



THE EFFECT OF WATER VAPOUR ON THE ADHESION OF OXIDE SCALES GROWN ON HIGH SPEED STEEL ¹

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Abstract

An investigation has been carried out into the effects of steam on the adhesion of oxide scales grown on two different chemical compositions of high speed steels. The oxidation tests were carried out in a thermobalance at 650 °C for up to 14,4 ks. The mass gain of the specimens increased with increasing contents of water vapour, and in no case were parabolic kinetics obeyed. Alloy composition had no effect on the oxidation rate in dry conditions, but the alloy containing increased vanadium had the lowest rate in moist conditions, however this effect was small. The “adhesion” of the oxide scale was determined using indentation with a Rockwell C diamond to determine the interfacial toughness. The results of the investigation indicated that oxide adhesion was lowest for the specimens exposed to dry conditions, and that with increasing water vapour content, the scale was more adherent. It is noteworthy that whereas the scale formed in dry conditions spalled at the metal oxide interface, that formed in moist gas failed cohesively within the scale. Indentation test results showed that an increase in the vanadium concentration was deleterious to oxide adhesion in both the dry and wet environments.

Key words: Steam oxidation; Adhesion; Kinetics; High speed steels.

EFEITO DO VAPOR DE ÁGUA NA ADESÃO DA CAMADA DE ÓXIDO FORMADA DURANTE A OXIDAÇÃO DE AÇO RÁPIDO

Resumo

O efeito do teor de vapor de água na adesão da camada de óxido formada durante a oxidação de dois aços rápidos foi investigado. Os testes de oxidação foram realizados em uma balança termogravimétrica a 650°C durante 14,4 ks. O ganho de massa das amostras aumentou com o aumento do teor de umidade. A variação da composição química da liga não causou nenhum efeito na taxa de oxidação em condição de ar seco. A liga contendo maior teor de vanádio teve a menor taxa de oxidação em atmosfera úmida, entretanto esse efeito não foi acentuado. A adesão da camada de óxido foi determinada utilizando-se um indentador Rockwell C. Os resultados indicaram que a adesão da camada de óxido foi menor para camadas formadas em atmosferas secas e que com o aumento do teor de umidade a camada se tornava mais aderente. Foi observado que enquanto a camada de óxido formada em atmosfera seca falhava na interface metal/óxido a falha da camada formada em atmosfera úmida acontecia de maneira coesa. Os resultados dos testes de indentação mostraram que o aumento do teor de vanádio foi prejudicial à adesão da camada de óxido formada tanto em atmosfera seca quanto úmida.

Palavras-chave: Oxidação em atmosfera úmida; Cinética; Adesão; Aços rápidos.

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1 INTRODUCTION

The application of interest here is the behaviour of high-speed steels that are used in the surfacing of hot rolls. The steels are subjected to a complex set of conditions that include injection of steam for cooling, high temperatures and mechanical stress. In order to produce a high quality rolled product it is important to minimise surface defects on the rolls and thus a low oxidation rate is necessary for good performance. It is well known that most metals and alloys oxidize faster in air or combustion gases containing water vapour than in correspondingly dry gases.^(1,2) Performance could be improved by a better understanding of the factors that control oxidation, fracture and adhesion of the scale produced under these conditions.

There have been many investigations of the effect of water vapour on ferritic Fe-Cr steels but most have considered alloys with chromium concentrations in excess of about 10 % and current research is driven to a very large extent by development of interconnects for solid oxide fuel cells.⁽³⁻⁵⁾ There are three main factors that may contribute to the observed increase in the oxidation rate of ferritic Cr-containing steels. Firstly, volatile chromium- and iron-containing compounds can form in oxygen-rich⁽⁶⁾ and oxygen-lean atmospheres [**Erro! Indicador não definido.**] respectively, which lead to formation of less protective oxides either by loss of the protective element, chromium, or the development of a more porous scale. Secondly, the transport properties of chromia and iron oxides can be modified by the presence of protons, or effectively OH^- , derived from water vapour.⁽⁷⁾ Thirdly, and in part as a consequence of the altered transport properties, the oxide scale is often observed to be more plastic and hence adhesion is improved compared with oxide scales formed in dry conditions.^(8,9)

Reactivity of the oxide toward water vapour is clearly important and in this respect the acid base nature of the oxide is believed to be a controlling factor. Galerie *et al.*⁽¹⁰⁾ have suggested that the more acid the oxide is, the less likely it is to react with water vapour and vice versa. Acid base data of oxides is frequently derived from room temperature measurements⁽¹¹⁾ and unfortunately at present there are insufficient data about the behaviour of thermally formed oxides at high temperature to fully develop this argument. Furthermore, dissociation of any gas molecule is favoured by surface defects, and dissociation of water seems to be more rapid at lower temperatures than, for example, oxygen. Thus it is clear that alloy composition, water vapour content and temperature are important parameters that control alloy behaviour under these conditions.

An increase of the oxidation rate for the high-speed steels oxidized in wet atmospheres was observed by Monterio *et al.*⁽¹²⁾ and Pieraggi *et al.*⁽¹³⁾ The present paper aims to extend these investigations to study the effect on the oxidation rate and on scale adhesion of water vapour content of the atmosphere and alloy composition.

2 EXPERIMENTAL

2.1 Materials

The compositions of two high-speed steels used in this study alloys are listed in Table 1. The alloys were prepared as cast ingots and the chemical composition was determined by wet chemical analysis.

Table 1. Composition of alloys, % mass fraction

	C	Cr	Mo	W	V	Fe
A1	1,5-2,5	4,06	2,02	1,96	4,79	Bal
A2	1,5-2,5	4,19	2,07	2,02	8,09	Bal

Figure 1 shows a typical microstructure of high speed steel used for the manufacture of hot rolling rolls. Two types of carbides are observed; MC carbides, which are rich in vanadium and M_2C carbides, which are rich in chromium.

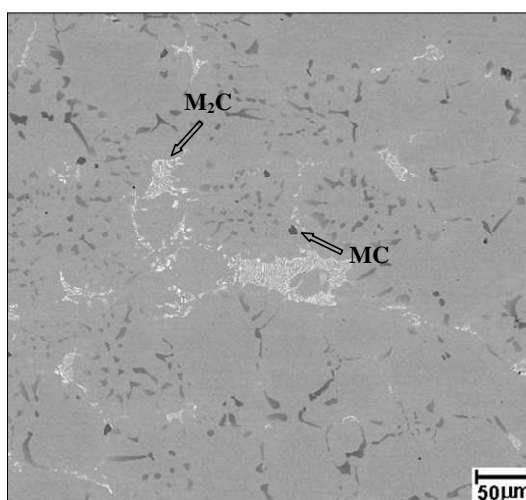


Figure 1 – Backscattered scanning electron micrograph showing typical microstructure of high speed steel used for the manufacture of hot rolling rolls.

Cylindrical samples ($\varnothing 9,2 \times 1$ mm) with about $1,6 \text{ cm}^2$ surface area were cut from ingots, abraded with 600 grade SiC paper and then polished with $3 \mu\text{m}$ diamond paste. Immediately before oxidation tests, the test specimens were cleaned for 10 minutes in acetone using ultrasonic agitation.

2.2 Oxidation

Oxidation tests were carried out in a Setaram thermobalance at 650°C for 14,4 ks. The dry oxidation atmosphere was provided by a flowing nitrogen (99,999% pure) – 20% oxygen (99,97% pure) gas mixture. The wet mixed gas was obtained by passing $\text{N}_2 - \text{O}_2$ (ratio 4:1) through distilled water by means of a bubbler and then 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°C , 40°C and 50°C , producing a water vapour concentration of 4,2 %, 7,3 % and 12,2 %, respectively.

In order to prevent the water vapour from condensing on the measuring system of the thermobalance, a counterflow of dry Ar, (99,999% pure) was maintained through the upper part of the thermobalance. The specimens were suspended in the furnace tube that was heated at $50^\circ\text{C min}^{-1}$ to 650°C in Ar with a volumetric flow rate of 20 ml min^{-1} . When the specimen reached 650°C , the oxidation gas mixture was introduced and flow maintained at 60 ml min^{-1} . After oxidation the specimen was cooled in flowing Ar and placed in a desiccator.

2.3 Adhesion Tests

The type of adhesion test carried out in the present investigation was the high load indentation in which an estimate of the interfacial fracture strength can be obtained.⁽¹⁴⁾ Adhesion tests were carried out on in triplicate, using a single specimen.

Indentation tests were performed using a Rockwell hardness test according to ASTM 1994 with a preload of 100 N and a maximum load of 1.500 N. All specimens were tested approximately 24 hours after completion of the oxidation test during which period the specimens were stored in a desiccator. Images of the indent and damaged region were obtained in a scanning electron microscope, and using an image analysis system, the maximum extent of oxide cracking around the indent was defined manually and the area of the disbonded oxide calculated.

3 RESULTS

3.1 Oxidation Tests

Alloy A1 was exposed to four different conditions, dry air and air with additions of 4,2%, 7,3% and 12,2% water vapour, while alloy A2 was exposed to dry air and air containing 12,2% water vapour. Both alloys were exposed for 4 h at 650°C. Figure 2 shows the effect of water vapour on the kinetics of the oxidation for alloy A1. For all oxidation conditions, the initial oxidation was rapid before a transition to a slower rate, but when water vapour was present, “breakaway” occurred, and the time to breakaway decreased as the water vapour content increased. In no case were parabolic kinetics obeyed, and power law kinetics gave “n” values less than ½ that indicated sub-parabolic kinetics for the dry atmosphere, whilst “n” values of up to 2 were found for the moist conditions. Table 2 shows the average mass gain data for alloy A1 oxidised in all conditions.

Figure 3 shows the effect of water vapour on the kinetics of the oxidation for alloy A2. The behaviour is similar to that reported to alloy A1.

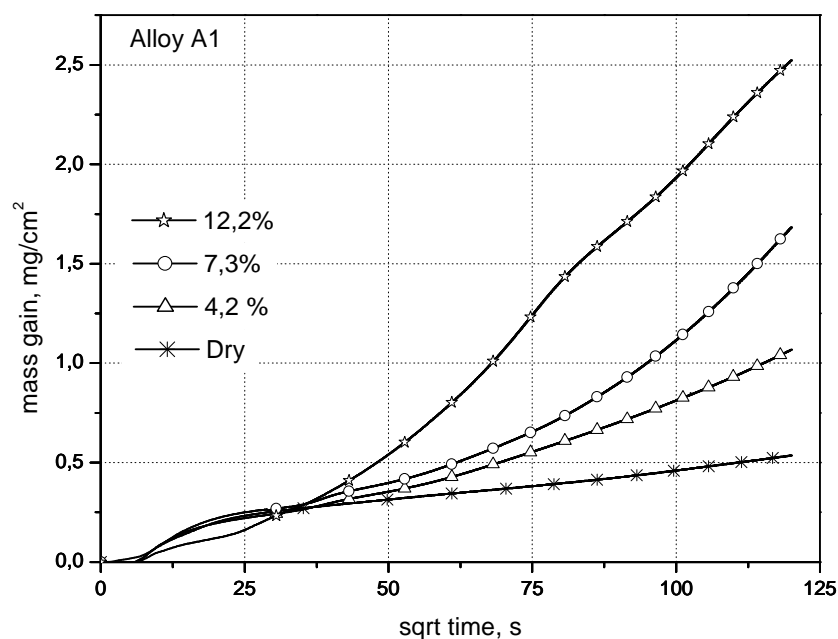


Figure 2 - Mass gain versus time curves for alloy A1 oxidised at 650 °C in dry synthetic air and with various water vapour additions.

Table 2. Average mass gain data for alloy A1 investigated after 4 h at 650°C in dry and moist air, mg cm⁻²

	0%	4,2%	7,3%	12,2%
A1	0,55±0,018	0,97±0,057	1,72±0,132	2,54±0,022

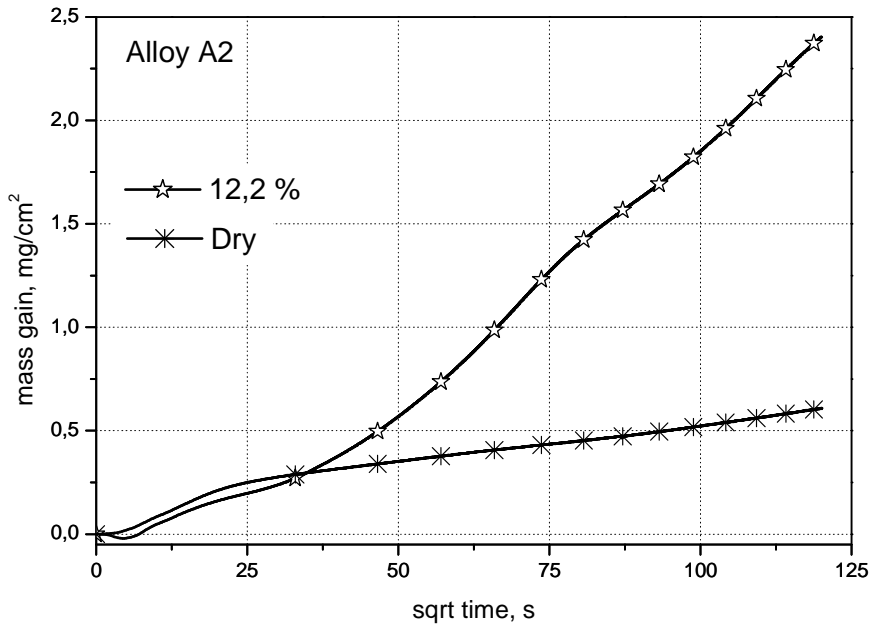


Figure 3 - Mass gain versus time curves for alloy A2 oxidised at 650 °C in dry synthetic air and 12,2% water vapour.

Table 3 lists the mass gain data, and as can be seen, increasing the water vapour content resulted in about a five-fold increase in the mass gain of all alloys. For the tests carried out in dry conditions, increasing V content had no effect in mass gain. For the tests with 12,2% water vapour there was a small statistical difference between the two alloys, the highest mass gain was observed for alloy A1.

Table 3. Average mass gain data for all alloys investigated after 4 h at 650 °C in dry and moist air, mg cm⁻²

	0%	12,2%
A1	0,55±0,018	2,54±0,022
A2	0,58±0,061	2,33±0,062

3.2 Adhesion Tests

Figure 4 shows scanning electron microscope images of the indent and damaged region of alloy A1 oxidised in dry, 4,2%, 7,3% and 12,2% water vapour atmospheres, respectively, after hardness testing. The red lines delimit the maximum extent of oxide cracking around the indent.

Table IV shows the indentation test results for alloy A1. In the case of alloy A1, where three levels of water vapour were used, the area disbonded decreased almost linearly with increasing water vapour content.

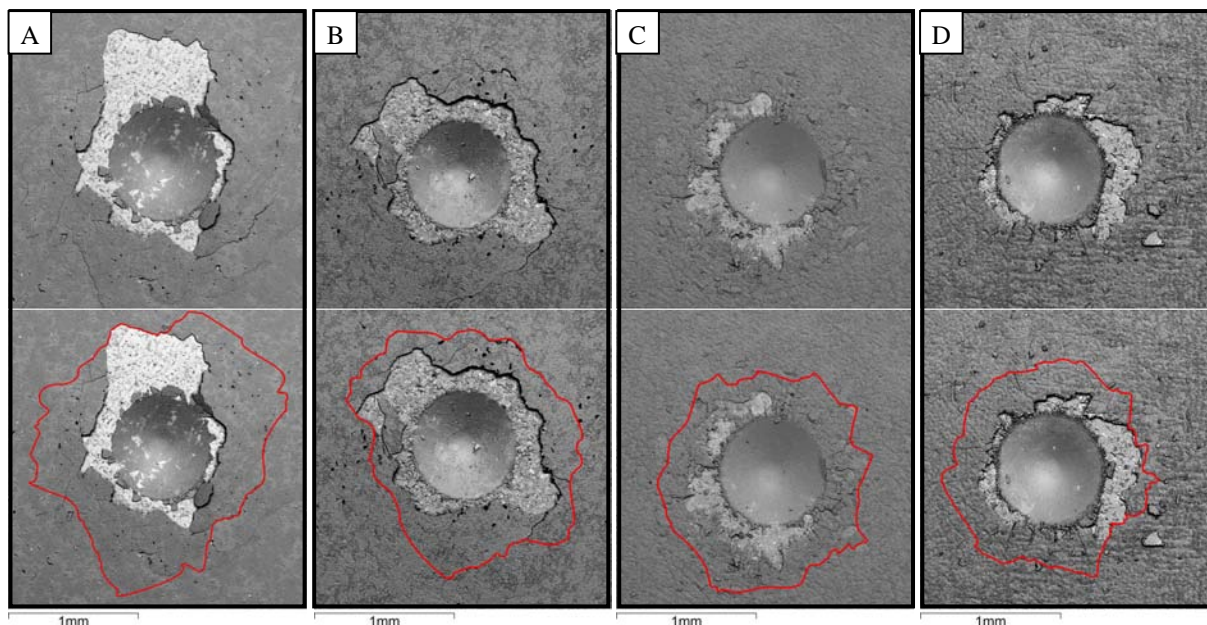


Figure 4 - Backscattered scanning electron micrographs of alloy A1 oxidised for 4 h at 650 °C (A) in dry synthetic air; (B) in 4,2 water vapour atmosphere; (C) in 7,3 water vapour atmospheres and (D) in 12,2 % water vapour atmospheres after Rockwell B hardness testing – the red line delineates the maximum extent of oxide cracking around the indent.

Table 4. Average area disbonded during indentation testing of alloy A1 as a function of water vapour content (%) of the atmosphere, mm²

	0%	4,2%	7,3%	12,2%
A1	2,43±0,24	1,79±0,35	1,38±0,07	1,18±0,04

Table 5 shows the indentation test results for all alloys. It can be seen that the area disbonded decreased when water vapour was present in the atmosphere. For both dry and wet conditions. Alloy A2 had the largest disbonded area.

Table 5. Average area disbonded during indentation testing as a function of alloy type and water vapour content (%) of the atmosphere, mm²

	0%	12,2%
A1	2,43±0,24	1,18±0,04
A2	3,10±0,14	1,79±0,34

Figures 5 and 6 show secondary scanning electron micrographs and associated X-ray maps of the fractured region around an indent for the case of alloy A1 exposed to dry and air with 12,2% water vapour addition, respectively. Note that for the case of oxidation in dry air, fracture occurred mainly at the alloy oxide interface, as indicated by the absence of oxygen. For the specimen oxidised in 12,2% water vapour, however, the fracture appeared to be largely cohesive and occurred at Cr-spinel/magnetite interface. Similar results were observed for the alloy A2 exposed to dry and wet conditions.

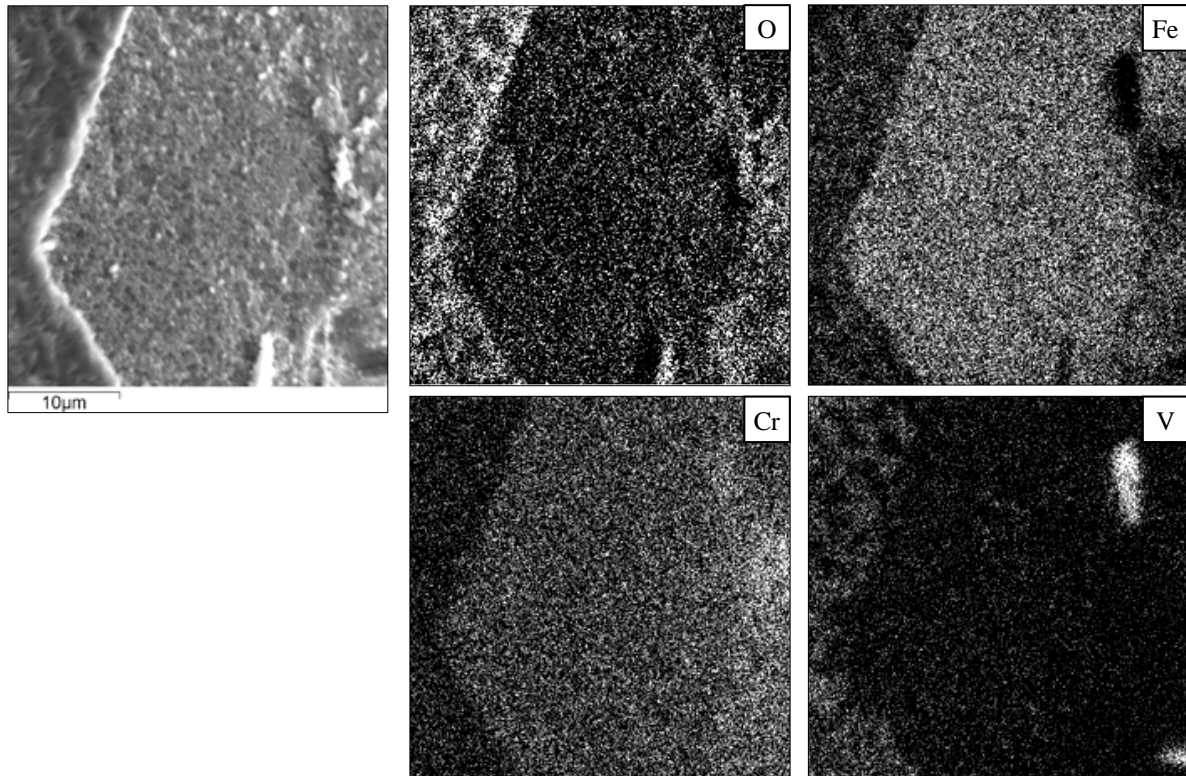


Figure 5 - Secondary scanning electron image and associated X-ray maps of the fractured region of alloy A1 oxidised for 4 h at 650 °C in dry air after indentation.

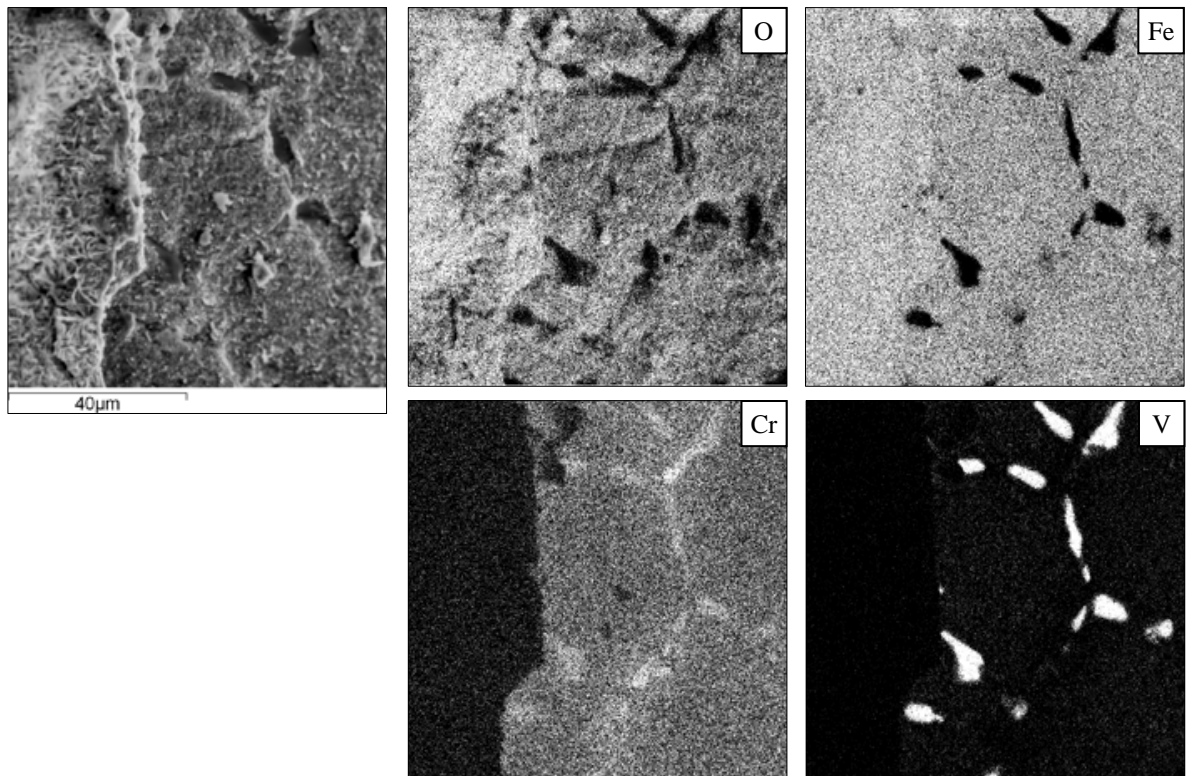


Figure 6 - Secondary scanning electron image and associated X-ray maps of the fractured region of alloy A1 oxidised for 4 h at 650 °C in air containing 12.2% water vapour after indentation.

Figure 7 shows SEM images of the fractured region of the oxide formed on alloy A1 and A2 after exposure to air 12,2% water vapour after indentation. Note the porous nature of the other layers formed on alloys A1 and A2.

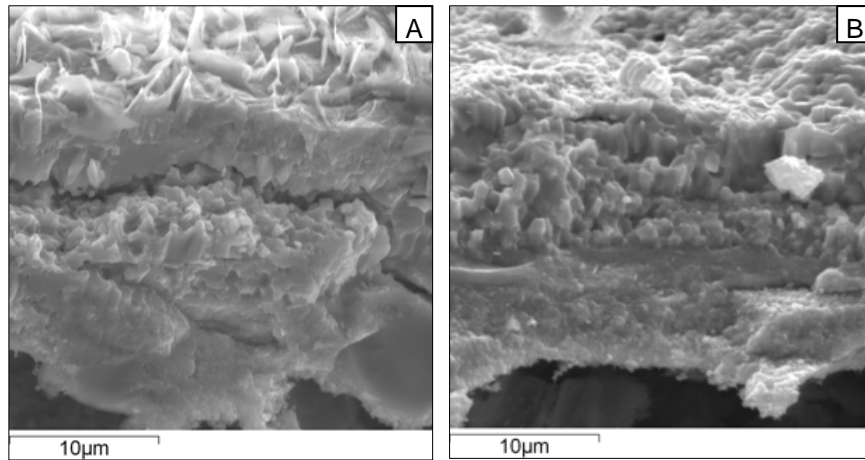


Figure 7 - Secondary scanning electron images of fractured regions after indentation (a) alloy A1 and (b) alloy A2 after exposure to air 12,2% water vapour for 4 h at 650°C.

Figures 8 and 9 show micrographs and corresponding X-ray maps showing cross-sections of alloy A1 and A2, respectively, after oxidation in 12,2% water vapour containing atmosphere. The inner oxide was slightly Cr-rich and contained unoxidised vanadium carbides.

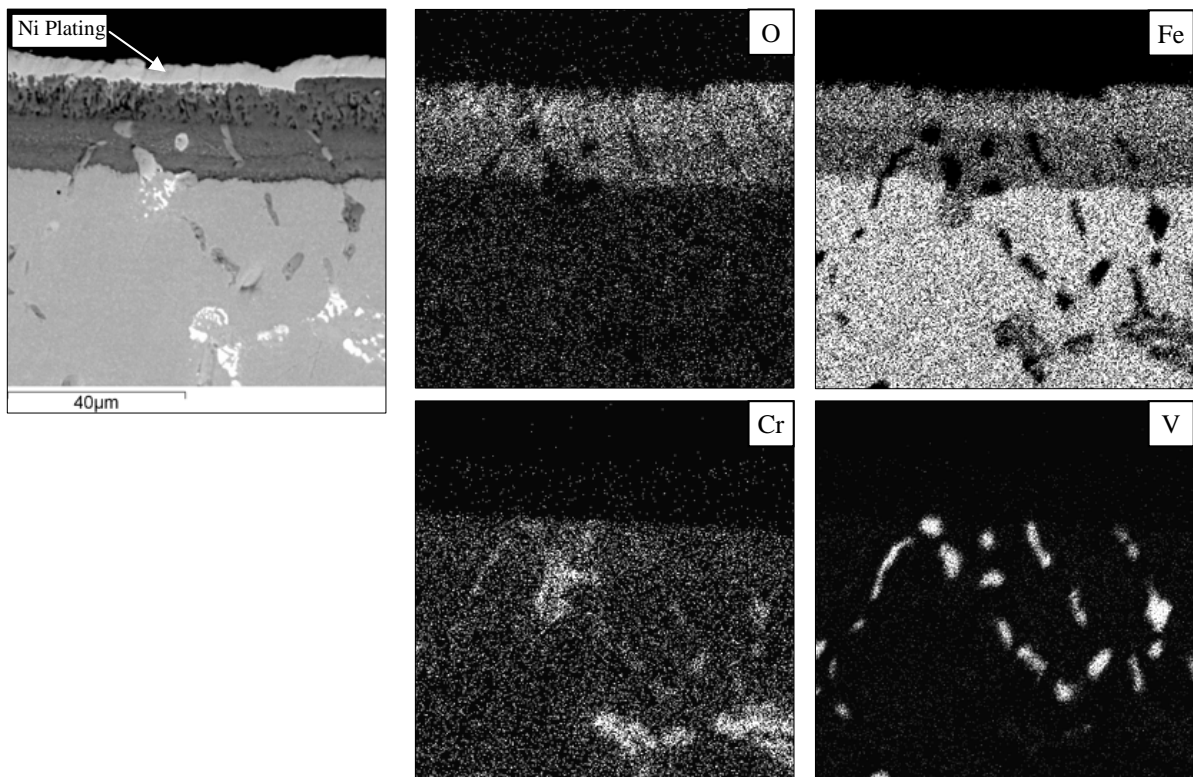


Figure 8 - Scanning electron micrograph of a cross-section of alloy A1 after 4 h at 650 °C in air 12,2% water vapour.

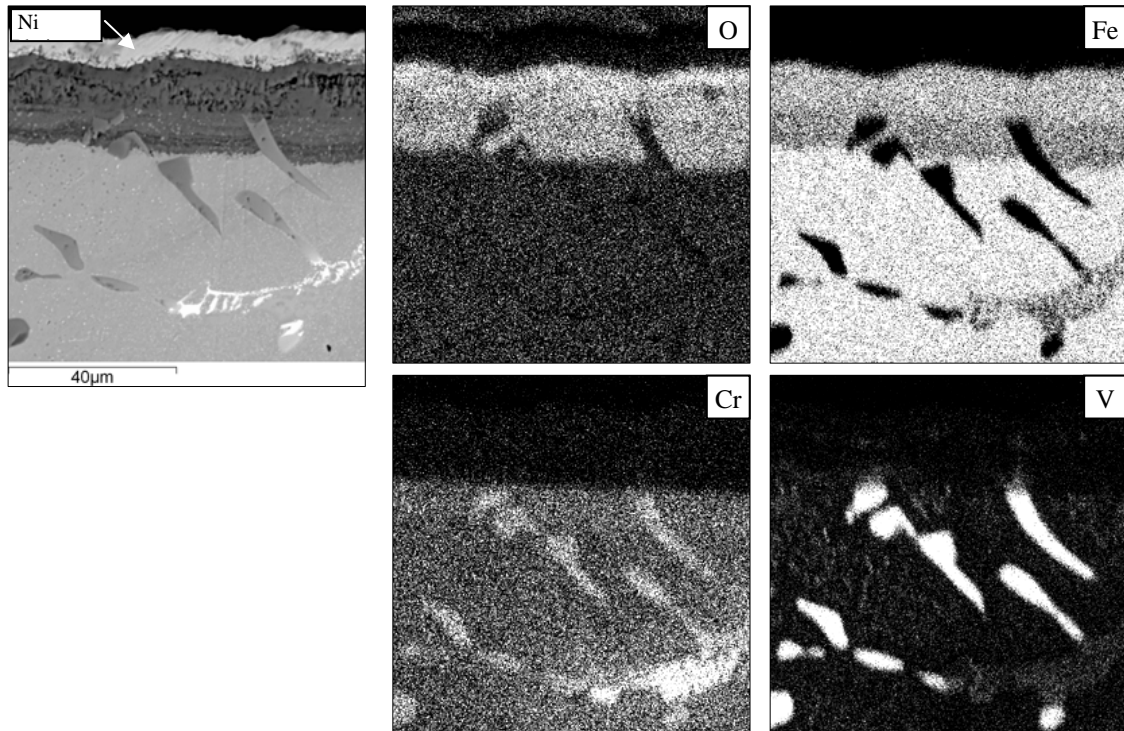


Figure 9 - Scanning electron micrograph of a cross-section of alloy A2 after 4 h at 650 °C in air 12,2% water vapour.

Cross-sections of the specimen showing the disbonded region of samples A1 and A2 are present in Figures 10 and 11, respectively. These images indicate cohesive failure within the oxide.

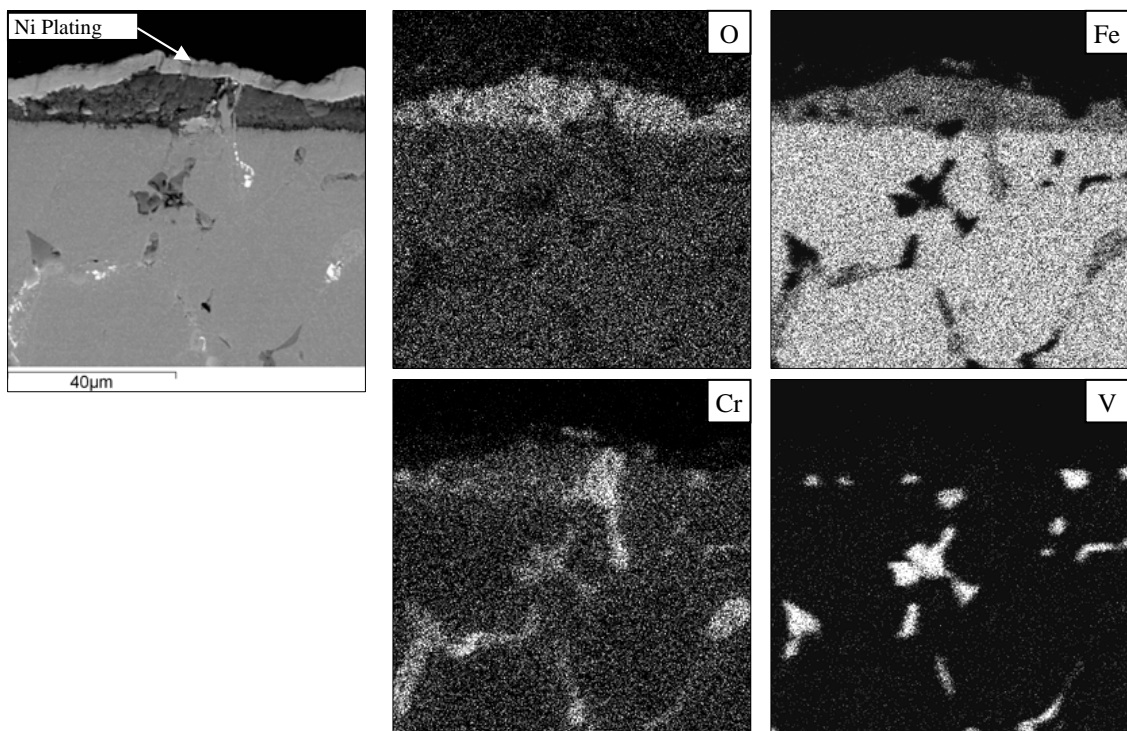


Figure 10 - Scanning electron micrograph of the disbonded region of alloy A1 after 4 h at 650 °C in air 12,2% water vapour.

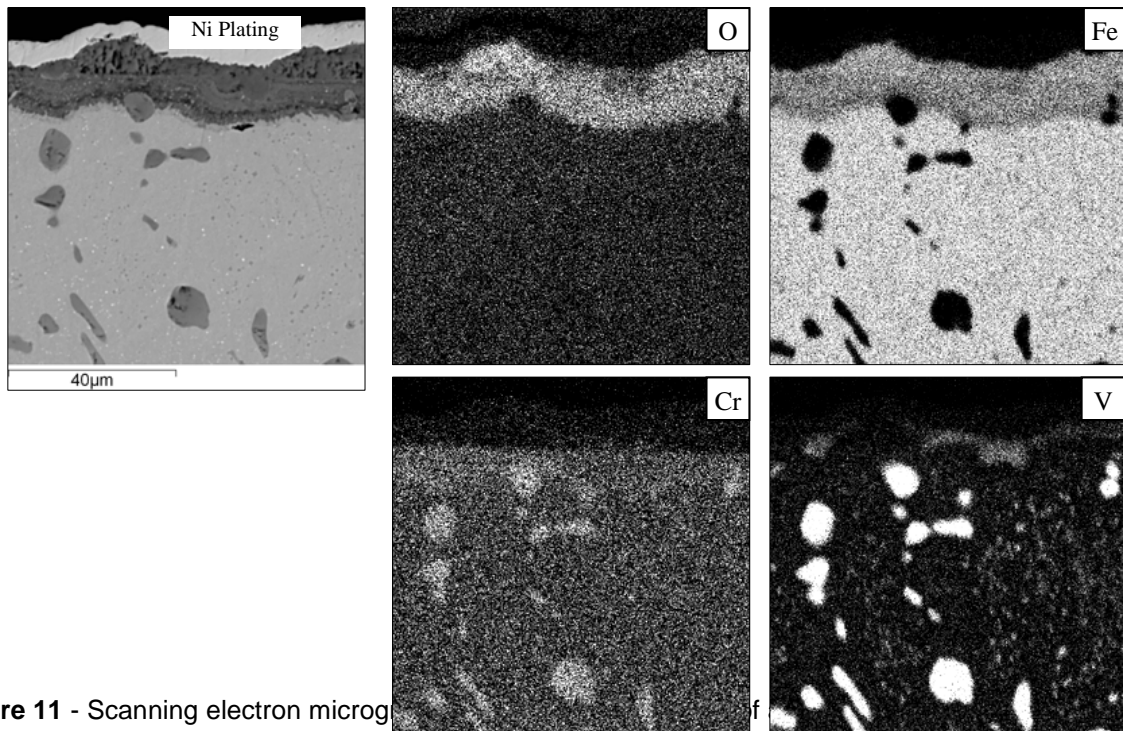


Figure 11 - Scanning electron micrographs of a Ni-plated surface oxidized in an atmosphere containing 12,2% water vapour.

4 DISCUSSION

Addition of water vapour increased the oxidation rate of the two alloys and there was a corresponding increase in scale adhesion. This observation is consistent with previous work^(2,8,9) and it could be related to the fact that water vapour encourages inward scale growth thereby inhibiting void formation at the alloy oxide interface that would arise during cation controlled oxide growth. Alternatively, stress relief cracking during oxide formation in water vapour-containing atmospheres has been observed by Schütze *et al.*,⁽¹⁴⁾ and it is possible therefore that the enhanced fracture resistance could be attributed to the presence of such cracks, thus giving rise to an apparent increase in deformation resistance.

Alloy composition had little effect on the oxidation rate in both dry and wet conditions. For the indentation test carried out, more damage was evident for the alloy high in vanadium oxidised in dry and wet conditions, so the scale adhesion could be ranked as follows: A2<A1. For the two alloys considered here, it appears that scale adhesion is not a function of scale thickness, since there was very little difference in oxidation rate for the alloys when exposed to the same conditions, so that oxide composition or microstructure probably had a greater influence. Generally, for specimens oxidised in wet conditions, failure was cohesive and occurred at the magnetite/Cr-containing spinel interface. It was observed in the cross-sections that the large carbide particles remain largely unoxidised and were found within the inner oxide layer as expected. It is proposed that these carbide particles act as stress raisers and as such initiate failure within the inner scale or at the inner/outer scale interface.

Considering now the effect of alloy composition. The vanadium content of alloy A2 was increased by approximately 60%. The chromium carbides were dendritic in nature with a fine microstructure, the vanadium carbides were coarse, and thus the vanadium carbides might be expected to act as stress raisers, and the oxide formed on the alloy high in vanadium exhibit the lowest fracture toughness. The indentation



adhesion test is a measure on interfacial fracture toughness [**Erro! Indicador não definido.**], and thus it seems reasonable that the high vanadium alloy showed the greatest damage.

5 CONCLUSIONS

The investigation into the effects of steam on the adhesion of oxide scales grown on two different chemical compositions of high speed steels oxidised at 650 °C for up to 14,4 ks allows the following conclusions:

- The mass gain of the specimens increased with increasing contents of water vapour;
- Alloy composition had no effect on the oxidation rate in dry conditions, but the alloy containing increased vanadium had the lowest rate in moist conditions;
- The oxide adhesion was lowest for the specimens exposed to dry conditions, and the scale was more adherent with increasing water vapour content;
- Indentation test results showed that an increase in the vanadium concentration was deleterious to oxide adhesion in both the dry and wet environments;
- For specimens oxidised in wet conditions, failure was cohesive and occurred at the magnetite/Cr-containing spinel interface.

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