rate of the same alloys[3-6].

The benefits of adding reactive elements to improve the oxidation resistance of alloys used at high temperature is quite well documented. These reactive elements include Y, Hf, Ti or Zr and many other elements that have high affinity for oxygen. The reactive elements have been added to these alloys in elemental form, as an oxide dispersion or applied to their substrates. The effect of these additions on sulphidation behavior has not been adequately documented. Some researchers[7] reported improvements in sulphidizing behavior of iron based alloys with addition of Y, whereas others[8], reported an increase in sulphidation rate with the addition of Y.

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*e-mail: mfpillis@net.ipen.br

2. Methods and Materials

Fe-20Cr and Fe-20Cr-0.7Y alloys were prepared in a vacuum induction furnace. These ingots were hot forged at 980 °C and specimens cut to size. Sulfidation measurements were carried out in a thermobalance, in a flowing H_2-2%H_2S gas mixture at 700 °C and 800 °C. The specimens were heated in an inert atmosphere up to the test temperature and then the H_2/H_2S mixture was introduced. Cooling the specimens from the test temperature was also carried out in an inert atmosphere. Two sets of experiments were carried out: (a) To study the initial stages of sulfidation. The specimens were polished to 1 µm before exposure to the H_2-2%H_2S gas mixture at 700 °C for 3, 5, 15 and 30 min; (b) To study the sulfidation kinetics of the alloys. The specimens were ground to 220 mesh before exposure to the H_2-2%H_2S gas mixture at 700 °C and 800 °C for up to 5 h. The Sulfidation kinetics of the alloys at these temperatures were determined from the mass gain curves as a function of exposure time. To calculate the mass gain, the mass of the scaled reaction product was also considered, where relevant.

Scanning electron microscopy (SEM) and energy dispersive analysis (EDS) of micro-regions, as well as X-ray diffraction analysis (XRD) were used to characterize the reaction products.

3. Results and Discussion

The mass gain curves of the two alloys as a function of sulphidizing time at 700 °C and 800 °C are shown in Fig. 1. The figure clearly shows that with addition of yttrium, the sulphidation rate of the alloy decreased significantly. At 700 °C, both the alloys revealed parabolic behavior, whereas at 800 °C, the alloys showed linear behavior. The rate constants of the alloys at the two temperatures are given in Table I.

The two alloys scaled considerably at 700 °C and 800 °C in the sulphidizing atmosphere. A large number of cracks, both intergranular and transgranular were observed on the surfaces of these alloys. The grain size of the oxide formed on the alloy with yttrium addition was smaller than that on the alloy without Y.

Figure 2 shows a region of the reaction product that remained adhered to the substrate. Figure 2a shows the surface of the FeCr alloy. In Fig. 2b, which shows the alloy FeCrY, a region with a quite distinct morphology (arrow) can be seen. In this region, yttrium was detected. Figure 3a shows a transverse section of alloy FeCr sulphidized at 700 °C. It can be observed that the surface layer is made up of two "sublayers". The inner layer close to the metal/sulphide interface is richer in chromium, and also contains iron, as shown in Fig. 3b, a chemical composition profile along a horizontal line across the sulphide layer and as determined by EDS. This analysis also revealed that the external sublayer contained only iron and sulphur. The line L in Fig. 3b indicates the visual separation between the two sublayers. The average total thickness of the layer is 120 µm. Thickness measurements were carried out at a region where the sulphide remained adhered to the substrate. The metal/sulphide interface is planar. The external sublayer is made up of alternated light and dark lamellas. EDS analysis revealed that the dark lamellas are richer in chromium compared to the light lamellas. It has been reported in literature[9] that this layer was formed by iron sulpho-spinels ($Fe_{2-x}Cr_xS_4$) and that during cooling, decomposition of this phase took place. Variations in sulphur content were not detected. Large cracks have been observed in the external layer.

X-ray diffraction analysis of the outer layer of the reaction product formed on FeCr alloy after 5 h of sulphidation at 700 °C revealed only peaks pertaining to the $Fe_{1-x}S$ phase and X-ray diffraction analysis of the reaction product that remained adhered to this substrate after scaling, revealed

Table I. Parabolic and Linear Sulfidation Constants of the Alloys.

Alloy	Temperature (°C)	K_p ($g^2.cm^{-4}.s^{-1}$)	K_l ($g.cm^{-2}.s^{-1}$)
FeCr	700	1.20×10^{-8}	-
	800	-	1.62×10^{-6}
FeCrY	700	3.25×10^{-9}	-
	800	-	8.69×10^{-7}

Where: K_p = parabolic rate constant
K_l = linear rate constant

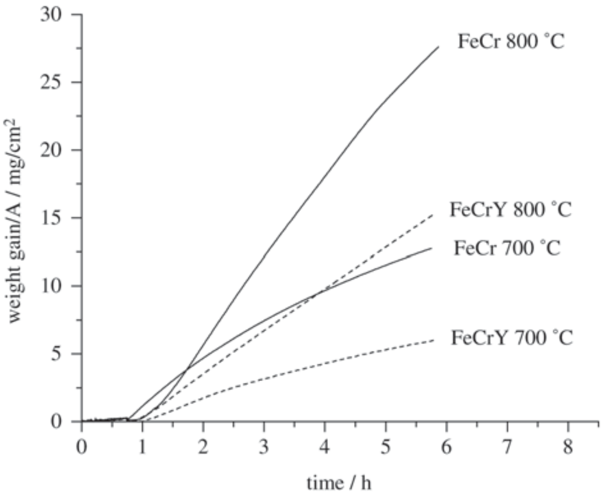

Figure 1. Weight gain versus time curves of FeCr and FeCrY alloys, sulphidised at 700 °C and 800 °C.

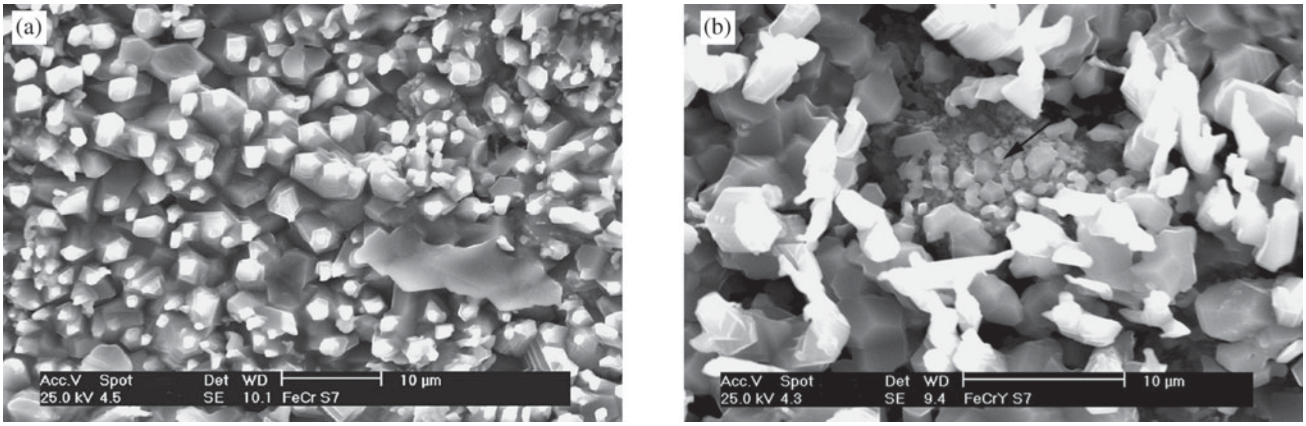

Figure 2. Scaled oxide still sticking to the alloy surface after sulphidation at 800 °C. a) FeCr; b) FeCrY.

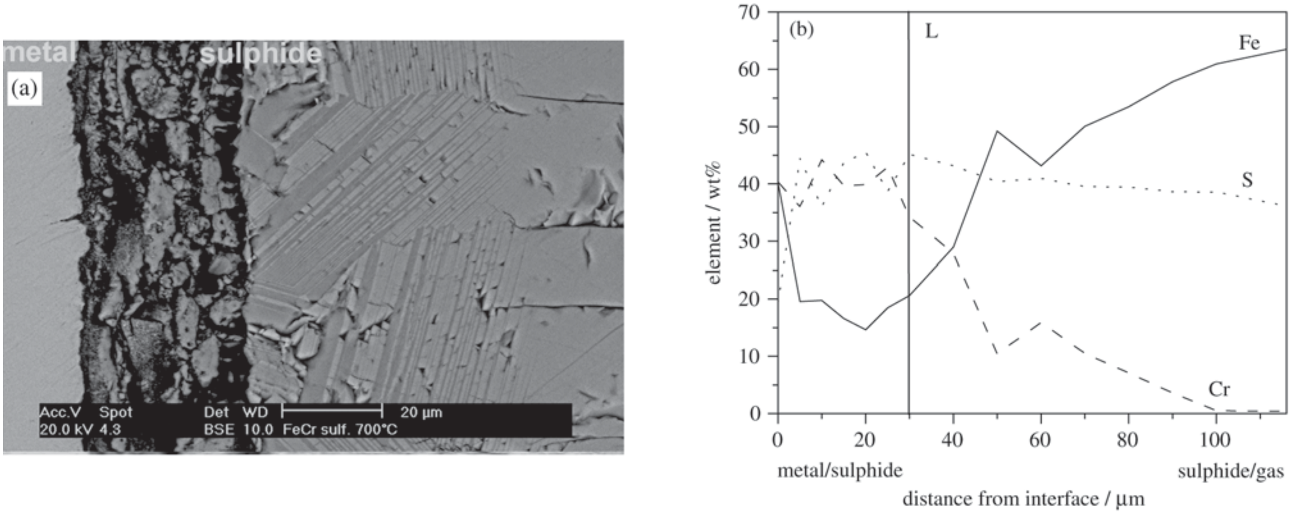

Figure 3. a) Cross-section of FeCr alloy sulphidised at 700 °C; b) composition profile through a).

besides $Fe_{1-x}S$, the phases Fe_7S_8 and Cr_2S_3.

Figure 4a presents the transverse section of FeCrY alloy sulphidized at 700 °C. A chemical composition gradient can be observed in the sulphide layer shown in Fig. 4b. The line L in Fig. 4c indicates a visual separation between the two sublayers. The average thickness of the layer is 75 µm, much less than that found on the FeCr alloy. It can be observed that the sublayers have alternating regions of higher or lower penetration of the sulphide into the metallic substrate. In the alloy without yttrium, (Fig. 3a) the sulphide layer was uniform. The light regions in the interior of the sulphide layer are rich in yttrium. It can be observed that these particles are not present in the external sulphide layer.

Figure 5 presents a transverse section of alloy FeCrY sulphidized for 2 h at 700 °C. The light regions within the alloy (arrow) were identified by EDS as the Fe-Y phase. In the sulphide layer, the presence of this phase (in sulphidized form) was observed up to a certain depth within the layer. In the external layer, where EDS analysis was carried out, the presence of only $Fe_{1-x}S$ was indicated. There were no nodules of the sulphidized phase of Fe-Y. Thus it can be stated that sulphidization took place initially by predominant cationic diffusion, forming the external layer and then by predominant anionic diffusion, with the sulphidation front progressing into the metallic substrate. In this case, the Fe-Y phase functions as a "marker" indicating the direction of growth of the sulphide. X-ray diffraction analysis of the reaction product that remained adhered to the surface of the FeCrY alloy sulphidized for 5 h at 700 °C, and after scal-

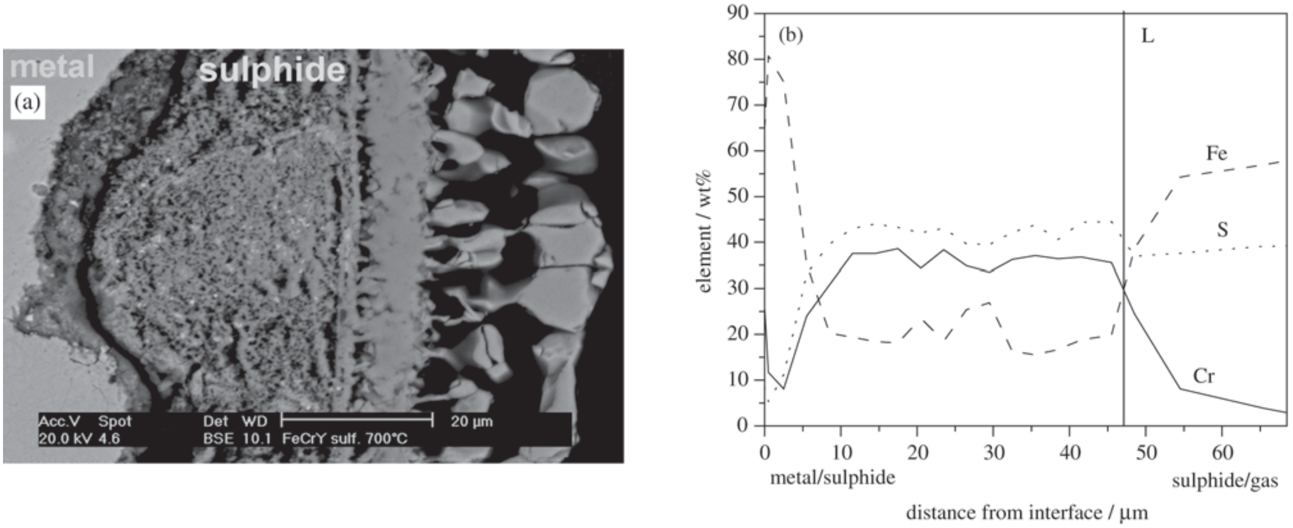

Figure 4. a) cross-section of FeCrY alloy sulphidised at 700 °C; b) composition profile through a).

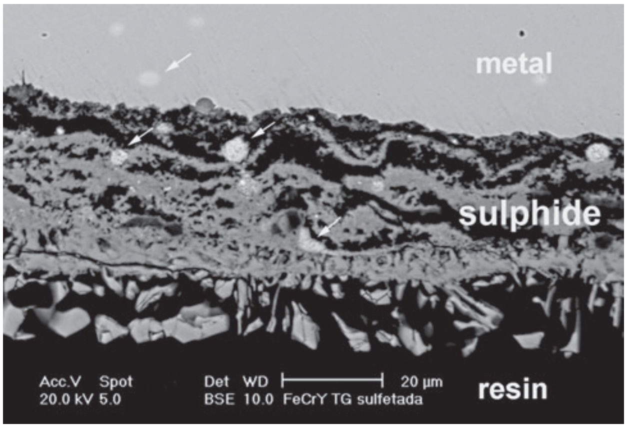

Figure 5. Cross-section of FeCrY alloy sulphidised at 700 °C for 2 h.

ing, revealed the phases $Fe_{1-x}S$, Cr_2S_3 and Fe_7S_8, similar to that found in specimens without yttrium. Y containing phases were not detected. The reaction product was very fragile and scaled during specimen handling.

Specimens of FeCr alloy were sulphidized for very short durations, 3, 5, 15, or 30 min at 700 °C to help understand the initial stages of sulphidation. The surfaces of the specimens were observed in an SEM and specific regions were analyzed using EDS. After 3 min of sulphidation the alloy showed scaling in certain regions, many cracks and grain growth, as shown in Fig. 6. After 5 min of sulphidation (Fig. 7a) the ridges grew even more. EDS measurements indicated high iron content on the surface and that the dark regions contained more chromium than the light regions. The cracks seen in Fig. 7b probably occured during cooling, since there was no penetration of sulphur and consequent growth of ridges. Growth of iron sulphide probably caused cracks during the initial stages and these cracks generated new surfaces for the diffusion of sulphur. The cracks relieved thermal stresses and stresses associated with the growth of sulphides. After 15 min (Fig. 8a) a compact surface can be observed, as though the oxide ridges grew and occupied the whole surface. EDS measurements revealed high iron content on the surface and that the dark regions contained more chromium than the light regions. The specimen sulphidized for 30 min (Fig. 8b) shows severe scaling. A small region of the sulphide layer can be found still adhering to the substrate. EDS measurements carried out at this region revealed high iron content in the outer layer along with some chromium. The chromium content in the inner layer close to the interface with the substrate was significantly higher.

The surface of the alloy FeCrY sulphidized for 5 min at 700 °C is shown in Fig. 9a. It can be observed that sulphur attack took place preferentially along the alloy grain boundaries. Y was not detected even on these grain boundaries. A large particle (region 1) can be seen on the left in Fig. 9b and EDS measurements revealed high iron and low chromium content. At regions 2 and 3 in Fig. 9b, EDS analysis revealed high iron and chromium content close to that in the alloy, indicating thus the strong influence of the matrix, or the very fine oxide on the results. A nodule can be observed in Fig. 9c that formed in region 2. EDS analysis of region 4 indicated large amounts of Y, S and Cr. The light sulphides in acicular form (region 5) contained high iron content. This apparently indicates that the Y containing phase acted as nucleation sites for the sulphides. Figure 9d shows the growth of iron sulphide needles. The micrographs were obtained from different regions of the same specimen and these indicate sulphide growth sequence on the metallic surface.

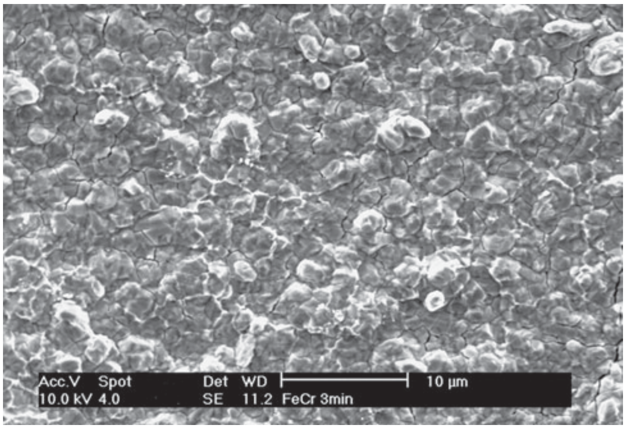

Figure 6. Surface of the FeCr alloy sulfidized for 3 min at 700 °C.

The surface of alloy FeCrY sulphidized for 30 min can be seen in Fig. 10. Under these conditions, the specimen scaled. It is possible to identify the grains from the orientation of the sulphide during growth in Fig. 10a. Yttrium was however not detected at all. A region of the sulphide layer still adhering to the substrate after scaling is shown in Fig. 10b. Grain boundaries can be seen and high amounts of Y were detected. The Cr and Fe contents at these regions were close to each other. Away from the grain boundary, Y was not detected and the Cr content was more than that of Fe. Apparently during short periods of sulphidation, yttrium diffuses in large quantities to the interface metal/reaction product, and concentrates at the grain boundaries of the metal, close to the interface. Y was detected in the nodules after 5 min of sulphidation, but not in the grain boundaries.

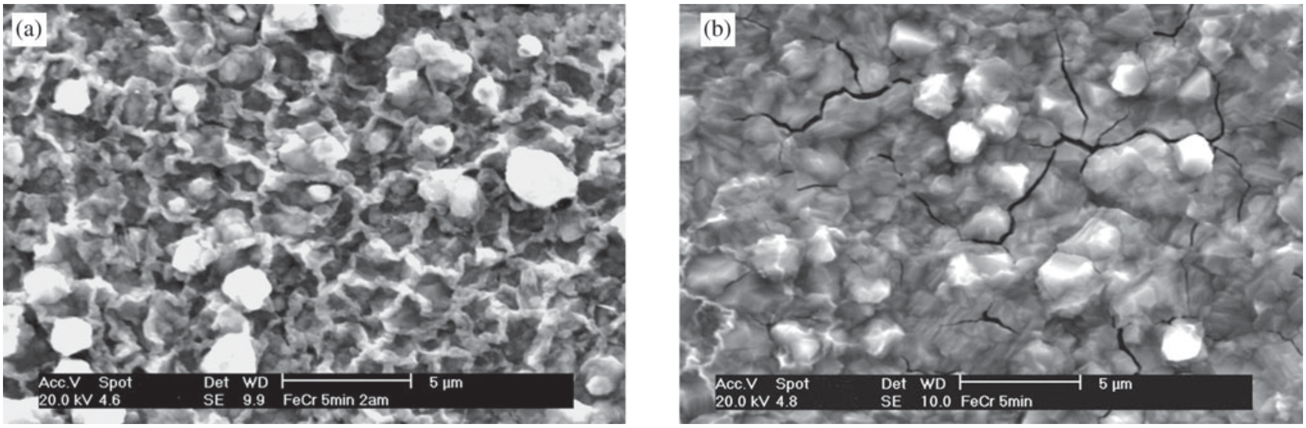

Figure 7. Surface of the FeCr alloy sulfidized for 5 min at 700 °C.

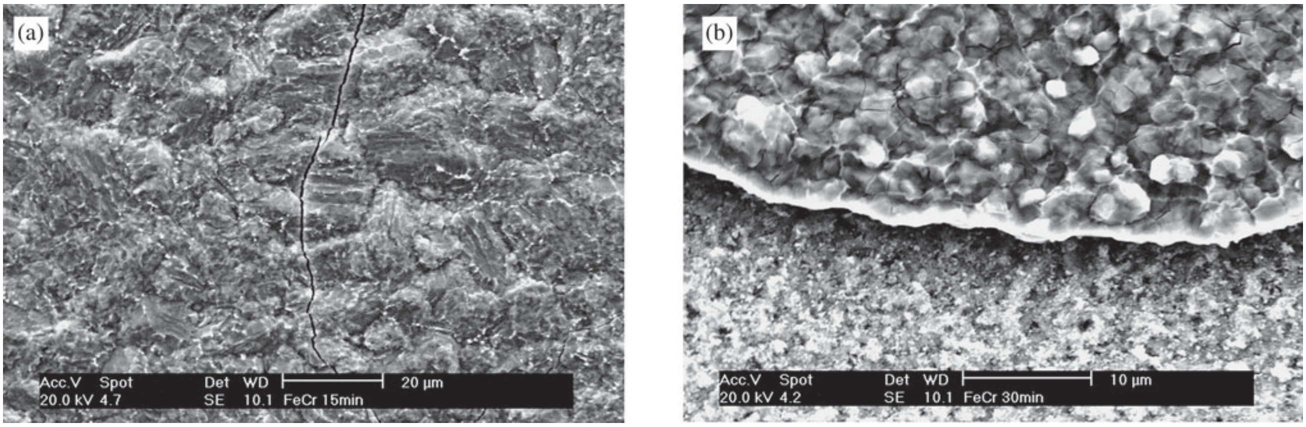

Figure 8. Surface of the FeCr alloy sulfidized at 700 °C. a) for 15 min and b) for 30 min.

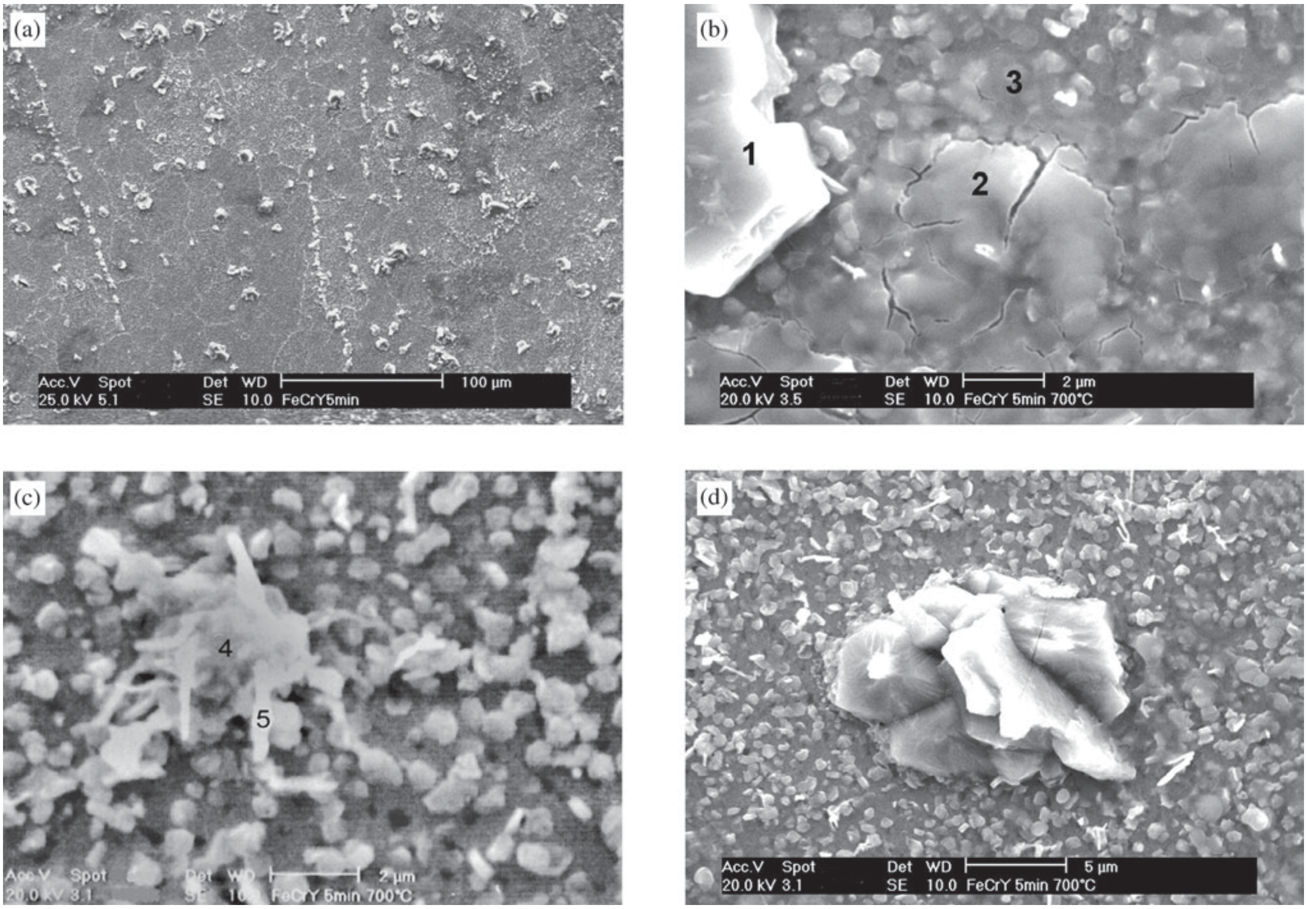

Figure 9. Surface of the FeCrY alloy sulfidized for 5 min at 700 °C.

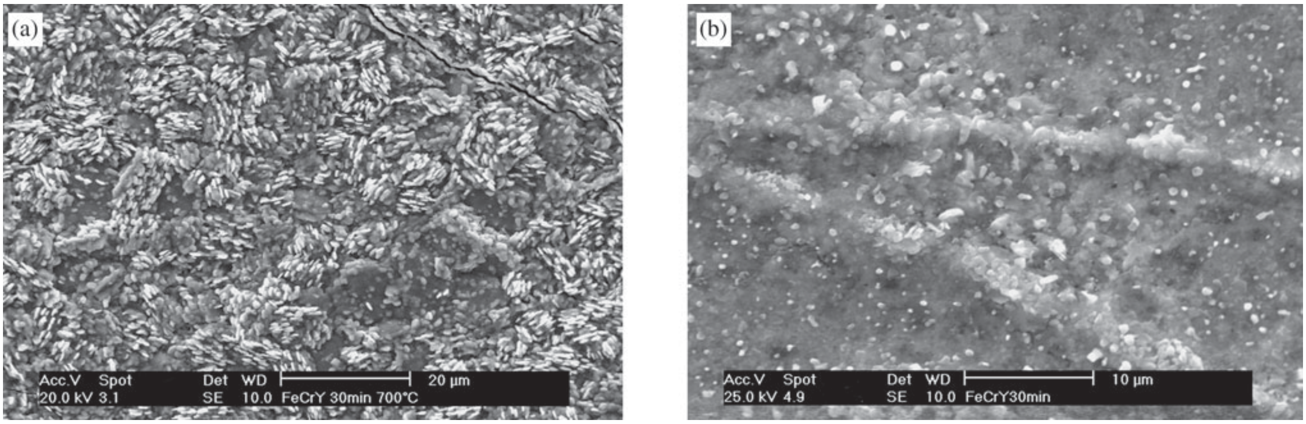

Figure 10. Surface of the FeCrY alloy sulfidized for 30 min at 700 °C.

The main effect of yttrium is reduction in the grain size of the alloy. The FeY phase sulphidizes first, and these act as the nucleation sites for other sulphides. The growth of sulphides inside the grains is inhibited and it concentrates at the grain boundaries. Thus growth rate and consequently that of sulphidation decreases. In the alloy without Y, Fe and Cr are quickly sulphidized, whereas in the alloy with yttrium, selective sulphidation of chromium takes place as internal sulphidation. The diffusion rate of the species through the chromium sulphide is much less than in iron sulphide, as this is less stoichiometric.

4. Conclusions

1. The addition of Y increased the sulphidation resistance of the Fe20Cr alloy.
2. The sulphidation kinetics of alloys Fe20Cr and Fe20Cr0.7Y follow parabolic rate laws at 700 °C and linear rate laws at 800 °C.
3. The grain size of the sulphide formed on alloy Fe20Cr is larger than that formed on the alloy containing Y.
4. The sulphidation of the Y containing alloy takes place essentially via grain boundaries whereas in the alloy without Y the influence of the grain is easily observed, especially during the initial stages of the process.

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