THE EFFECT OF WATER VAPOUR ON THE HIGH-TEMPERATURE OXIDATION OF A HIGH SPEED STEEL[1]

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Abstract

The effect of altering the water vapour content on the oxidation rate of a high speed steel (HSS) at 650 °C in synthetic air for times up to 14.4 ks was investigated. At all levels of water vapour addition studied up to a maximum of 12.2 vol% the oxidation rate was increased but the increase was most marked at water vapour contents greater than about 7.5%. The oxide microstructure and composition was examined using SEM, EDX and XRD. This investigation showed that water vapour encouraged the formation of whiskers and platelets on the surface of the oxidized steel, and that at this early stage of the oxidation process the large carbide precipitates present in the steel remained unoxidized. In the absence of water vapour a protective duplex oxide layer was formed with an inner chromium-rich oxide. Addition of the water vapour transformed this layer into a thick scale, also duplex in nature, but there was no evidence of chromium enrichment in the scale. These observations are interpreted in terms of the current understanding of the effects of water vapour and it is concluded that the main effects are related to the production of volatile chromium and iron compounds and the ingress of hydrogen-containing species through pores in the scale. This leads to a breakdown of the protective chromium-rich layer and a change in the oxide growth mechanism from predominantly cation transport to one dominated by inward migration of oxidant.
Key words: Oxidation; Water vapour; High speed steels

EFEITO DO VAPOR DE ÁGUA NA OXIDAÇÃO EM ALTA TEMPERATURA DE UM AÇO RÁPIDO

Resumo

O efeito da mudança do teor de vapor de água na taxa de oxidação de um aço rápido a 650 °C em ar sintético por 14,4 ks foi investigado. Com o aumento do teor de vapor de água, até o máximo estudado de 12,2 %, a taxa de oxidação aumentou, porém, este aumento foi mais significante em teores de vapor de água maiores do que 7,3%. A microestrutura e a composição das camadas de óxido foram examinadas por MEV, EDX e DRX. Foi verificado que a presença de vapor de água favorece a formação de óxidos com morfologia de whiskers e de plaquetas na superfície do aço e que, neste estágio inicial de oxidação, os carbetos presentes no aço permaneceram sem ser oxidados. Em atmosfera sem a presença de vapor de água, uma camada protetora de oxidação dupla contendo uma região interna de óxido rico em cromo foi formada. A adição de vapor de água trasformou esta camada em uma camada dupla mais espessa e sem evidências de enriquecimento de cromo na região interna. Estas observações foram interpretadas com base no atual conhecimento dos efeitos da presença de vapor de água na oxidação em altas temperaturas. Foi concluído que os principais efeitos estão relacionados com a produção de compostos voláteis de cromo e de ferro e com o ingresso de espécies contendo hidrogênio através de poros da camada de óxido. Estes fatores acarretaram na não formação de uma camada protetora rica em cromo e na mudança do mecanismo de crescimento da camada de óxido de predominantemente transporte catiônico para um mecanismo dominado pela migração da espécie oxidante.
Palavras-chave: Oxidação; Vapor de água; Aço rápido.

1   INTRODUCTION

It is well known that the presence of water vapour may significantly affect the high-temperature oxidation behavior of some metals and alloys. Thus, most technical steels oxidize faster in air or combustion gases containing water vapour than in correspondingly dry gases.[1]

There is no satisfactory explanation on the effects of water vapour. Kofstad[2] reviewed the effects of water vapour on oxidation of pure iron and iron-base alloys. For iron-base Cr_2O_3 and SiO_2 forming alloys, the protective scale, which developed in dry oxygen, failed to develop or was broken down in oxygen containing sufficiently large amounts of water vapour.[2-3] Similar results have been obtained for Fe-Cr alloys with Cr contents up to 14% or 15% oxidized at 1000 °C in an Ar + H_2O mixture (3,4). Chromium was not selectively oxidized when water vapour was present in contrast to the behaviour in dry air/oxygen; rather the scale consisted of a seemingly dense outer layer of magnetite and an inner layer of wüstite and Fe-Cr spinel. A compact, protective chromia layer was, however, formed on a high-purity Fe-28% Cr alloy in the same conditions.[3,4] A study of Fe-Cr alloy oxidation at 900-1000 °C showed that the reason for the increase of oxidation in the presence of water vapour is that an initially-formed Cr_2O_3 scale cannot be maintained.[5]

An increase of the oxidation rate was observed for the high speed steels oxidized in wet atmospheres due, probably, to the same mechanism observed in Fe-Cr alloys.[6] However, some aspects of the oxidation behavior of these steels are still not well understood.

The present paper investigated the oxidation rate and the scale microstructure of a high speed steel, which contains 4.06 weight percent of chromium, at 650 °C, with different amounts of water vapour.

2   EXPERIMENTAL

Table 1 shows the nominal chemical composition, determined by wet chemical analysis, of the high-speed steel used in this study. Cylindrical samples ($\varnothing$ 9.2 $\times$ 1 mm) with about 1.6 cm^2 surface area were cut from ingots, abraded with 600 mesh SiC paper and then polished to 3 μm diamond paste. Just before oxidation tests, the samples were cleaned for 10 minutes in acetone using ultrasonic agitation.

Table 1. Nominal Composition of the high-speed steel (wt. %).

Sample	C	Cr	Mo	V
A1	1.5 – 2.5	4.06	2.02	4.79

The oxidation tests were carried out in a thermobalance at 650 °C for up to 14.4 ks. The dry oxidation atmosphere was provided by a flowing nitrogen (99.999% pure) – 20% oxygen (99.97% pure). The wet mixed gas was obtained by passing N_2 – O_2 (ratio 4:1) through distilled water by means of a bubbler. The wet mixed gas passed through a pipe preheated at 80 °C before being admitted to the thermobalance. A hygrometer linked to a computer was connected to the gas pipe in order to monitor, on line, the water vapour concentration during the tests. The distilled water temperatures were thermostatically

controlled at 30 $^{\circ}$C, 40 $^{\circ}$C and 50 $^{\circ}$C, producing a water vapour concentration of 4.2 vol%, 7.3 vol% and 12.2 vol%, respectively[1].

In order to prevent the water vapour from condensing on the measuring system of the thermobalance, a counterflow gas (Ar, 99.999% pure) was maintained through the upper part of the thermobalance. The samples were suspended in the furnace tube which was heated at 50 $^{\circ}$C/min up to 650 $^{\circ}$C in the protecting gas with a volumetric flow rate of 20 ml/min, controlled by a flow meter. When the samples reached 650 $^{\circ}$C, the oxidation gas was introduced into the themobalance. The oxidation gas flow was controlled to a volumetric flow rate of 60 ml/min. After oxidation the sample was cooled in flowing Ar gas.

Subsequent to oxidation, the samples were further examined using X-ray diffraction with Cu – Kα radiation and scanning electron microscopy with energy dispersive X-ray analysis (SEM / EDX).

3 RESULTS

Kinetics

Figure 1 shows the mass gain plots for the alloy as a function of the water vapour content of the atmosphere, where it can be clearly seen that the presence of water vapour increases the oxidation rate by up to a factor of about 10. It is of interest to note that the observed increase in rate is not directly proportional to the water vapour content, with a small increase being observed for the 4.2% water addition and a larger incremental change in rate when 7.3% water vapour was added, and then again a small increase for the 12.2% water.
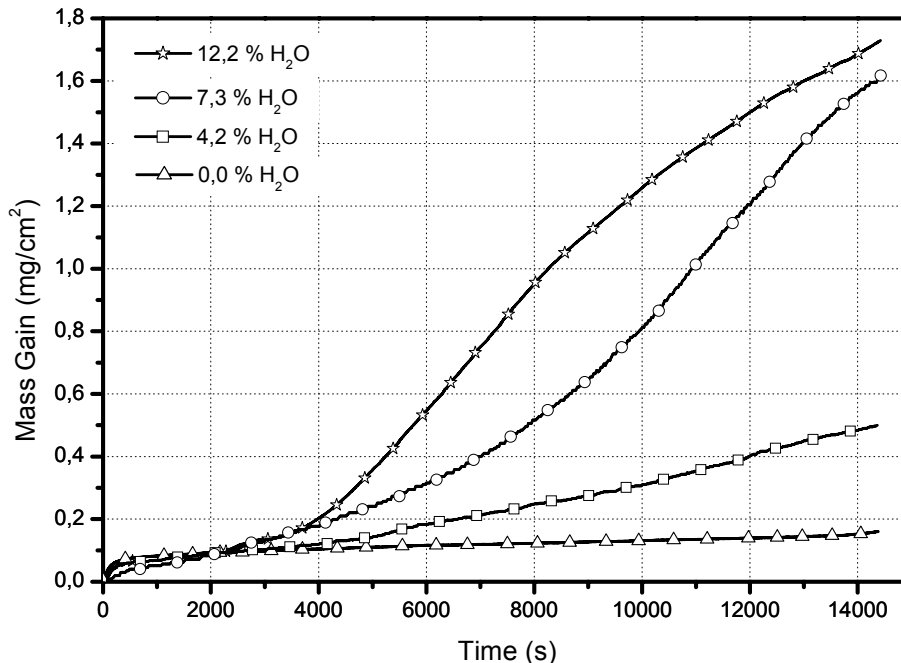

Figure 1. Mass gain plots for the HSS as a function of the water vapour content of the atmosphere

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[1] In all future references to gas composition "%" will be taken to mean volume percent

Scale Microstructure and Analysis

The morphology of the surface of the scale was greatly affected by the presence of water vapour. Figure 2 contrasts the structures found on the scales grown in 4.2% and 7.5% water vapour, where it can be seen that the scale formed in the drier gas mixture had only a very few whiskers whereas that formed in the 7.5% water vapour was almost entirely covered in whiskers and platelets. It can also be observed in Figure 2 that some spallation and oxide cracking occurred in the drier gas mixture.
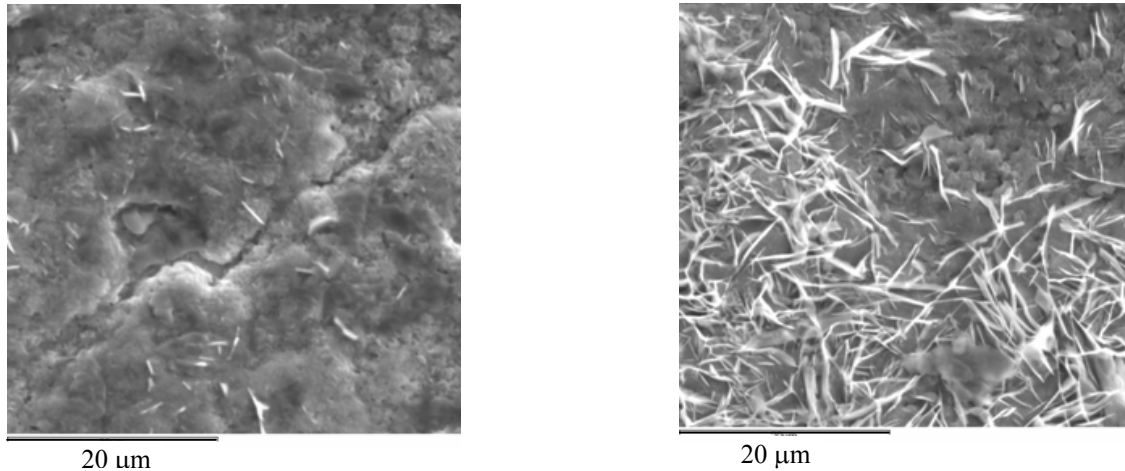

20 um   20 μm

Figure 2. Secondary electron images of the surface of HSS specimens oxidized for 14.4 ks at 650 °C in air (a) with 4.2% and (b) with 7.5% water vapour.

Other features of interest from these specimens are shown in Figures 3 and 4. The regions beneath the spalled areas of the specimen oxidized in the 4.2% water vapour gas mixture were chromium-rich indicating the presence of a chromium rich inner oxide layer (Figure 3). For both the 4.2% and 7.5% atmospheres, vanadium-rich regions were observed (Figure 4). For the specimens oxidized in the drier gas these vanadium-rich regions appeared to be associated with carbides which had not been oxidized, while for the specimen oxidized in the gas mixture containing 7.5% water vapour whiskers or platelets did not form in these carbide regions.
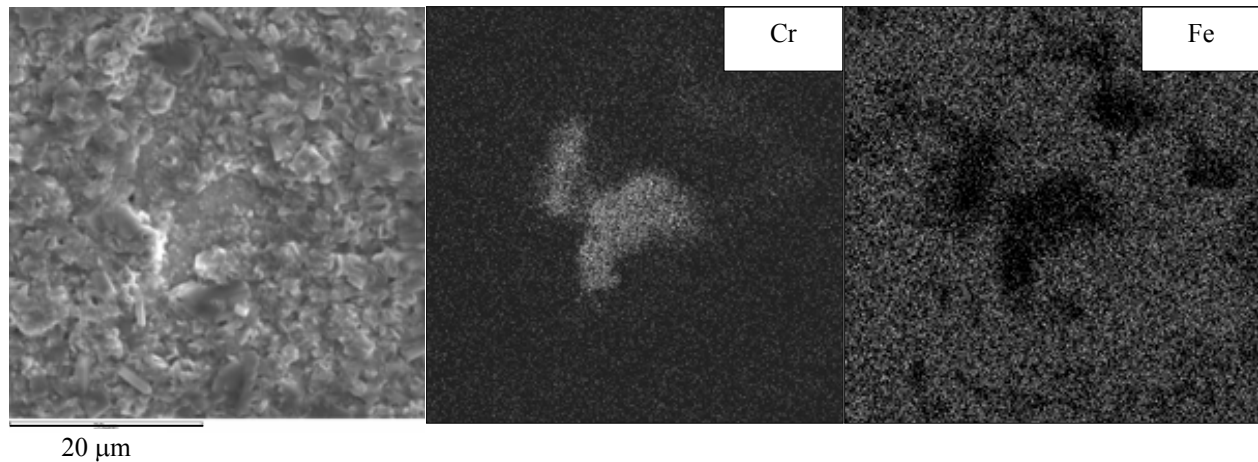

Cr   Fe

20 μm

Figure 3. Secondary electron micrograph and associated elemental maps of the surface of the HSS specimen oxidized for 14.4 ks at 650 °C in the air 4.2% water vapour gas mixture.
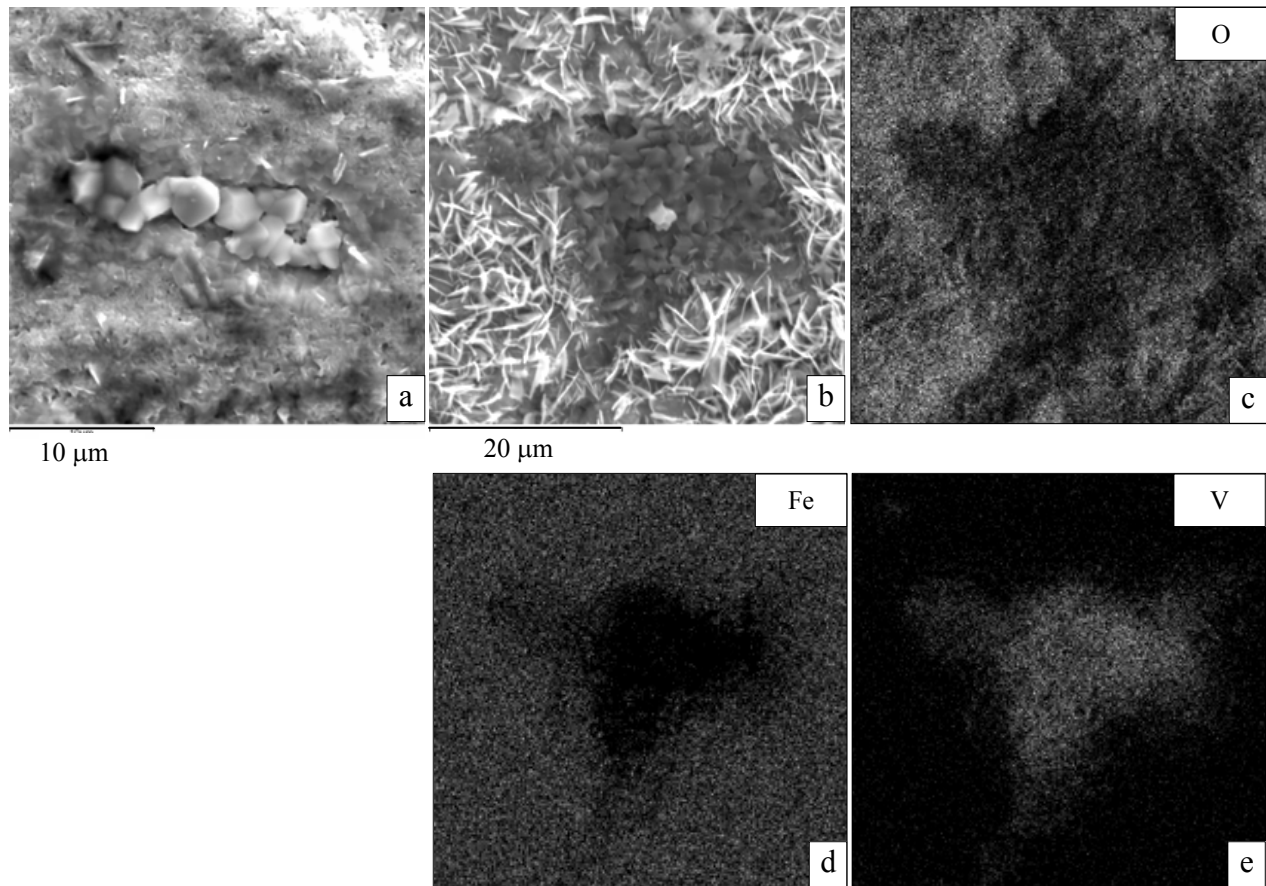
10 μm

20 μm

Figure 4. Secondary electron images and associated elemental maps of the surface of HSS specimens oxidized for 14.4 ks at 650 °C in air 4.2% water vapour mixtures (a) and air 7.5% water vapour mixtures (b), (c), (d) and (e).

Cross-sections were prepared of the specimens oxidized in dry air and the air 12.2% water vapour mixture and micrographs and analysis are shown in Figures 5 and 6. The specimen oxidized in dry air had a duplex structure with an outer iron-rich layer and a chromium-rich inner layer (Figure 5). The scale formed in the air 12.5% water vapour atmosphere was much thicker, but again duplex in nature; the outer layer was voided and was iron-rich, while the inner layer consisted of an iron chromium oxide mixture and unoxidized vanadium-rich carbides (Figure 6).
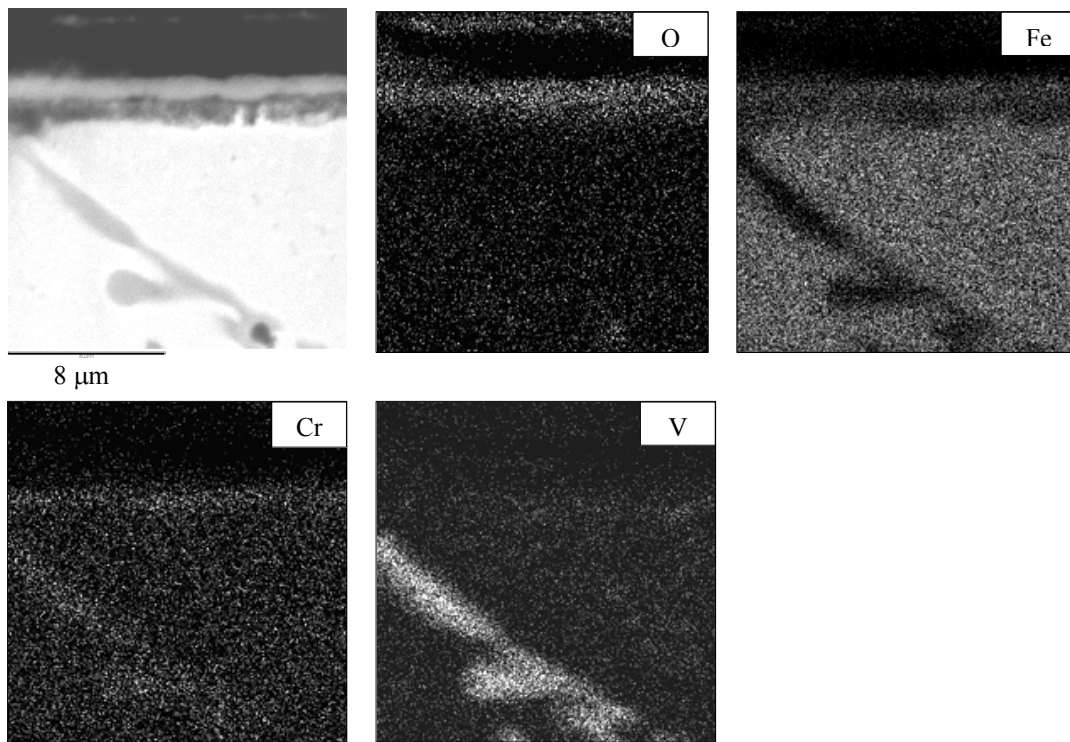
8 μm

Figure 5. Secondary electron image and associated elemental maps of a cross-section of a HSS specimen oxidized for 14.4 ks at 650 °C in dry air.
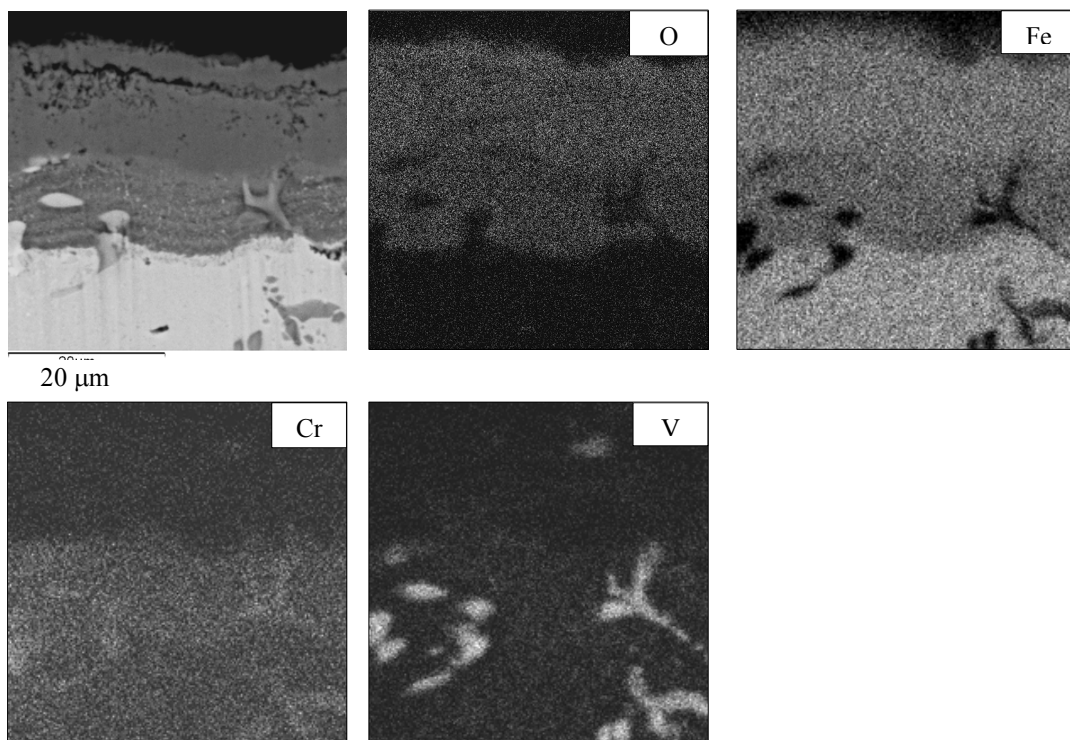

20 μm

Figure 6. Secondary electron image and associated elemental maps of a cross-section of a HSS specimen oxidized for 14.4 ks at 650 °C in an air 12.2% water vapour mixture.

X-ray diffraction confirmed the results obtained in the SEM. Figure 7 shows diffractograms obtained from specimens oxidized in air plus 4.2% and 7.5% of water vapour. The scale formed on the specimen oxidized in the atmosphere containing 4.2% water vapour consisted entirely of M_2O_3. The diffraction pattern corresponding to the iron matrix was detected in the diffractogram and the only oxide was consistent with the pattern for Fe_2O_3, but only small shifts would be expected for a dilute chromium containing oxide, so that it is not surprising that this was not detected. The XRD pattern for the HSS oxidized in 7.5% water vapour showed the presence of Fe_2O_3, Fe_3O_4 and $FeCr_2O_4$ in agreement with the analysis of the cross-section of the specimen oxidized in the atmosphere containing 12.2% water vapour (Figure 6).
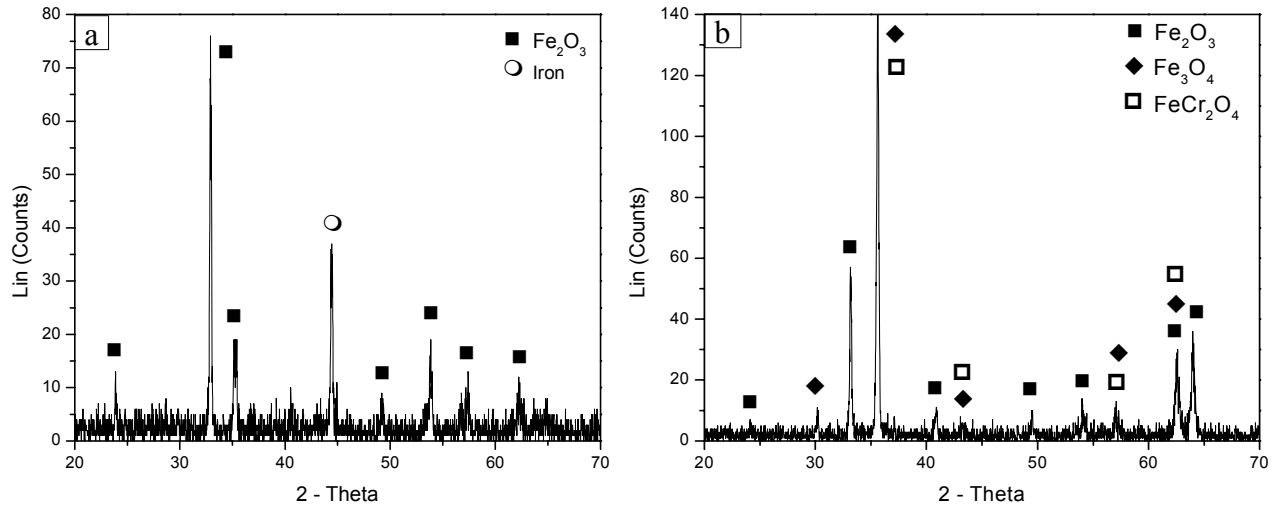

Figure 7. X-Ray diffraction patterns for scales formed at 650 $^\circ$C after 14.4 ks. (a) 4.2% water vapour mixture, (b) 7.5% water vapour mixture.

4 DISCUSSION

This work, in common with that of many other workers,[1-8] has demonstrated that the presence of water vapour results in a significant increase in the rate of oxidation of iron chromium alloys compared with that observed in dry air. The results for the HSS studied here indicate that this effect becomes more pronounced when the water content is greater than about 7.5%, although possibly if longer exposures were carried out the effect of the addition of the 4.2% water vapour may have been more marked. The microstructures also correlate well with the observed kinetics; a thin duplex scale with a protective chromium-rich inner layer was transformed into a thick non-protective scale with an outer porous magnetite layer and an inner iron chromium oxide. Also in agreement with the observations of other workers,[9-11] the presence of water vapour appears to improve the adhesion of the oxide layer. It was noted that oxide cracking and spallation was observed for the specimens oxidized in the dry conditions and with low moisture levels, whereas for the thicker scales formed with water contents of at least 7.5% no spallation was observed. Furthermore, for the HSS studied here, the carbides were often not oxidized in the relatively short exposures used for this work, and there is an indication that the presence of carbides in the surface may have prevented the development of a protective oxide layer in that region.

The steel under investigation has a relatively low chromium content (4.06 wt%) and the matrix concentration is further reduced to about 3.0 wt% due to chromium incorporation in the carbide precipitates. Nevertheless this low level of chromium is able to confer some degree of protection in dry atmospheres. For example, compared with the oxidation of rate of mild steel at 650 °C in dry air where a mass gain of about 1 mg cm^{-2} was observed[12] after 14.4 ks, the addition of chromium reduced the mass gain by a about a factor of 3-4. The XRD data indicated that only M_2O_3 was formed with an inner chromium-rich layer and no magnetite formation, again confirming the formation of a protective layer.

There are several effects of water vapour addition on the oxidation of the HSS studied in this research. Firstly, whiskers and platelets were observed, secondly, there was no chromium enrichment in the scale; instead the chromium was apparently immobile and was oxidized *in situ*, thirdly the outer iron-rich scale contains voids, fourthly scale adhesion (plasticity) is improved and finally, the rate of oxidation was increased. Gulbransen and Copan[13] demonstrated that whiskers only formed in the early stages of oxidation and were then converted into platelets, as appears to have been the case for the HSS studied here. Raymond and Rapp[14] have proposed that whisker formation is initiated at dislocations and rapid diffusion takes place along the central core to form whiskers.. It is proposed that the reason why these morphological features form in water-containing atmospheres is that water is more easily dissociated than oxygen and thus rapid growth takes place at the tip of the whiskers. It has also been proposed that whiskers and platelets can result from chemical vapour deposition processes, and volatile $Fe(OH)_2$ could have formed and then been oxidized at the higher oxygen pressures at the surface to form Fe_2O_3 platelets, although as shown by Davies and Dinsdale,[15] the vapour pressure would be quite low in the pressure range of interest (0.04-0.12 atm.).

It is noteworthy that the surface of the iron-rich layer appeared to be porous. Thus when water vapour was added to the atmosphere direct access to the chromium-rich layer may have been possible. Asterman *et al.*[8] observed evaporation of $CrO_2(OH)_2$ at 600 °C from 310 stainless steel and that this was flow rate dependent. Thus, if as just suggested, water vapour had direct access to the chromium-rich layer the formation of the volatile hydrated chromium oxide would be a possibility, and thus removing chromium from the protective inner layer and leading to the observed high rates of oxidation. Tuck et al.[11] proposed that enhanced plasticity of iron-based scales grown in water vapour containing atmospheres was due to dissolved hydrogen providing additional sources and sinks to increase dislocation mobility. Indeed this effect may also be responsible for the observed whisker and platelet formation. For the iron chromium-base alloys it is established that hydrogen is frequently observed in the alloy and also can be found dissolved in the inner Cr/Fe spinel layer.[9,16] By encouraging inward diffusion of oxidant fewer pores are generated at the alloy oxide interface which also contributed to improved scale adhesion. Voids were, however, formed in the outer iron-rich layer probably by a vacancy condensation mechanism[17] where according to the proposal of Rahmel and Toboloski[10] continued growth is dependent upon oxidant species being transported across the voids by "H_2/H_2O bridges".

It is concluded that the main effects are related to the production of volatile chromium and iron compounds and the ingress of hydrogen-containing species through pores in the scale. This leads to a breakdown of the protective chromium-rich layer and a

change in the oxide growth mechanism from predominantly cation transport to one dominated by inward migration of oxidant. It is clear that many of the observations reported here are consistent with those of other workers, but that the details of the processes involved in the breakdown of the protective layer require a more fundamental study.

5 CONCLUSIONS

- The oxidation rate of a 4.06%Cr HSS was increased by the addition of up to 12.2% water vapour to a synthetic air mixture in short-term tests at 650°C
- Water vapour encouraged the formation of whiskers and platelets on the surface of the HSS.
- The oxide formed under dry condition had a tendency to crack and spall during cooling, whereas that formed in the presence of water vapour appeared to be more plastic and adherent.
- The protective scale formed under dry conditions had a chromium-rich inner layer, but when water vapour was present a thick duplex scale was formed that was not enriched in chromium.

REFERENCES

1 Douglass, D.L., Kofstad, P., Rahmel, A., Wood, G., International Workshop on High-Temperature Corrosion, Oxidation of Metals, v. 45, n. 5/6, p. 529-620, june 1996.
2 Kofstad, P., High-Temperature Corrosion, London: Elsevier Applied Science, 1988.
3 Fujii, C. T., Meussner, R. A., Journal of Eletrochemical Society, v.110, p.1195, 1963
4 Wood, G.C., Wright, I.G., Hodgkiess, T., Whittle, D. P., Werkst. Korros., v.21, p. 900, 1970.
5 Kvernes, I., Oliveira, M., Kofstad, P., High Temperature Oxidation of Fe-13Cr-xAl alloys in air/H_2O vapour mixtures, Corrosion Science, v. 17, n. 3, p. 237-252, 1977.
6 Jianian, S., Longjiang, Z., Tiefen, L., High-Temperature Oxidation of Fe-Cr Alloys in Wet Oxygen, Oxidation of Metals, v. 48, n. 3/4, p. 347-356, January 1997.
7 Monteiro, M. J., Rizzo, F.C., Effect of Chromium Content on the Oxidation Behaviour of High-Speed Steels Under Dry and Moist Air Environments, International Symposium on High Temperature Oxidation & Corrosion 2005 - ISCHOC 2005, 2005.
8 (8). Asteman, H., Svensson, J.-E., Johansson, L.-G, Oxidation of 310 Steel in H_2O/O_2 Mixtures at 600 °C: the Effect of Water-Vapour-Enhanced Chromium Evaporation, Corrosion Science, v. 44, p. 2635–2649, 2002.
9 Quadakkers, W.J, Norton, J.F, Penkall, H.J, Beuer, U., Gil, A., Rieck, T., Hänsel,M., 3rd International Conference Microscopy of Oxidation, p. 221, 1996.

10 A. Rahmel, A., Toboloski, J., Einfluss von Wasserdampf unf Kohlendioxid auf die Oxidation von Eisen in Sauerstoff bei hohen Temperaturen, Corrosion Science,v. 5 p. 333-340, 1965.

11 Tuck, C. W., Odgers, M., Sachs, K., The Oxidation of Iron at 950 °C in Oxygen/Water Vapour Mixtures, Corrosion Science, v. 9, p. 271-285, 1969.

12 Haibin, L., Kaiming,L., Lefu, M., Shoure, G., Shuangxi, W., Materials Letters, v. 51, p. 320-324, 2001.

13 Gulbransen, E. A., Copan, P, Proc. European Conf. on Electron Microscopy, Delft, p. 225, 1960,

14 Raymond G. M., Rapp, R. A, In situ Observation of Whiskers, Pyramids and Pits During High Temperature Oxidation of Metals, Oxidation of Metals, v. 21 p. 89-102. 1984

15 Davies, H., Dinsdale, A., Theoretical Study of Steam Grown Oxides as a Function of Temperature, Pressure and $p(O_2)$, Materials at High Temperatures, v. 22, p.15-25, 2005.

16 Dieckmann, R., Materials at High Temperatures, v. 22, p.93-103, 2005.

17 Quadakkers, W. J., Ennis, P.J., Zurek, J., Michalik, M., Materials at High Temperatures, v. 22, p.47-60, 2005.