ISSN 2179-3956

EFFECT OF MOLYBDENUM AND CHROMIUM CONTENTS ON SLIDING WEAR OF HIGH-CHROMIUM WHITE CAST IRON AT HIGH TEMPERATURE[1]

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Abstract
High-chromium white cast irons are commonly used in applications requiring excellent abrasion resistance, as in the mining and mineral ore processing industry. Their excellent abrasion resistance is mainly due to their solidification microstructures. In this study, 15 experimental high-chromium white cast alloys containing different chromium and molybdenum contents and a ratio Cr/C of 10 are examined. The wear experiments are carried out on a pin-on-disc tribometer at 700 ºC. Microstructure has the most important role in dictating friction. It is observed that the wear loss is insignificant compared to that obtained at room temperature. The mean friction coefficient is also lower than that observed at room temperature sliding wear.
Key words: High-chromium cast iron; Friction; Sliding wear; Gigh temperature.

EFEITO DA COMPOSIÇÃO DO FERRO FUNDIDO BRANCO ALTO CROMO E MOLIBDÊNIO NO DESGASTE POR DESLIZAMENTO À ALTA TEMPERATURA

Resumo
Ferros fundidos branco alto cromo são ligas geralmente utilizadas em aplicações que requerem excelente resistência à abrasão, como, por exemplo, nas indústrias de processamento mineral. Sua excelente resistência à abrasão é principalmente devida a suas microestruturas decorrentes da solidificação. Neste estudo, 15 ligas experimentais de ferro fundido branco contendo composições distintas de cromo e molibdênio e uma razão Cr/C de 10 são avaliadas. Os experimentos são realizados em um tribômetro pino-disco à temperatura de 700 ºC. Os resultados à alta temperatura mostram que a microestrutura tem papel fundamental no comportamento do atrito. O desgaste observado é insignificante comparado ao observado à temperatura ambiente, assim como os valores de coeficiente de atrito se apresentam mais baixos.
Palavras-chave: Ferro fundido branco alto cromo; Atrito; Desgaste por deslizamento; Alta temperatura.

[1] *Technical contribution to the First International Brazilian Conference on Tribology – TriboBr-2010, November, 24th-26th, 2010, Rio de Janeiro, RJ, Brazil.*
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ISSN 2179-3956

1 INTRODUCTION

Tabrett, Sare and Ghomaschil[1] gave a range of chromium and carbon contents to define high-chromium white cast irons alloys. The respective content of these elements is between 11 to 30 wt.% for chromium and 1.8 to 3.6 wt.% for carbon. The microstructure of these alloys has been studied by several authors.[1-5] It is composed of hard primary and/or eutectic carbides (M_7C_3 type) in a softer iron matrix (i.e. austenitic, martensitic, ferritic, pearlitic or bainitic). By adding alloying elements such as molybdenum, vanadium, niobium, etc., additional carbides such as M_6C or M_2C and MC are formed. These alloys are widely used in the mining, cement, steel making and ceramic industries that require materials with excellent abrasion resistance.

Generally, wear resistance is dependant on matrix microstructure, carbide type and characteristics (size, morphology, distribution, orientation[6]) as well as the volume fraction, fracture toughness and hardness of the alloys.[7,8] It also depends on loading conditions, the features of the tribological environments, and type and size of the abrasive bodies. However, there have been only a few investigations dealing with sliding wear at high temperature.[9-11]

The addition of molybdenum, in quantities of more than 3 wt.%, to a high-chromium white cast iron leads to the formation of M_2C or M_6C carbides depending on the Cr/C ratio.[12] Furthermore, the molybdenum content (0.5–3 wt.%) prevents the pearlitic transformation of the austenite and increases the hardenability of alloyed cast irons.[1,2] A molybdenum content grater than 3 wt.% could improve the high-temperature wear resistance. Ikeda et al.[9] have performed sliding wear experiments on a cast iron with a ratio Cr/C of 5. It is shown that, by adding molybdenum, M_2C carbides are formed which contribute to enhancing high temperature abrasion resistances.

The general purpose of this study is to investigate the high temperature sliding wear behavior of 15 experimental white cast alloys containing different chromium (16 wt.% Cr to 32 wt.% Cr) and molybdenum (Mo-free to 9 wt.% Mo) contents and a Cr/C ratio of 10, which leads to the formation of M_6C carbides instead of M_2C carbides.[12]

2 MATERIALS AND METHODS

2.1 Experimental Procedure

Friction tests are carried out on a pin-on-disc tribometer in dry conditions (Figure 1). The disc has a continuous rotating movement and the linear velocity depends upon radius of wear track. The loading is applied using dead weights. The disc is heated by high frequency induction and its surface temperature is controlled by an infrared pyrometer. The tribometer and pin and disc geometries complete descriptions are reported in literature.[11,13]

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(a)

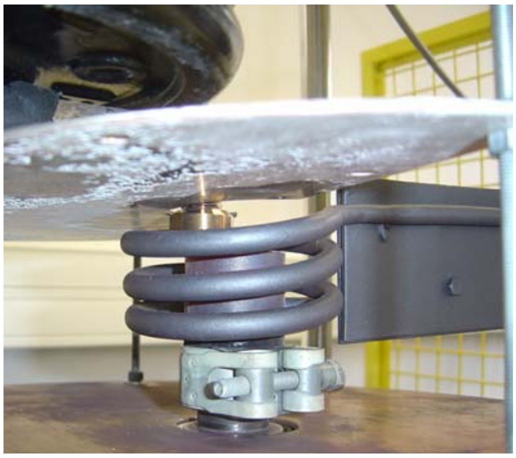
(b)

Figure 1 - General view of the pin-on-disc tribometer (a) and detail of inductive heating system (b).

The disc is heated during 1 h at the test temperature (pre-oxidation). During pre-oxidation, the pin is kept at room temperature. After disc pre-oxidation, the pin is put on the disc and experiment starts. A strain gauge sensor continuously records the friction forces. The pin height loss (h) is calculated from the variation between the initial diameter of the contact surface (D_i) and its final diameter (D_f) (Equation (1)). All diameters are measured by optical microscopy.

$$h = \frac{D_i - D_f}{2} \tag{1}$$

All friction experiments are performed under same testing conditions, summarized in Table 1. Each friction test is carried out twice for repeatability considerations.

Table 1 – Frictional experimental conditions

Sliding speed	Normal load	Test duration	Temperature
0,1 m/s	20 N	1800 s	700 ºC

The worn surfaces are examined by optical and scanning electronic microscopy (SEM).

2.2 Materials

The disc material is a low-carbon SAE 1020. Pins are composed of white cast irons with different chromium and molybdenum contents. The chromium/carbon ratio is always 10.

Four alloys groups have been studied: two groups are hypoeutectic alloys (16 and 24 wt.% Cr); one group is an eutectic alloy (28 wt.% Cr); and the last one is a hypereutectic alloy (32 wt.% Cr). For each group, four alloys with different Mo content (0, 3, 6 and 9 wt.%) are investigated. The 28 wt.% Cr – 6 wt.% Mo specimen has not been studied.

The complete characterization of these alloys had been determined in a previous study (12) and their microstructures and type of carbides are illustrated in Figure 2.

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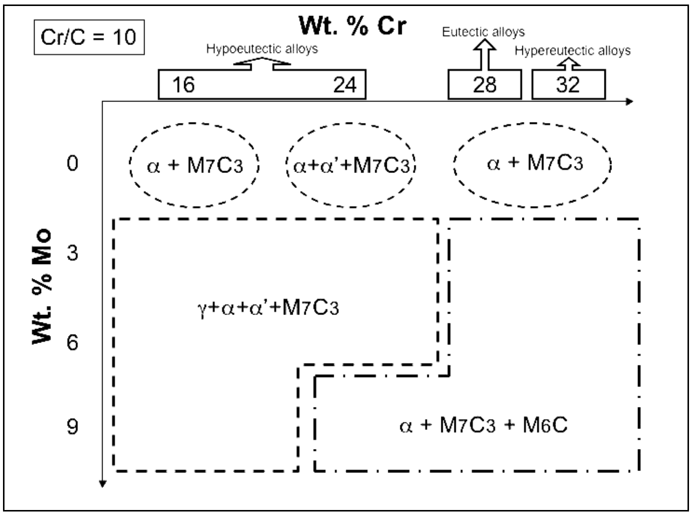
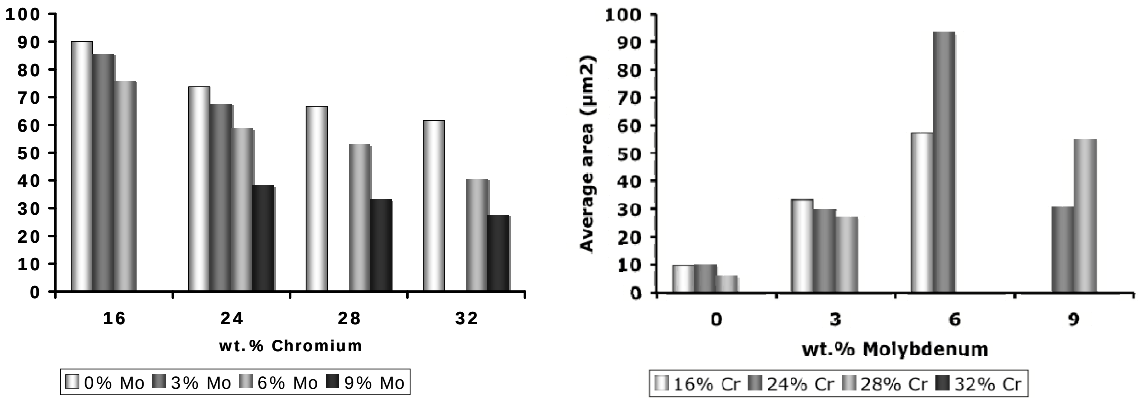


Figure 2 –Phases of different experimental white cast alloys as a function of chromium and molybdenum contents (wt.%).[12]

The volume fraction of the matrix and carbides are determined by image analysis.[12] The volume fraction of the matrix decreases as the content of the alloying elements increases, since M_7C_3 and M_6C eutectic carbides are formed, as well as M_7C_3 primary carbides (Figure 3a).

The average area of M_7C_3 carbides is strongly influenced by the Mo content, reaching a maximum value for the 6 wt.% Mo alloys (Figure 3b). The average areas of hypereutectic alloys (32 wt.% Cr) have been discarded due to its primary carbides population present much higher dimensions.[12]



(a) (b)

Figure 3 – (a) Volume fraction of matrix (%) as a function of chromium and molybdenum contents (wt.%); (b) average area of M_7C_3 carbides (μm^2).[12]

3 RESULTS AND DISCUSSION

3.1 Friction Results

Friction results are shown in Table 2.

For Mo-free alloys, the mean value of the friction coefficient is practically constant, except for the hypoeutectic Mo-free - 24 wt.% Cr alloy that shows a lower value. Eutectic and hypereutectic alloys display slightly higher values. For multiphased matrix alloys (hypoeutectic alloys with any molybdenum content, except the 24 wt.% - 9 wt.% Mo alloy), friction coefficient depends on molybdenum content.

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Previous studies[13-15] obtained friction results around 0.5 for similar materials and test conditions.

Table 2 - Mean friction coefficient values after sliding wear at high temperature

FRICTION COEFFICIENT					
		wt.% Cr			
		16	24	28	32
wt.% Mo	0	0.5	0.2	0.45	0.45
	3	0.1	0.2	0.5	0.5
	6	0.5	0.5	-	0.55
	9	0.35	0.5	0.5	0.55

Figure 4 illustrates the general aspect of the evolution of friction coefficient versus test duration. Joos et al.[15] relate similar friction curves behavior with no running-in or stability period.

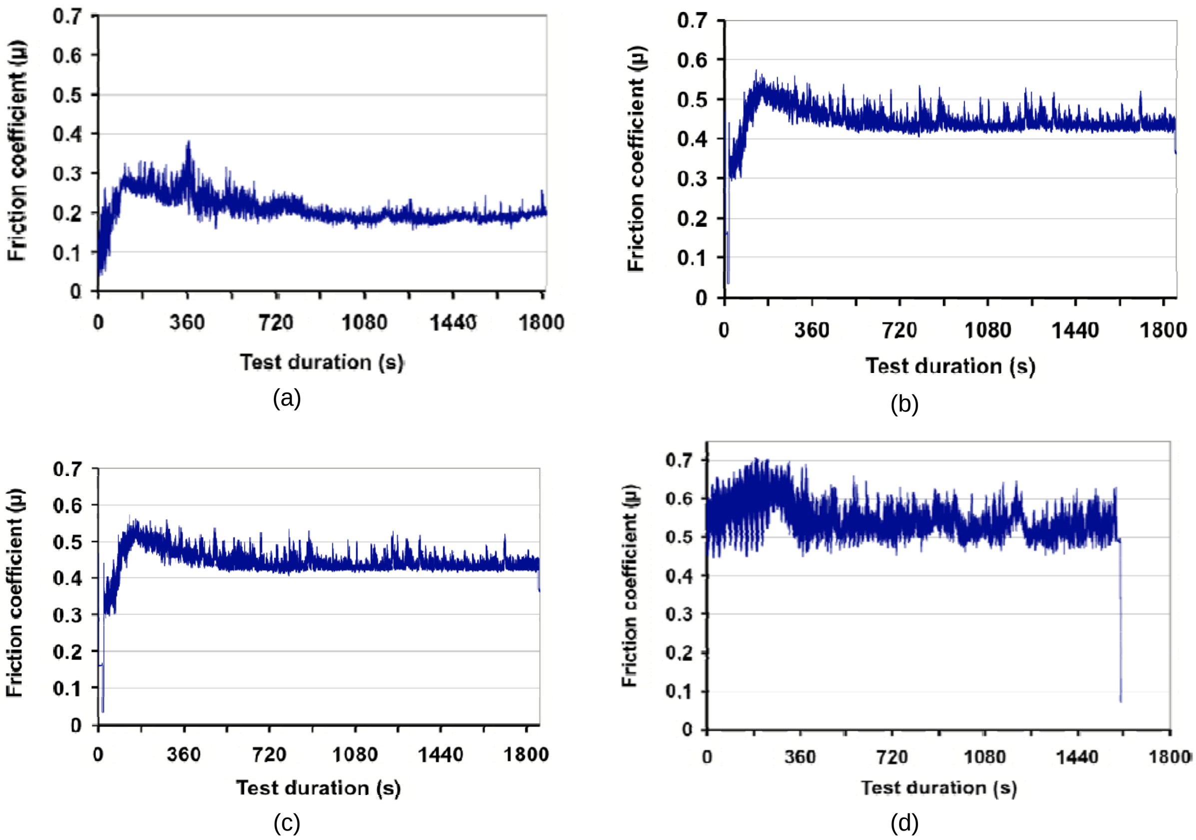

Figure 4 - Friction coefficient versus test duration for: (a) Mo-free alloy with martensitic matrix; (b) Mo-free alloy with ferritic matrix; (c) hypoeutectic alloy 16 wt.% Cr – 6 wt.% Mo; (d) hypereutectic alloy 32 wt.% Cr – 9 wt.% Mo.

At this point, it is important to remark that the mean value of the friction coefficient obtained at high temperature is lower than that observed at room temperature.[11]

3.2 Role of Microstructure on Friction

SEM examinations of worn surfaces of the pins reveal that there is a preferential transference of oxides from the disc and, then, adhesion to the matrix of the pin,

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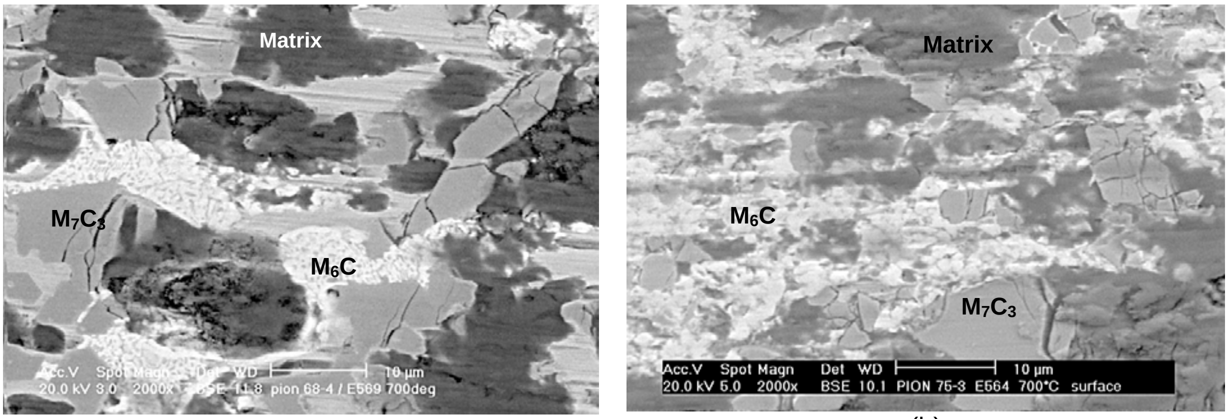
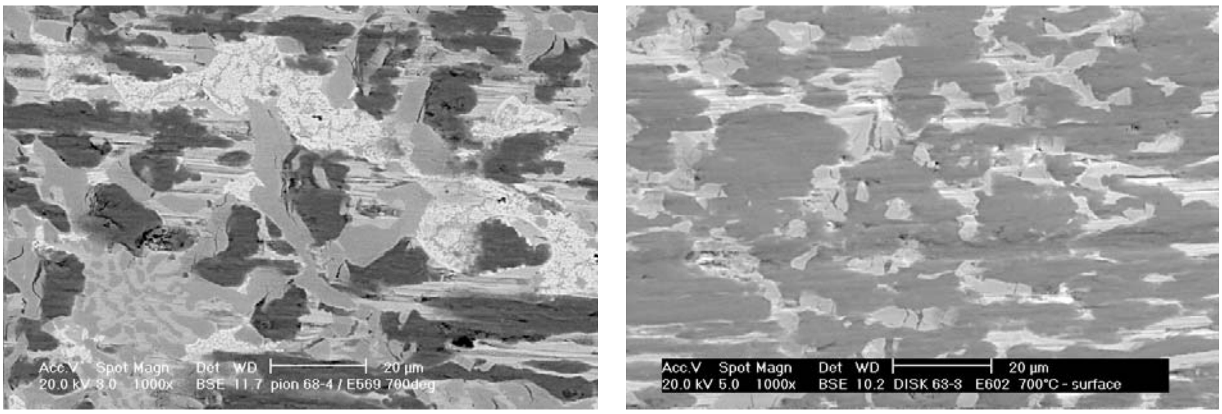
specifically on the α-Fe, due to its ductile characteristic. Occasionally, the oxides transferred are found attached to the M_7C_3 carbides, but never to the M_6C carbides of the pin. Moreover, microcracks are always clearly observed with M_7C_3 carbides and rarely with M_6C (Figure 5). This is a trend that seems to rule the coefficient friction values.



(a) (b)

Figure 5 – SEM observations of microcracks in M_7C_3 carbides, intact M_6C carbides and oxides from the disc attached to the matrix in: (a) hypoeutectic alloy (24 wt.% Cr – 6 wt.% Mo); (b) hypereutectic alloy (32 wt.% Cr – 9 wt.% Mo). Darker areas correspond to matrix covered by oxides; lighter areas, to M_6C carbides; and, medium grey areas, to M_7C_3.

An increase in the volume fraction of the matrix or M_6C carbides of hypoeutectic alloys tends to reduce the friction coefficient probably due to: (1) the adhesion of oxides transferred from the disc in the matrix forms an oxide film that avoid the contact between surfaces; (2) physical characteristics of M_6C carbide – because ceramic-ceramic contacts present lower friction coefficient than in metals sliding and present a great hardness combined to an excellent wear resistance, since this type of carbide with a "fishbone" morphology exhibits no fracture. In opposition, microcracking of M_7C_3 carbides leads to increased friction because the occurrence of fracture provides an additional mechanism for the dissipation of energy at the sliding contact.[16]



(a) (b)

Figure 6 – Microstructure of hypoeutectic alloys with the same chromium content: (a) 24 wt.% Cr – 6 wt.% Mo; (b) 24 wt.% Cr – 3 wt.% Mo. Darker areas correspond to matrix covered by oxides; lighter areas, to M_6C carbides; and, medium grey areas, to M_7C_3.

The relationship between the mean friction coefficient and the volume fraction of the matrix and carbides in hypoeutectic alloys can be observed in Figure 6. For the

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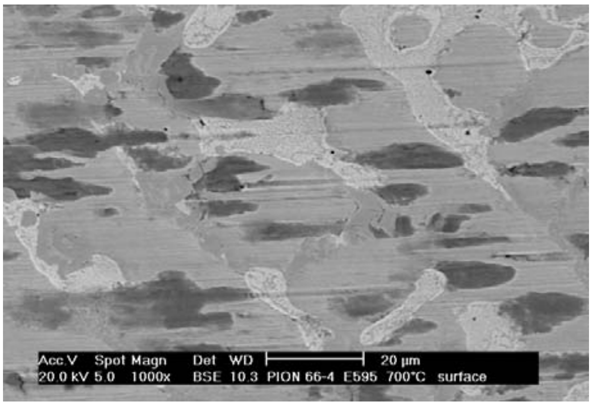
same chromium content alloys, the higher is the volume fraction of the matrix – and then, the higher the area covered with oxides – in contrast with the volume fraction of M_7C_3 carbides, the lower is the mean value of the friction.

Another remarkable observation is that, besides volume fraction of matrix and carbides, the carbide size and the distribution of phases in microstructure have a great influence on friction coefficient results. An evidence of that can be pointed out in a comparison between the 24 wt.% Cr – 3 wt.% Mo and 16 wt.% Cr – 6 wt.% Mo alloys characteristics (Table 3).

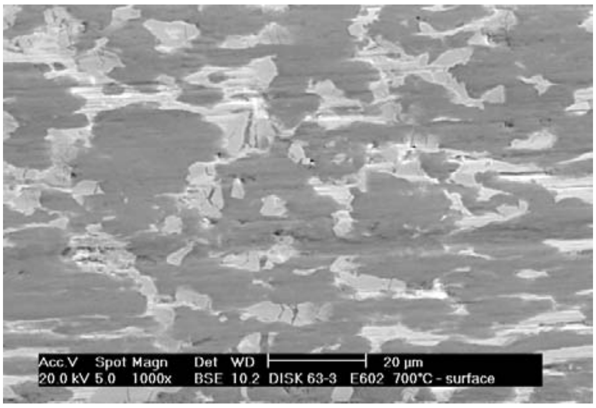
Table 3 - Characteristics of two hypoeutectic alloys with different chromium contents as a function of volume fraction of phases, hardness and friction coefficient(12)

	16 wt.% Cr – 6 wt.% Mo	24 wt.% Cr – 3 wt.% Mo
Vickers hardness (HV_{10})	557	583
Volume fraction of matrix (%)	75.9	67.6
Volume fraction of M_7C_3 carbides (%)	14.5	27.1
Volume fraction of M_6C carbides (%)	9.6	5.3
Friction coefficient	0.5	0.2

Despite of the higher volume fraction of matrix and M_6C carbides and the lower volume fraction of M_7C_3 carbides of the 16 wt.% Cr – 6 wt.% Mo alloy, it has a greater friction coefficient. This fact is probably due to the distinct distribution of phases in its microstructure, that forms a more discontinuous oxide film – and, then, a less protective oxide layer – than that observed in the 24 wt.% Cr – 3 wt.% Mo alloy (Figure 7).



(a)



(b)

Figure 7 - Distribution of phases in hypoeutectic alloys: (a) 16 wt.% Cr - 6 wt.% Mo; (b) 24 wt.% Cr - 3 wt.% Mo. Darker areas correspond to matrix covered by oxides; lighter areas, to M_6C carbides; and, medium grey areas, to M_7C_3**.**

Another relevant consideration in the friction behavior of the former alloy is that the average area of M_7C_3 carbides is about two times higher (Figure 3b). Thus, microcracking of M_7C_3 carbides seems to be more significant in dictating friction particularly when their average area is higher than 50 μm^2, as in the eutectic and hypereutectic alloys, as well as 6 wt.% Mo alloys, which display slightly higher values of mean friction coefficient.

For hypereutectic alloys, the friction curves versus test duration display large amplitude fluctuations (Figure 4d) probably due to microcracking of large primary M_7C_3 carbides.

For Mo-free alloys, the mean value of the friction coefficient is practically constant except for the hypoeutectic Mo-free - 24 wt.% Cr alloy that shows a lower value

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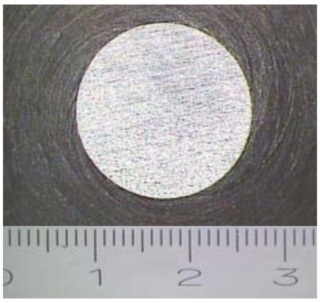
probably due to its duplex ferritic-martensitic matrix in place of a ferritic single-phased one. The martensitic phase shows lower plasticity what could explain the lower friction coefficient, since it provides mechanical support for the oxide film.[17]

3.3 Wear Results

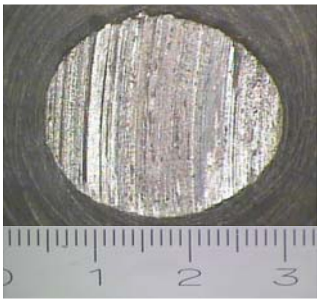
For the tested conditions and alloys, the wear loss is insignificant no matter the composition or hardness of the alloy (total pin height loss between 0 and 70 µm). Once the oxides are transferred from the oxide layer formed during pre-oxidation of the disc to the matrix of the pin surface, the contact of bulk materials are prevented and little or none wear occurs.

Many previous studies[13-15,18,19] tested similar materials and conditions. Therefore, the results emphasize mainly the wear mechanisms involved in sliding wear. Barrau et al.[14] tested a martensitic tool steel (AISI H11) against AISI 1018 at various tribological conditions and, for a similar experimental condition tested in this work (700 ºC, 20 N), the total pin height loss was 55 µm.

Moreover, lower wear loss are expected in sliding at high temperatures due to surface oxidation, since a substantial oxide film can suppress the plasticity-dominated mechanisms by reducing the shear strength of the interface.[17] A comparison can be made between the worn surfaces of the present study and the previous one at room temperature (Figure 8), in which the pin height loss (h) can be higher than 0.8 mm.[11]



(a)



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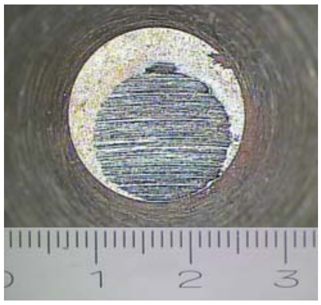

(c)

Figure 8 – Eutectic alloy (28 wt.% Cr – 3 wt.% Mo): (a) before test; (b) after test at room temperature; (c) after test at 700 ºC.

4 CONCLUSIONS

The oxides are always observed attached to the matrix – avoiding the contact between the bulk materials and, therefore, reducing the wear loss – and occasionally to the M_7C_3 carbides, but never to the M_6C carbides. Besides that, microcracks are always observed with eutectic or primary M_7C_3 carbides, but rarely with M_6C.

Microcracking of M_7C_3 carbides seems to contribute greatly to friction results due to dissipation of energy at sliding contact. As the volume fraction of this type of carbides and, specially, its average area increase, the mean friction coefficient values tend to be higher. In opposition, the presence of M_6C carbides tends to reduce friction.

The friction coefficient values obtained at high temperature are lower than that observed at room temperature sliding wear.

The wear results highlight that, for the tested conditions and alloys, the wear loss tends towards zero in contrast with the room temperature wear results.

ISSN 2179-3956

Acknowlegments

The authors would like to acknowledge the contributions of DSc. Pedro Carneiro.

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