Heat Treatment Effect on the Microstructure and Tribological Behaviour of a High Chromium Cast Iron with 0.5% of Niobium

Leonardo Menezes de FARIA,¹)* Ismael Nogueira Rabelo de MELO,²) Anderson Júnior dos SANTOS³) and Ivete Peixoto PINHEIRO³)

1) Master’s Programme in Materials Engineering, Federal Center for Technological Education of Minas Gerais, Belo Horizonte, MG, Brazil.
2) Federal Institute of Minas Gerais, Ibirité, MG, Brazil.
3) Department of Materials Engineering, Federal Center for Technological Education of Minas Gerais, Belo Horizonte, MG, Brazil.

(Received on November 30, 2019; accepted on May 15, 2020)

A high chromium cast iron (HCCI) with 0.5%Nb was subjected to destabilization heat treatments (950°C, 1 000°C, and 1 050°C) for 2 hours. Specimens were characterized by optical and scanning electron microscope (SEM). It was found coarser secondary carbides as the temperature treatment increased. Niobium carbides were found agglomerated in petal-like and blade-like forms. Abrasion tests using a Dry Rubber Wheel Abrasion Tester (DRWAT) were carried out. Results indicated that the wear resistance was proportional to the matrix microhardness, the 1 000°C and 1 050°C temperatures presented the best wear resistance. SEM images have shown wear by plastic deformation preferentially on the matrix. The worn surfaces were scanned by a contact profilometer. Specimens which had more removed material presented a higher average roughness (Sₐ). Also, the average roughness (Sₐ), maximum values of peaks (Sₚ) and pits (Sᵥ) tended to be lower as the temperature of the heat treatment increased. This can be related to the plastic deformation caused by the wear. The presence of pits was predominant on the worn surfaces.

KEY WORDS: high chromium cast iron; niobium; destabilization treatment; wear resistance; roughness.

1. Introduction

High chromium cast irons (HCCI) are commonly used in industrial applications for their high abrasion resistance, such as mining and mineral processing. The HCCI outstanding abrasion resistance results from the morphology, distribution and amount of a hard phase (carbides) embedded in a matrix, which is predominantly martensitic or austenitic.¹–³

Many studies have been done in order to improve HCCI abrasion resistance. Some works have demonstrated that the addition of carbide-forming elements, such as niobium, enhance wear resistance.⁴,⁵) Niobium forms hard carbides,⁴–⁶) increases matrix hardness⁵,⁶,⁹) and refines the M₇C₃ carbides.⁶–⁸) These characteristics have positive potential effects on wear resistance. Low concentrations of Nb (less than 1%) has been studied in structural carbides.²,⁴,⁶,⁹) and it has indicated the beneficial effects of niobium on the resistance matrix.⁸–⁶

The microstructure of the HCCI has strong influence on its properties. Hence, some researchers are focused on optimizing the composition of the microstructure in order to further improve hardness and wear resistance. The as-cast microstructure can significantly be altered by destabilization, which has two objectives: precipitation of secondary carbides and transformation of primary austenitic matrix to martensitic, predominantly.¹,¹⁰)

Regarding heat treatments, characteristics of secondary carbides have been investigated. The stoichiometry of these carbides (M₇C₃, M₇C and M₂₃C₆) depends on the chemical composition (mainly Cr) and destabilization temperature.¹,¹⁰) The morphology and amount of carbides are strongly related to the time and temperature¹,¹²) and are mostly described as rod-type or cubic-type.¹⁰–¹²)

The effect of the destabilization on matrix structure is, also, an ongoing discussion. It is stablished in the literature¹) that the matrix provides mechanical support to resist abrasion, but the optimal temperature of destabilization to wear resistance depends not only on martensite/austenite correlation, but, also, the presence of strong carbide former, such as niobium.⁸–⁶

There are no studies focused on heat treatment of HCCI with low percentage of niobium. This element forms strong carbides altering the chemical composition and microstructure of the material, and therefore, the optimum destabilization heat temperature should be investigated. Also, an
analysis of the wear impact on surface texturing of HCCI is not found on literature. This paper addresses these issues.

This paper aims to assess the effect of different temperatures of destabilization on the microstructure and tribological behaviour of a HCCI with 0.5%Nb. The implications of the performed heat treatment on the microstructure and on the wear mechanisms are explored. In addition, roughness parameters ($S_a$, $S_z$, $S_q$, $S_p$, $S_v$, $S_{ku}$ and $S_{sk}$) were measured, according to ISO 25178, and their relation with wear resistance was investigated.

2. Experimental

2.1. Materials

Pieces of a rotor and scraps of a Fe–Nb alloy were casted in an induction furnace. The chemical composition was determined by optical emission spectroscopy (Spectromaxx) and it is given in Table 1. In order to obtain suitable sample dimensions to the dry rubber wheel test, the blocks were further cut by electro discharge machining (Servspark Eletroplus EDM-540).

Some samples were heat-treated in an electrical resistance furnace (Brasimet KR-170). They were destabilized at 950, 1000 and 1050°C for 2 hours, cooled to room temperature in forced air and, then, tempered at 200°C for 2 hours. The chosen destabilized temperatures cover the main temperature range of the performed heat treatment in the HCCI's.1,10,13,14)

2.2. Microstructural Characterization

Specimens were mounted, grounded and polished. They were chemically etched using Villela’s regent (1 g picric acid + 5 ml hydrochloric acid + 100 ml ethanol) for around 15 s.

The microstructure was examined by an optical microscopy (Platinum Microscope Fortel IM713) and scanning electron microscopy (JSM-IT300LV for secondary-electron images and Jeol JSM 6360LV for back-scattered electron images) equipped with an energy dispersive X-ray spectrometry (EDS) apparatus.

The volume fraction of carbides (CVF) was measured using the software Fiji Is Just Image J. The optical micrograph images were used to quantify carbides in heat-treated samples while SEM images were used to quantify the CVF of as-cast samples.

X-Ray Diffraction (XRD) were executed with a SHIMADZU XRD-7000, Cu-Ka at 40 KV and 30 mA. The scanning speed was 1°/min over a 2θ range of 30–110°. TheICDD powder diffraction file (PDF) number used to identify phases are given in Table 2. The martensite phase was identified using a ferrite PDF file, as they have same intensity peaks.

2.3. Hardness and Abrasive Wear Tests

The bulk hardness and microhardness were performed on Vickers Scale in a Shimadzu instrument HMV-2T. The applied load was 2.0 and 0.05 Kgf, respectively; and the dwell time was 15 seconds.

The abrasive wear test was carried out on a Dry Rubber Wheel Abrasion Tester (DRWAT). A view of the testing machine is shown in Fig. 1. The samples were fixed in a holder and compressed against a rotating rubber wheel. Silica sand is thrown in the contact wheel and specimen. The applied load was 130 N and the revolution of the wheel was kept constant (200.3 rpm) during the tests. The abrasive particles granulometry, silica sand, were 50 mesh. The total time test was 60 min, but weigh measurements of the samples were made from 15 to 15 min with a weighing machine (OHAUS AR2140), in order to investigate the variation of the wear rate over the time.

The worn surfaces of the specimens were examined by SEM and EDS to identify wear mechanisms. A profilometer, Hommelwerk T8000, and the software Hommelmap 6.2 were used to trace the 3d shape and measure the surface roughness parameters ($S_a$, $S_z$, $S_q$, $S_p$, $S_v$, $S_{ku}$ and $S_{sk}$), according to ISO 25178.15) The profilometer has scanned an area of 38×8 mm² of each tested surface, approximately 32% of each worn surface.

3. Results and Discussion

3.1. Microstructure

The microstructure of the hypoeutectic alloy is shown in
The microstructure is basically an austenitic matrix with eutectic carbides comprising it and austenite dendrites. There are layers of martensite surrounding the eutectic carbides as well, as denoted in Figs. 2(a) and 2(b). These observations are common in some papers. It can also be noticed the formation of niobium carbides colonies in Figs. 2(b) and 2(c). Figure 2(c) reveals niobium carbides in petal-like and as fine blade-like form. These carbide shapes are in agreement with findings in references, respectively.

Niobium is a strong carbide former and the niobium carbide formation is expected to occur before the eutectic reaction. They have the tendency towards agglomeration and growth acting as heterogeneous nuclei for austenite dendrites.

In Fig. 3, it is illustrated the microstructure of the alloys subjected to the destabilization for 2 hours at temperatures 950, 1 000 and 1 050°C. After the destabilization heat treatment, the matrix structure changed from predominantly austenite to martensite, the heat-treated microstructures were composed by martensitic matrix, eutectic and secondary carbides. Also, retained austenite was identified in the micrographs and detected on the XRD experiments in all tested alloys. The heat-treated microstructures are composed by martensite matrix, M7C3 carbides (eutectic and secondary) and niobium carbides (NbC).

The retained austenite appears as plates surrounding martensite. Apparently, according to the SEM images of Fig. 3, the amount of retained austenite seems to be higher in the specimen treated at 950°C than 1 000°C or 1 050°C. At 950°C, the secondary carbides were found mostly in discrete rod-type shape. These carbides became coarser as the destabilization temperature increased, in agreement with references. Temperature increase led the carbides to become more elongated, described in references. Regarding the amount of secondary carbides, apparently, there are no differences among the heat-treated samples by SEM analysis.

3.2. XRD Analysis
The XRD profiles of the as-cast sample and heat-treated samples are displayed in Fig. 4. In the as-cast condition, the phases austenite, martensite, M7C3 and NbC carbides were detected. There is no evidence of M23C6 in the structure. It is clearly that the main phase changed from austenite to martensite after the heat treatment, and there is still a small amount of austenite, as previous indicated by the SEM images. Also, the X-ray diffraction indicates that there are M7C3-type precipitated carbides in the heat-treated specimens.

Furthermore, it can be noted higher peaks of martensite (64.7° and 82.4°) and M7C3 (39.1°) for 1 000°C and 1 050°C comparing to 950°C. These observations are evidence that, possibly, the martensite volume fraction was higher in the specimens of 1 000 and 1 050°C in response to the precipitation of secondary carbides during heat treatment. The precipitation of secondary carbides leads to lower concentrations of Cr and C in the austenitic matrix, raising martensite start temperature. As a result, martensite volume fraction increased.

3.3. Carbide Volume Fraction
The carbide volume fraction in as-cast and heat-treated conditions are displayed in Fig. 5. In the as-cast condition, the eutectic carbides correspond to 36.5% (±2.2) of the specimens, which is closed to the number calculated using the empirical formula based on the bulk carbon and chromium composition, 34.3%, described in reference.

\[
\%CVF = 12.33 \times (\%C) + 0.55 \times (\%Cr) \quad (1)
\]

It was noted that CVF has increased from as-cast condition comparing to the heat-treated alloys, due to the precipitation of secondary carbides. However, the CVF among the heat-treated samples have showed no significant differences, according to the statistical test ANOVA. According to this test, the average volume fraction of secondary carbide lays around 3.4–5.5%, in agreement with reference.
3.4. Hardness

In Fig. 6, the effect of the heat treatment is shown on the hardness of the material. The bulk hardness and matrix microhardness values of the heat-treated specimens are higher than those of the as-cast condition. The bulk hardness has increased, compared to the as-cast samples, an average of 30.3% for the 950°C treated samples, 32.9% for 1000°C and 30.6% for 1050°C. The matrix hardness has increased an average of 41.0% for 950°C, 59.1% for 1000°C and 62.7% for 1050°C, comparing to the as-cast samples.

There are no significant differences in bulk hardness among the heat-treated samples, according to the statistical test ANOVA. Regarding matrix microhardness, it had a relevant increase from 950°C to 1000°C and 1050°C. This happened probably due to a higher martensite formation evidenced by the XRD analysis.

3.5. Abrasive Wear Tests

In Fig. 7, it is showed the wear rate of the tested samples. The destabilized alloys have clearly a lower wear rate than the as-cast condition. Also, among the treated samples, the wear rate has dropped significantly comparing 950°C destabilized samples to 1000°C and 1050°C. There is no significant difference in wear resistance among 1000°C and 1050°C treated samples, according to the statistical test t-student.

The matrix microhardness was determinant on the material wear resistance. Regarding abrasive wear caused by plastic deformation, the volume of material removed is inversely proportional to material hardness.\textsuperscript{17,18} The matrix has an important role in providing mechanical support to the carbides. A harder martensite matrix has the potential to reduce wear matrix, therefore, the fracture rate of carbides.\textsuperscript{19} A hard matrix, but not brittle, provides the best abrasion resistance under certain abrasion conditions, such as the rubber wheel test, as commented by Zum Gahr and Doane.\textsuperscript{19}

A coarser morphology of the secondary carbides of the 1000°C and 1050°C heat-treated samples might have helped in a better wear resistance. Carbides have a capac-
ity to absorb energy during friction. Then, according to reference, it would be reasonable to expect that larger secondary carbides provide a better load support and hence a higher wear resistance.

The volume lost for each period (15, 30, 45 and 60 min) were plotted on Fig. 8 and linear regression was conducted for each heat-treatment condition. The equations and R-squared are displayed on Table 3. All R-squared values were higher than 0.9. The graph makes it clear the behavior of the wear over the time. The good fitness of the linear regression indicates that the wear rate of the specimens was approximately constant during the test. The wear rate of which condition is represented by the slope of the equations. The constant value of the equations corresponds to a residual error related to the linear fitting.

The worn surfaces are represented on Fig. 9. The acting wear mechanism is plastic deformation in which the matrix was preferentially removed, this can be noted especially on Figs. from 9(a) to 9(d). Niobium carbides can be seen on the wear surfaces of Figs. 9(b) and 9(c), they can act as a barrier to cracks and grooves propagation, as other carbides do.

Craters from destabilized specimens at 1 000°C and 1 050°C appear to have smaller size and, also, are less abundant, as depicted in Figs. 9(g) and 9(h). A predominance of microcutting can be observed. These facts can be related to a higher matrix microhardness of these alloys, since plastic deformation and, consequently, grain pull-out is less likely to occur in those materials.

The results have shown that the microstructure correlation between martensite, retained austenite and carbides (Niobium and M7C3) reaches its optimum wear resistance in the range of 1 000°C and 1 050°C. At these temperatures, there is a higher martensite content and less retained austenite in the tested samples, leading to better wear resistance results. Also, secondary carbides became larger which has a positive effect regarding abrasion resistance. Niobium carbides remained stable, but plays an important role as a barrier to wear mechanisms in all heat-treated specimens.

### Table 3. Linear equations of the lost volume over time.

<table>
<thead>
<tr>
<th>Heat-treated condition</th>
<th>Linear equations</th>
<th>R²</th>
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<tbody>
<tr>
<td>As-cast</td>
<td>Vol. (mm³) = 3.3495 t (min) + 3.3204</td>
<td>0.9318</td>
</tr>
<tr>
<td>950°C</td>
<td>Vol. (mm³) = 2.1446 t (min) + 1.3825</td>
<td>0.9587</td>
</tr>
<tr>
<td>1 000°C</td>
<td>Vol. (mm³) = 1.6026 t (min) + 1.2452</td>
<td>0.9649</td>
</tr>
<tr>
<td>1 050°C</td>
<td>Vol. (mm³) = 1.6316 t (min) + 0.2612</td>
<td>0.9626</td>
</tr>
</tbody>
</table>

3.6. Profilometer

The 3D profile of the worn specimens is shown on Fig. 10. It can be noted deeper regions where the contact of the wheel and the specimen was more intensive, around the center of the tested materials; therefore, the plastic deformation in those areas tend to be higher as the applied normal load is higher. In deeper regions, scratches seem to be sharper than in shallower regions. There is a notable difference of texture among different regions.

The roughness was measured on the worn surface. The roughness parameters are shown in Table 4. According

![Fig. 6. Effect of the destabilization temperature on the bulk hardness and matrix microhardness.](image)

![Fig. 7. Wear rate of the specimens.](image)

![Fig. 8. Lost volume over time. (Online version in color.)](image)
Fig. 9. SEM images of the worn surfaces: as-cast (a and e), destabilized at 950°C (b and f), destabilized at 1000°C (c and g) and destabilized at 1050°C (d and h).

Fig. 10. 3D profiles of the worn surfaces of each heat-treated condition: a) As-cast, b) Destabilized at 950°C, c) Destabilized at 1000°C, d) Destabilized at 1050°C. (Online version in color.)
to the results, the mean roughness, $S_m$, and the root mean square roughness, $S_{sq}$, were proportional to the wear rate. This can be related to the intensity of the plastic deformation caused by the wear. These two parameters represent the overall measure of the surface texture.

A higher matrix microhardness from specimens treated at 1000°C and 1050°C, due to the higher martensite volume fraction, can explain a more uniform overall texture of these samples after the wear tests. Due its hardness, martensite can be more effective in preventing plastic deformation and providing better mechanical support to the carbides and, therefore, avoiding the acting wear mechanisms and leading to less irregularities on the surface. This shows the importance of the matrix microhardness to prevent surface degradation of the material.

Also, the other roughness parameters ($S_p$, $S_z$ and $S_q$) were lower at the 1000°C and 1050°C destabilized samples, which are the specimens with better wear resistance. $S_p$, $S_z$ and $S_q$ correspond to maximum roughness values: peak, depth and maximum difference between peaks and pits. The negative values of $S_k$ indicate the predominance of pits on the worn surfaces, due to the action of the wear mechanisms. According to $S_k$ values ($S_k < 3$), the worn surfaces seem to vary smoothly, with no extreme values of peaks and pits.

4. Conclusion

(1) An investigation of destabilization heat-treatment performed on a HCCI with 0.5%Nb has been done. An analysis covered the heat-treatment impact on the microstructure and on its tribological behavior. An optimum destabilized temperature aims to guarantee a hard matrix with NbC and $M_23C_6$ carbides able to resist wear mechanisms. The martensite/austenite matrix should be able to provide mechanical support for the carbides, avoiding carbide pull-out during abrasion.

(2) The optimal temperatures for the destabilization heat treat HCCI with low percent of niobium, regarding wear resistance, were 1000°C and 1050°C. As the treatment temperature increased, the precipitated carbides became coarser and rod-like carbides became more abundant.

(3) The specimens wear rate was inversely proportional to its matrix microhardness. The higher microhardness to the destabilized temperatures 1000°C and 1050°C is probably related to a higher martensite formation, as indicated in XRD tests. The coarser morphology of the secondary carbides of the 1000°C and 1050°C samples might have played a significant role in the abrasion resistance.

(4) The detected wear mechanism was plastic deformation by microploughing and microcutting. Regarding heat-treated samples, craters were larger and more abundant in the 950°C. As they presented lower matrix microhardness, they are more susceptible to plastic deformation and, hence, the acting wear mechanisms are facilitated, causing the craters, especially by microploughing and grain pull-out.

(5) The roughness parameters, in general, showed a tendency to decrease as wear rate decreases. Also, there was a predominance of pits over the worn surfaces, as $S_k$ values were negative for all conditions.

Acknowledgements

This work was partially financed by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES). Authors are grateful to the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for providing financial support.

REFERENCES


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<th>Heat- treated condition</th>
<th>$S_p$</th>
<th>$S_v$</th>
<th>$S_z$</th>
<th>$S_{sk}$</th>
<th>$S_{ku}$</th>
<th>$S_a$</th>
<th>$S_q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td>226</td>
<td>301</td>
<td>527</td>
<td>−0.333</td>
<td>1.62</td>
<td>149</td>
<td>167</td>
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<tr>
<td>950°C</td>
<td>297</td>
<td>343</td>
<td>641</td>
<td>−0.226</td>
<td>1.87</td>
<td>142</td>
<td>164</td>
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<tr>
<td>1000°C</td>
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<td>417</td>
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<td>1.94</td>
<td>106</td>
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<td>1050°C</td>
<td>194</td>
<td>184</td>
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