

Oxide Structures Formed During the High Temperature Oxidation of Hot Mill Work Rolls

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Abstract The high temperature isothermal oxidation behaviour of work rolls and the oxide structures resulting from this process are presented. Oxidation of these alloys at 615 °C under various environmental conditions resulted in the formation of oxide crystals of different morphologies, depending on the chemical composition of the alloys and the gases present in the oxidant atmosphere. Particularly, the surface oxidation of high speed steel and high chromium iron for work rolls in hot strip mills included the formation of whiskers, platelets, and crystallites. The composition of the oxidant atmosphere also influenced the oxidation rate of the specimens by promoting the formation of protective or non-protective oxides. The reasons for the development of the different oxide morphologies and the effect that the oxides formed on the surface exert on the behaviour of important tribological variables present in the hot rolling of steel such as friction are discussed.

Keywords Oxides · Work roll · Whiskers · Platelets

Introduction

Steel production can be considered as one of the most important processes in the world, if not the most important one, given the considerable amount of products that are manufactured from this material. It is difficult to imagine a scenario that does not include the presence of steel despite that aluminium, titanium and nickel based alloys try to replace steel products for certain applications. It is for this reason that

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the quality of steel related to mechanical and surface properties represents a key aspect that would keep its advantage against other materials. Surface finish of steel products is strongly related to the many operational variables operational present in forming processes [1, 2]. Temperature can be considered as the most important and detrimental one because at the same that facilitates the transformation of steels to many shapes, it also promotes the formation of oxides which represent material losses and increase the cost of the final product [2–5]. In the hot rolling of steel strip, oxides are formed on the surface of both, stock and work rolls, given that the chemical reactions established between iron and oxygen are catalysed by the high temperature of the stock [6].

Information on the oxidation behaviour of work rolls is scarce mainly because studying the oxidation of work rolls represents a difficult task. Practically, it is almost impossible to replicate the mechanical and thermal conditions found in a hot strip mill. Despite this fact, some investigations dedicated to study the oxidation of work roll materials have been conducted [7, 8].

Regarding the relationship between work roll metallurgy and oxidation resistance, several ferrous alloys have been developed, being high chromium irons and high speed steel the common materials used for this application, but unfortunately, the oxidation of work rolls is inevitable. The use of one or another alloy depends mainly on the temperature profile of the stock along the finish stands in hot strip mills but, there is a high uncertainty about the differences between the surfaces changes of both work roll alloys induced by oxidation. In this investigation, the surface structures formed after the isothermal oxidation of high chromium white cast iron and a high speed steel work rolls are presented. The morphology and the chemical characteristics of the oxides are explained in terms of both, the chemical composition of the alloys and the components of the oxidant atmosphere.

Experimental Procedures

For this investigation the most common work roll materials were studied namely, a high speed steel and a high chromium white cast iron. These alloys were especially manufactured for earlier work roll projects [8, 9] and their chemical compositions are presented in Table 1. The oxidation behaviour of these materials was studied using an oxidation reactor capable to perform tests under controlled atmosphere conditions. The details on the operation principle and characteristics of this rig can be described elsewhere [8]. Specimens of $15 \times 15 \times 5$ mm were cut directly from work rolls using spark erosion given the high hardness found in these components. For the oxidation tests as well as for microstructural characterisation, the samples were prepared following the standard route of grinding with various grades of abrasive SiC papers allowing final polishing of the specimens afterwards using diamond pastes of 6 and 1 μm respectively. After preparation, the microstructural components of the alloys were determined using both, light optical and scanning electron microscopy.

The oxidation tests consisted in exposure of the specimens to 615 °C for different oxidation times from 1 up to 6 h in atmospheres which contained either dry air or a

Table 1 Chemical composition of the alloys

Alloy	Alloying elements in % weight					
	Fe	C	Cr	Mo	V	Ni
Steel	Balance	1.55	7.70	2.08	4.90	0.52
Cast iron	Balance	2.50	17.20	1.80	–	1.70

mixture of dry air and water vapour. This gaseous mixture was produced by passing dry air through a flask containing water at a constant temperature of 85 °C. Oxidation kinetics was followed by gravimetric means using an electronic balance with an accuracy of 1×10^{-5} g. The composition of the oxides formed on the alloys was determined by means of X-ray diffraction coupled with Cu and Co *K* lamps for the high chromium iron and high speed steel respectively. The radiation was generated at 40 kV and 30 mA allowing scans to be taken for 2θ angles in the interval compromised between 20 and 80°.

After the X-ray diffraction analyses, the specimens were coated with a thin layer of sputtered gold to allow surface inspection using a field emission gun scanning electron microscope. Secondary and backscattered electron detectors were used during the analysis allowing energy dispersive X-ray analyses to be acquired when appropriate.

Results

Figure 1a, b shows light optical microscopy images of the microstructures of the alloys. For the high speed steel, the X-ray spectrum shown Fig. 2a suggests that its microstructure includes the presence of eutectic chromium-rich M_7C_3 , vanadium-rich, MC and molybdenum-rich, M_6C carbides dispersed in a martensitic matrix. Alternatively, the X-ray spectrum shown in Fig. 2b reveals that the microstructure of the high chromium white cast iron contains mainly chromium-rich M_7C_3 and molybdenum-rich M_2C carbides also dispersed in a martensitic matrix. The distribution of the elements present in each alloy is better appreciated in the EDX map analysis shown in Fig. 3 for high speed steel and high chromium iron respectively.

Figure 4 shows the oxidation kinetic plots of alloys obtained for all the environmental conditions. In all cases, oxidation followed parabolic relationships. It is worth noticing that the oxidation of the samples was greater in the mixture of dry air and water vapour than in dry air.

Figure 5a, b shows scanning electron micrographs taken from the surface of the alloys, after 3 h oxidation in dry air. Oxidation of the high chromium iron (Fig. 5a) revealed the martensitic matrix covered by iron-chromium rich oxide whiskers. It is worth mentioning that the carbides present in the microstructure do not seem oxidised as it suggested by the EDX spectra shown in the micrograph.

In contrast, oxidation of the high speed steel under this condition (Fig. 5b), revealed the existence of a various oxide structures on its surface. These included, iron-oxygen rich crystallites that grew on MC vanadium rich carbides together with

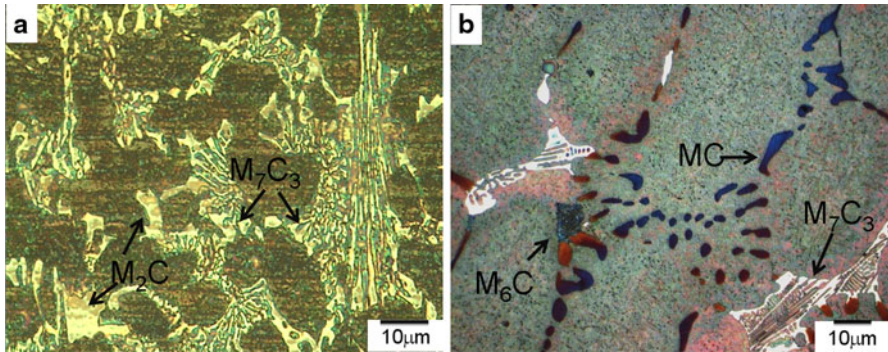


Fig. 1 Microstructure of the alloys. **a** high chromium white cast iron. **b** high speed steel

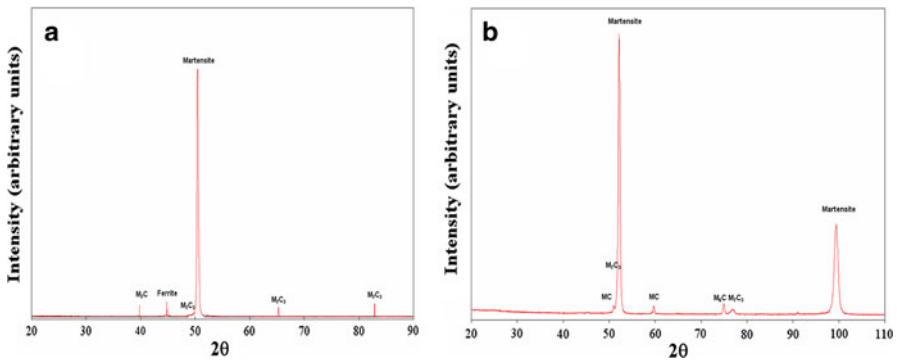


Fig. 2 X-ray diffraction spectra taken from the alloys. **a** high chromium white cast iron. **b** high speed steel

thin iron-chromium rich oxide whiskers that grew at the borders established between the martensitic matrix and eutectic M_7C_3 . Figure 6a, b show greater detail electron micrographs of the surface of the alloys after oxidation which allow a better appreciation of oxide morphologies developed.

In addition, the oxide structures formed during the oxidation of the specimens in the mixture dry air and water vapour are presented in Fig. 7a, b. Under this condition, the oxidation phenomenon of the high chromium white cast iron remained characterised exclusively by the formation of oxide whiskers (Fig. 7a). Alternatively, the surface of the high speed steel was completely covered by iron rich-oxide platelets. For this alloy, it was also possible to identify that vanadium-rich MC and chromium rich M_7C_3 carbides were not oxidised under this condition as it is indicated in the EDX spectra of Fig. 7b. Figure 8a, b give greater detail electron micrographs of the surface of the alloys after oxidation which allow a better appreciation of oxide morphologies developed in this experimental condition.

It is worth noticing mentioning that after 6 h oxidation, the iron-rich oxide platelets (Fig. 9) experienced an additional morphological transformation expressed as the formation of oxides structures similar to tree leaves (Fig. 10). Even after 6 h

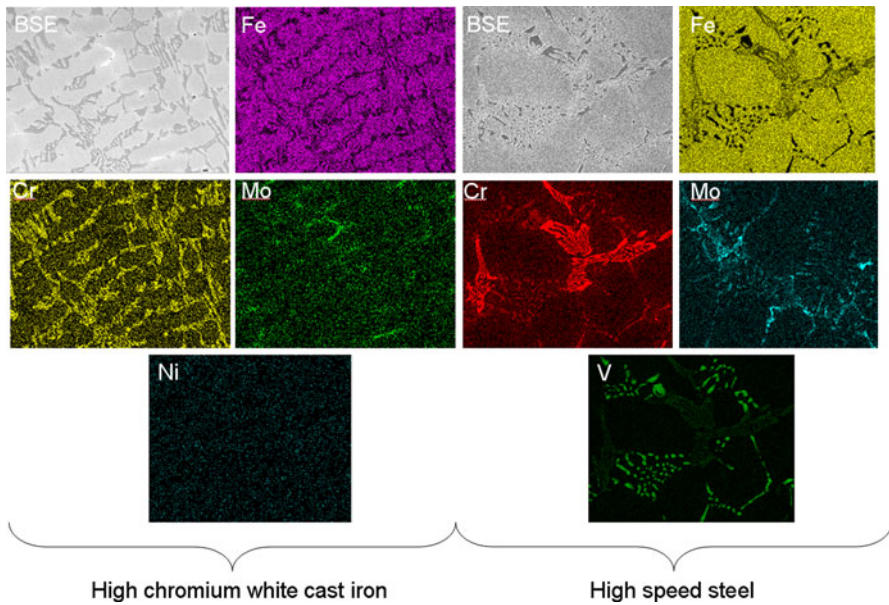


Fig. 3 EDX element mapping of both alloys

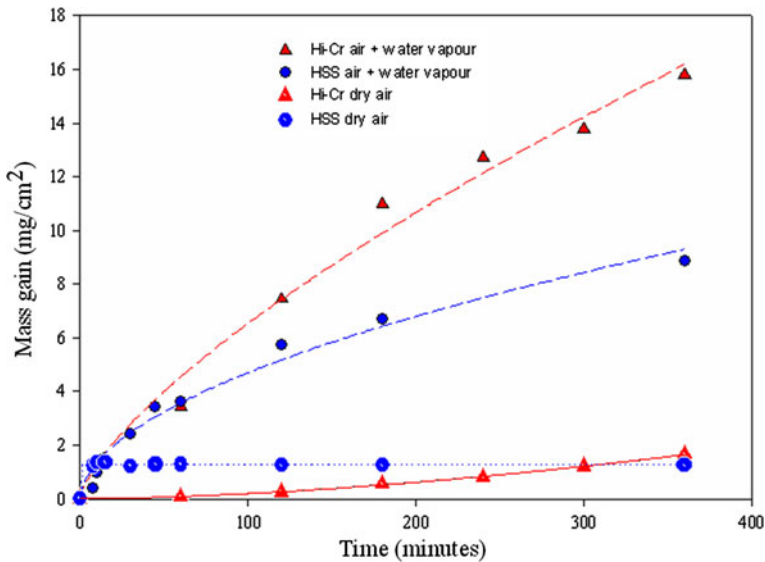


Fig. 4 Oxidation kinetics plots obtained from the tests

oxidation in water vapour, the morphology of the oxide scale formed on the surface of the cast iron did not changed and remained as dense oxide whiskers.

The X-ray diffraction spectra taken from the specimens after oxidation suggest the presence of two oxide species on the surface of the alloys. For the high chromium

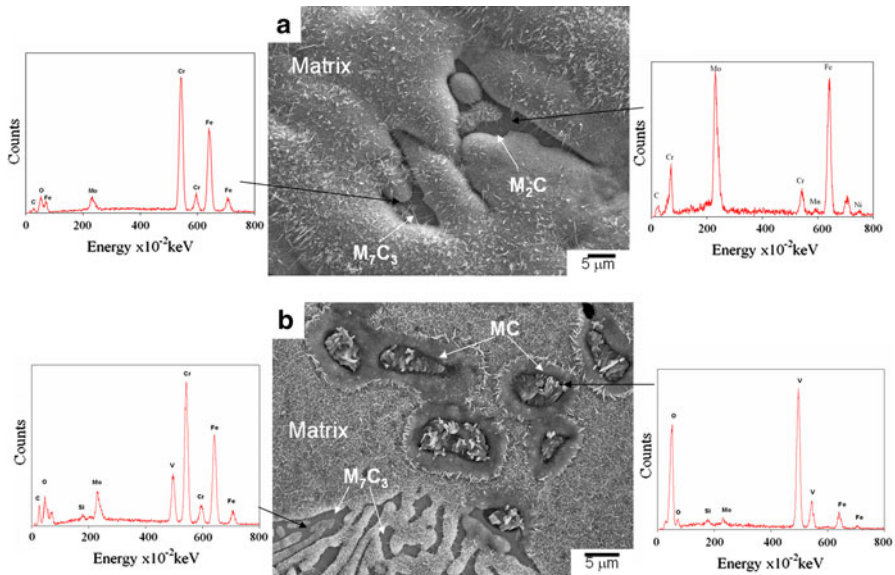


Fig. 5 Surface state of the alloys after oxidation in dry air. **a** high chromium white cast iron. **b** high speed steel

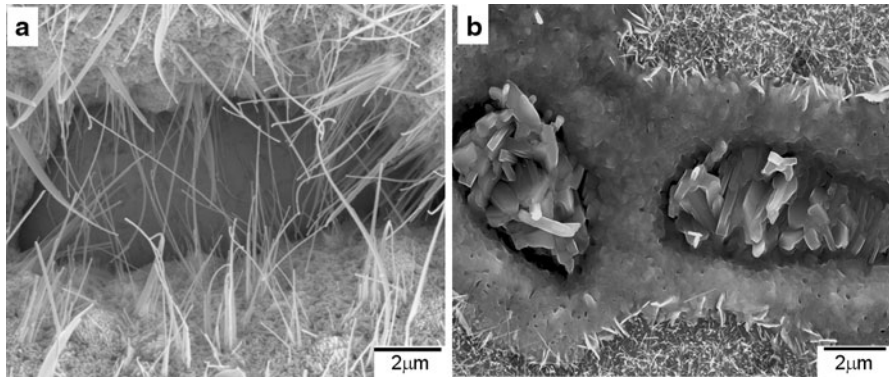


Fig. 6 Greater detail scanning electron micrographs of the alloys after oxidation in dry air. **a** high chromium white cast iron. **b** high speed steel

white cast iron, oxidation included the formation of $FeCr_2O_4$ and $(Fe,Cr)_2O_3$ oxides for all the environmental conditions studied (Fig. 11a). The phases found on the surface of the high speed steel for the environmental conditions studied included Fe_3O_4 and Fe_2O_3 as the main oxides present on the material (Fig. 11b).

Discussion

The differences in the oxidation rate and the oxide structures observed for both materials could be related with important variables present in the oxidation

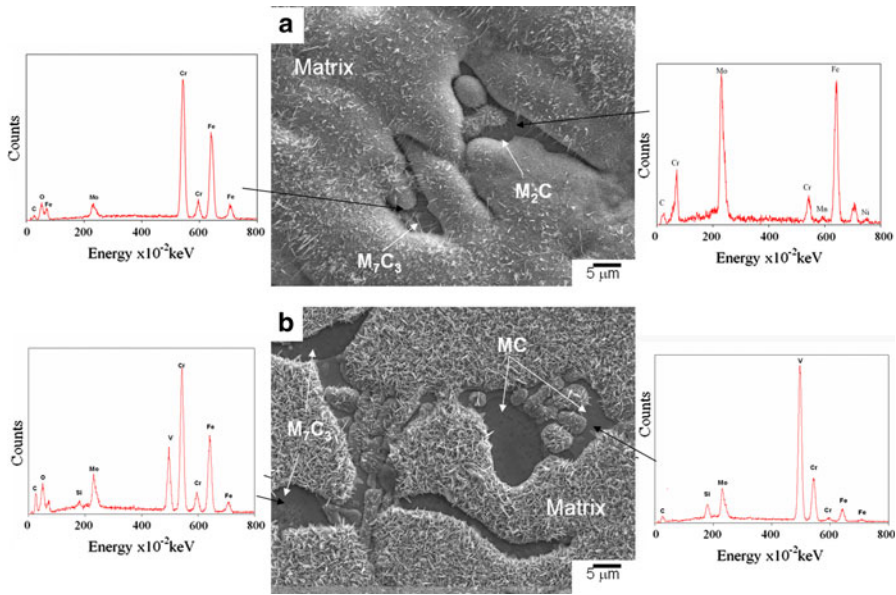


Fig. 7 Surface state of the alloys after oxidation in dry air and water vapour. **a** high chromium white cast iron. **b** high speed steel

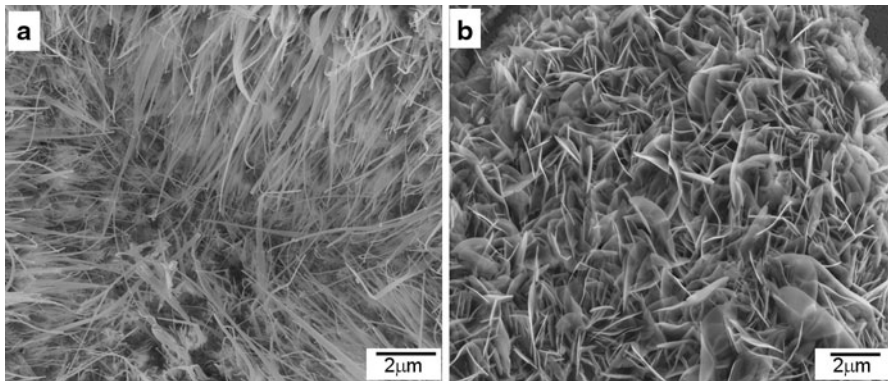


Fig. 8 Greater detail scanning electron micrographs of the alloys after oxidation in dry air and water vapour. **a** high chromium white cast iron. **b** high speed steel

experiments like: the microstructure and the chemical composition of the alloys, the gases present in the oxidant atmosphere and the time of exposure to these environments. Regarding the first variable mentioned, the presence of some elements in the alloys seems to favour the growth of certain oxide morphologies on their surfaces. For example, oxide whiskers grew preferentially on the martensitic matrix of the high chromium iron and in the regions near chromium rich M_7C_3 carbides in the high speed steel. Whisker growth has been observed in iron chromium alloys where the chromium content is substantial as it has been proposed

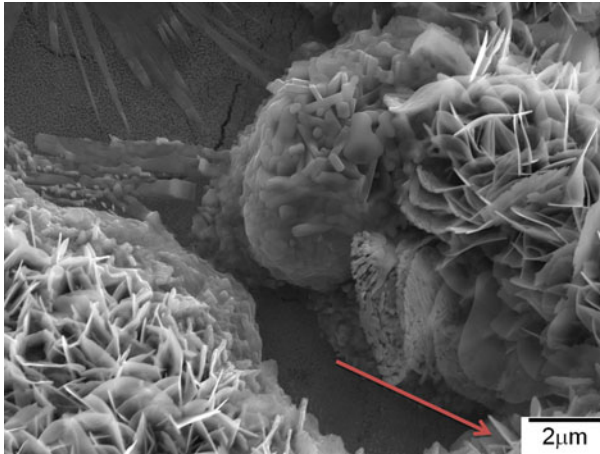


Fig. 9 Formation of oxide platelets from elongated crystallites during the oxidation of the high speed steel in dry air water vapour

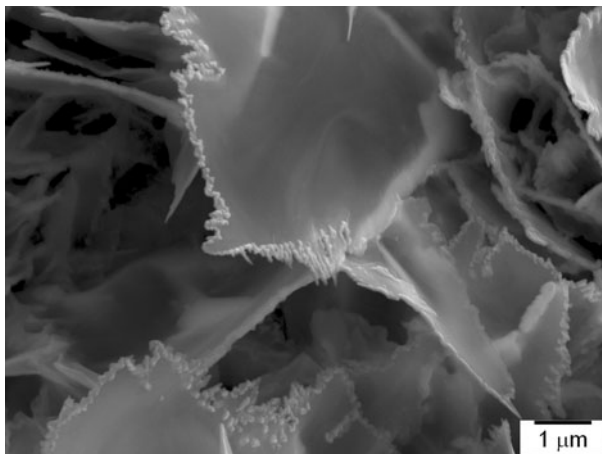


Fig. 10 Oxide morphology of the high speed steel after 6 h oxidation in dry air and water vapour

by Peraldi and Pint [10] and Othman et al. [11]. Particularly, Peraldi and Pint [10] proposed that whisker growth is representative of the formation of $(\text{Fe,Cr})_2\text{O}_3$ on the surface of Fe–Cr alloys with up to 20 %wt chromium. They also commented that this phase develops a different morphology when the chromium content of the alloy is less than 20 %wt allowing the growth of blade and platelet like oxide structures. Alternatively, Bertrand et al. [12] proposed that whisker and platelet formation is a characteristic phenomenon of the oxidation of iron alloys in atmospheres containing dry and moist air respectively.

Based on the information provided by these researchers and the morphological characteristics of the structures observed in this investigation, it is proposed that, for the alloys studied, high chromium contents favour the formation iron-rich oxide

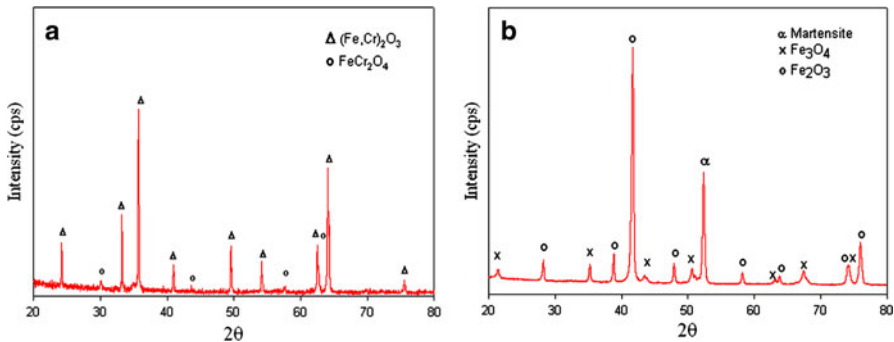


Fig. 11 X-ray diffraction spectra representative of both materials and the environmental conditions studied. **a** High chromium iron. **b** High speed steel

whiskers. These structures were found on the surface of the cast iron for both environmental conditions and, in the regions near to M_7C_3 carbides in the high speed steel where the chromium content is high.

Particularly, for the high speed steel, the lower chromium content premise proposed by Pierladi and Pint could be used to explain the growth of platelets instead of whiskers. This is, it is possible that the low amount of chromium in the alloy favours the solid state diffusion of ions and vacancies, exerted by the formation of less protective oxides which allow ionic travel across the scale [8]. If this was the case, other flow paths and growth directions existed in the initial structure of the oxide which are responsible of inducing this morphology to hematite as the reactions for oxide formation proceeded.

Contrary to premise used here to explain platelet growth, whiskers owe their morphology to the existence of a single screw dislocation in its basal plane which limits ionic motion only in the orthogonal direction to this plane which certainly restrict ionic flux in a particular direction [13].

The effect of the oxidant atmosphere is important not only for the morphology of the oxides but for the rate of oxide formation as it is suggested by the oxidation kinetic plots. Under the action of dry air + water vapour as oxidant atmosphere, the oxidation rate of the high chromium iron resulted greater than the oxidation rate of the high speed steel. It has been shown that the that presence of water vapour in dry air increases the diffusion of ionic species across the oxide scale in chromium alloys by increasing their plasticity [14, 15] but, this phenomenon also depends on the amount of chromium present in each alloy. The high chromium iron contains up to 11.60 %wt Cr (measured by EDX) which favours the formation of $(Fe,Cr)_2O_3$ oxide whiskers on its surface. The presence of chromium in iron-chromium alloys allows considerable increments to the oxidation rate of these alloys when exposed to water vapour. This compound favours the formation of chromium oxides and hydroxides which increase the ionic flux across the scale in the outer iron-rich layer as result of chromium depletion and consequently the oxidation rate of the base material as it was proposed by Asteman et al. [16]. These phases are volatile in nature and their formation may account mass losses rather that mass gains of specimens with high chromium contents. In this investigation it is proposed that the mechanism that

involved the transformation from a protective $(\text{Fe,Cr})_2\text{O}_3$ oxide layer to a chromium depleted hematite Fe_2O_3 which is not a protective phase [10–12, 14] increased considerably the oxidation rate of the high chromium iron.

In contrast, in the high speed steel, the chromium content was not high enough to promote the formation of Cr hydroxides and therefore, the presence of a dense layer of oxides platelets at the oxide-gas interface seems to be as the responsible mechanism for the reduction of the oxidation rate of this alloy in water vapour as it was proposed by Laverde et al. [15].

For the tests conducted in dry air, the oxidation rate resulted greater for the high speed steel than for the high chromium iron for the reason the chromium content of the steel is lower than the chromium content for the cast iron. This favours the formation of iron-chromium rich species of spinel FeCr_2O_4 and chromium doped hematite $(\text{Fe,Cr})_2\text{O}_3$ phases where ionic travel is limited hence the reduced mass gained experienced by the samples oxidised in this condition [17, 18]. Added to this phenomenon, it also worth considering that under this condition the formation of chromium hydroxides is discarded therefore; ionic mobility (which is the rate controlling mechanism given that oxidation kinetics is parabolic) was restricted resulting in the lower mass increments experienced by the specimens.

Previous studies on the oxidation of high speed steel under this environmental condition revealed the oxide scale formed on the surface of this alloy does not have a protective character allowing a fast diffusion of ionic species which increases the oxidation rate [8]. The fact that vanadium carbides do oxidised must be also considered as an additional reason which explains the greater mass gain observed for this alloy under this condition.

The effect of the oxidant atmosphere on the development of specific oxide morphologies seems to be more important for the high speed steel than for the high chromium white cast iron. When oxidation occurred in dry air, the surface of the high speed steel included oxide whiskers on the martensitic matrix and oxide crystallites on MC vanadium rich carbides. It was also found that M_7C_3 chromium rich carbides did not experienced considerable oxidation. When oxidation of the high speed steel occurred in moist conditions, the alloy did not experience carbide oxidation and the morphology of the oxide that grew on martensite consisted of hematite oxide platelets instead of whiskers. This behaviour could be also explained based on the diffusion of iron ions in hematite studied by Tallman and Gulbransen [19], which also points out that hematite whiskers definitely grow by the mechanism of single axial screw described earlier.

Regarding the oxidation of the carbides present in the microstructure of each alloy, it was appreciated that this phenomenon seems to be more important for the high speed steel than for the white cast iron given that the vanadium rich carbides present in its microstructure where oxidised when exposed to dry air only. Some investigations [8, 20] have proposed that even tough vanadium carbide has a considerable affinity for oxygen, its oxidation is not possible in environments with low oxygen partial pressure as it was the case when exposed to dry air + water vapour ($p = 0.06$ atm).

Alternatively the M_7C_3 chromium rich carbides present in both alloys did not developed oxidation. This phenomenon is probably related to the fact that the

chromium content in these carbides is considerable high (47.50 %wt Cr for those present in the high chromium iron and 36 %wt Cr for those present in the high speed steel) as to form a thick oxide layer that could be detected during the SEM analysis. It is worth mentioning that oxygen was detected in these carbides in the high speed steel (Figs. 5b and 7b), which can be considered as evidence that suggests the formation of a thin oxide film. The oxidation resistance exhibited by the chromium carbides present in both alloys agrees well with the information provided by Durham et al. [21] for iron-chromium alloys containing ~ 15 %wt Cr oxidised at 850 °C, where chromium-rich carbide oxidation is not developed but carbide decomposition is observed. It is clear that in this investigation, the temperature at which the tests were conducted was probably not high enough as to promote either considerable carbide oxidation or carbide dissociation.

In this investigation, the oxidation kinetics plots presented in Fig. 4 suggests that the diffusion of ions is greater for the cast iron than for the high speed steel when exposed to the mixture dry air + water vapour. Even though the presence of water vapour tends to enhance ionic diffusion for oxide growth at high temperature [10–12, 14–16] it could be possible that diffusion of chromium ions was not fast enough as to maintain a balance in the amount of single screw dislocations promoting the formation of very long whiskers instead of oxide platelets given that iron ions move faster than chromium ones.

Contrary to the phenomenon observed for the cast iron, hematite grows on the steel at the oxide-gas interface driven by an ordered diffusion of iron in the normal direction to this interface which causes the formation of oxide crystals. In order to form platelets, the diffusion direction of the iron ions should have been altered by mechanisms like: (1) The existence of less chromium in the martensitic matrix and (2) The presence of other alloying elements such as vanadium and molybdenum that could have increased the amount of dislocations present in the oxide, favouring the existence of other

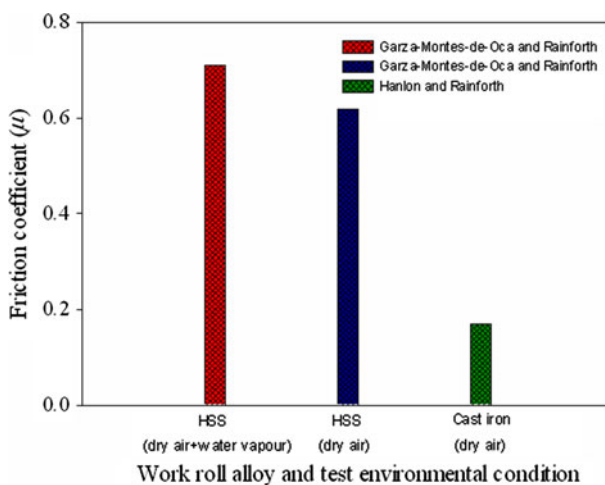


Fig. 12 Friction behaviour of both alloys under sliding conditions

diffusion directions. The reasons here proposed seem correct looking at the formation stages of hematite platelets expressed as a fusion of oxide crystallites in Fig. 9.

The study of the oxidation differences between high speed steel and white cast iron as work roll material is of considerable importance for fact that features like the rate of oxide growth and the chemical composition of the species present in the oxide scale formed on work rolls are strongly related to friction and wear in the finishing stands in hot strip mills [22–24]. An example of this is given in Fig. 12 where a comparison of the variation of the friction coefficient measured in wear experiments of these materials under sliding conditions at high temperature is given, showing that oxide growth and composition favours friction changes under dynamic conditions as it has been proposed by Garza-Montes-de-Oca and Rainforth [23] and Hanlon et al. [24] respectively. The effect of the presence of water vapour on the sliding friction and high temperature wear characteristics of the white cast iron alloy presented in this investigation is currently under investigation.

Conclusions

The differences in the oxidation rate and oxide morphology of high speed steel and high chromium irons as work roll alloys were studied. For this investigation, the morphology of the oxide structures formed at the oxide-gas interface depends on with the amount of chromium present in each alloy and the composition of the oxidant atmosphere in which the phenomenon occurred. The composition of the oxidant atmosphere controls the oxidation rate of the alloys leading to greater mass gains for the cast iron alloy when the materials is exposed to a water vapour containing environment by a mechanisms associated with the formation of Cr volatile species. The composition of the oxides formed on the surface seems to influence the value of the friction coefficient obtained when the alloys are exposed to high temperature rolling-sliding conditions as in hot strip mills.

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