Sulfidation of Fe-Cr binary alloys in H₂/H₂S atmosphere at 873- 1073 K

Z. Zurek, J. Gawel

► To cite this version:

Z. Zurek, J. Gawel. Sulfidation of Fe-Cr binary alloys in H₂/H₂S atmosphere at 873- 1073 K. Journal de Physique IV Proceedings, 1993, 03 (C9), pp.C9-327-C9-330. 10.1051/jp4:1993932 . jpa-00252370

HAL Id: jpa-00252370

<https://hal.science/jpa-00252370>

Submitted on 1 Jan 1993

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Sulfidation of Fe-Cr binary alloys in H_2/H_2S atmosphere at 873-1073 K

Z. Zurek and J. Gawel

Cracow University of Technology, 31-155 Krakow, Poland

Abstract. — Sulfidation of Fe-Cr binary alloys has been studied in H_2/H_2S atmosphere in the temperature range 873-1073 K. Alloys containing respectively 3, 10, 26 and 45%wt. of chromium were investigated. Sulfur partial pressure in the gas mixture was $p_{S_2} = 10^{-3}$ Pa. Morphology of the obtained scales was studied by SEM. In spite of the results of Narita, Smeltzer and Nishida who have found a two layer scale, scales in this survey consisted apparently of one layer in the entire range of temperatures and alloy compositions. Scale composition was determined by X-ray diffraction. Diffraction patterns of scales formed on Fe45Cr exhibited the presence of Cr_3S_4 whereas $FeCr_2S_4$ was found on Fe26Cr. The latter compound was also observed in scales formed on Fe10Cr and Fe3Cr, though in these spectra some peaks were difficult to interpret. Kinetic measurements taken by a spring microbalance confirmed the results of Narita *et al.* and the reaction rate increased only slightly with increases in chromium content in the alloy.

1. Introduction.

Chromium steels are a staple construction material in chemical industry. Although, Fe-based alloys have poorer high temperature oxidation resistance than Co- or Ni-based alloys, they are more widely used. Fe-Cr alloys exhibit satisfactory mechanical properties and quite good corrosion resistance at intermediate and also high temperatures. Unfortunately, this is true only for oxygen or air, because even small amount of sulfur in the ambient gas drastically accelerates corrosion. Industrial atmospheres usually contain some sulphur compounds, and even though modern technologies try to keep its contents low. Therefore it is important to simulate such conditions during high temperature oxidation tests. Several gas compositions of a low sulphur contents have been used in the literature, such as mixtures of COS and CO [1], or pure sulphur under a low total pressure [2]. In this paper a wide range of Fe-Cr binary alloys were investigated in H_2/H_2S at 600 and 800 °C to repeat the study of Narita *et al.* [3]. A great excess of H_2 in the mixture could be associated with reducing conditions, but it should be stressed that the samples were exposed to a positive sulfidizing atmosphere.

The aim of this study was to survey the reactive kinetics of various Fe-Cr alloys and evaluate the effect of increasing chromium content on the high temperature corrosion resistance of these alloys in H_2/H_2S atmosphere.

2. Experimental.

Fe-Cr binary alloys were prepared by melting of the pure metals at least 99.99wt.% pure in a Balzers vacuum oven. Following proportions were taken: 3, 10, 26 and 45 at.% Cr.

The ingots were scarfed and cold rolled in order to obtain 0.2 mm thick sheets. Samples 1.5×1.5 cm were cut out of the sheets and annealed in reducing atmosphere for 2 hours at 600 °C. Before placing in the reaction chamber the samples were polished to a mirror like appearance and degreased in acetone. Thermogravimetric measurements were carried out in a standard quartz microbalance [4] under a total pressure of 1 atm. Individual specimens were exposed to a H_2/H_2S gas mixture which flowed with a speed of 0.3 cm/s. H_2/H_2S mixture was prepared in the following manner. First, hydrogen was run through liquid sulphur and the mixture of hydrogen and sulphur vapour underwent a catalytic reaction in a pipe oven at 600 °C. This procedure was described in detail elsewhere [5]. The equilibrium partial pressure in the microbalance was $p_{S_2} = 10^{-3}$ Pa, at all reaction temperatures. In order to do this composition of the gas entering the microbalance was adjusted; the lower the reaction temperature, the higher the H_2S content in the nominal gas. H_2S content was constantly analyzed and kept at the desired level by controlling of the liquid sulphur temperature.

3. Results and discussion.

Reaction kinetics of all the investigated alloys obeyed a linear rate law for a relatively long time under all applied conditions. Mass gain was proportional to the reaction time as shown in figure 1. After this period samples started to gain mass more slowly accordingly to a parabolic rate law. Therefore, an overall parabolic reaction rate was calculated for all experiments. These values were compared to previous ones [6, 7] and shown in figure 2. Points representing this study are situated between points representing experiments made under lower and higher sulphur partial pressure. It can be seen that there is a slight increase of the reaction rate with the increases in chromium content in the alloy. The tendency appears more obvious under lower sulphur partial pressures [7]. On the contrary, under higher sulphur partial pressures, alloys richer in chromium were more resistant to sulphur attack [6].

Fig. 1. — Sulfidation kinetics of Fe-Cr alloys under $p_{S_2} = 10^{-3}$ Pa: A) Fe3Cr at 800 °C; B) Fe10Cr at 800 °C; C) Fe26Cr at 800 °C; D) Fe45Cr at 800 °C; E) Fe10Cr at 700 °C; F) Fe10Cr at 600 °C.

It is interesting to compare our results with the kinetics of pure chromium sulfidation. Parabolic reaction constant of Fe-Cr alloys sulfidation in H_2/H_2S under $p_{S_2} = 10^{-3}$ Pa is

Fig. 2. — The dependence of the parabolic sulfidation rate constants on the chromium contents of the Fe-Cr alloys at 800 °C in H_2/H_2S and pure sulphur vapour (10^5 Pa) [6].

between 1.0×10^{-6} and $1.9 \times 10^{-6} \text{ kg}^2 \text{ m}^{-4} \text{ s}^{-1}$ (this study). Parabolic reaction constant of pure chromium in H_2/H_2S under $p_{S_2} = 100$ Pa is about ten times lower and equals $2.2 \times 10^{-7} \text{ kg}^2 \text{ m}^{-4} \text{ s}^{-1}$ [8]. That fact indicates the role of iron in the reaction mechanism.

All in all, the kinetic data remain in a good agreement with the results of other surveys. However, when the morphology is concerned, this study has shown a quite different scale appearance. Narita *et al.* have obtained two layer scales. Both thickness and porosity of the inner layer increased with the increasing alloy chromium contents. In this study one layer scale was observed as shown on the SEM in figures 3 and 4. The entire scale is compact, built from columnar grains and adheres well to the sample core. It is disputable, whether a thin subscale exists close to the alloy surface, but surely, scale morphology did not depend on alloy contents.

Fig. 3. — SEM of the scale formed on Fe45Cr in H_2/H_2S under $p_{S_2} = 10^{-3}$ Pa at 800 °C. Magnification 250 $\times$.

Fig. 4. — Cross section of the scale formed on Fe26Cr in H_2/H_2S under $p_{S_2} = 10^{-3}$ Pa at 800 °C. Magnification 200×.

X-ray diffraction analysis of sample scales were carried out and the entire sample was placed on the goniometer head. The results were not distinct. In scales built on Fe3Cr, Fe10Cr and Fe26Cr presence of $FeCr_2S_4$ spinel was revealed, whereas on Fe45Cr chromium sulfide Cr_3S_4 was found to be main constituent.

Acknowledgements.

The authors are gratefully Dr. S. M. Dubiel for supplying the alloys and for stimulating discussions.

References

- [1] RAHMEL A., GONZALES J., *Werkst. Korros.* **22** (1971) 283.
- [2] DANIELEWSKI M., MROWEC S., *J. Thermal. Anal.* **29** (1984) 1021.
- [3] NARITA T., SMELTZER W.W., NISHIDA K., *Oxid. Met.* **17** (1982) 299.
- [4] MROWEC S., STOKLOSA A., *Oxid. Met.* **3** (1971) 291.
- [5] ZUREK Z., *J. Therm. Anal.* **39** (1993) 15-20.
- [6] MROWEC S., WALEC T., WERBER T., *Oxid. Met.* **1** (1969) 93.
- [7] NARITA T., NISHIDA K., *Oxid. Met.* **6** (1973) 157-181.
- [8] DAVIN A., COURTSOURADIS D., *Cobalt* **17** (1962) 23.