Wear resistance of high chromium white cast iron for coal grinding rolls

Desgaste de fundiciones de hierros blancos de alto cromo usados en rodillos de molinos de carbón

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ABSTRACT: High chromium white cast iron alloy used in coal grinding components is a material that may present different wear resistance depending on the thermal treatment used in its manufacturing. In this context, the properties of this alloy, containing 22% chromium and 3% carbon, were investigated after applying different heat treatments and their influence on the abrasion wear resistance was evaluated. For the characterization of the alloy, several experimental tests were performed using the following laboratory equipment: durometer, microdurometer, optical microscope, scanning electron microscope (SEM), X-ray diffraction, emission spectral photometry and equipment for wear testing according to the ASTM G65-04 (2010) standard. The results obtained reveal that the wear resistance of the selected alloy increases when a lower amount of austenite is retained in the matrix and high precipitation of secondary chromium carbides occurs. They also suggest that it is not necessary to use long times for the alloy destabilization in order to obtain higher hardness values and good wear resistance when the alloy is previously annealed, in contrast to what is practiced in the industry.

RESUMEN: Las fundiciones blancas al alto cromo utilizadas en componentes de molinos de carbón son materiales que presentan diferentes resistencias al desgaste, dependiendo del tratamiento térmico usado en su fabricación. Las propiedades mecánicas, microestructurales y tribológicas de la aleación con 22% de cromo y 3% de carbono (II D ASTM A532-10) y su influencia en la resistencia al desgaste fueron investigadas. Para la caracterización de la aleación fueron realizados diversos ensayos, utilizando los siguientes equipos de laboratorio: durómetro, microdurómetro, microscopio óptico, microscopio electrónico de barrido, difracción de rayos X, espectrofotómetro de emisión óptica, y equipo para ensayo de desgaste abrasivo de acuerdo con la norma ASTM G65-04 (2010). Los resultados encontrados mostraron que la resistencia al desgaste incrementa cuando la matriz tiene una baja fracción volumétrica de austenita retenida y una alta fracción de carburos secundarios. También indican que no es necesario usar largos tiempos durante la desestabilización en la aleación II D para obtener una óptima resistencia al desgaste, cuando la aleación fue previamente recocido. Estos resultados indican que la industria puede usar tiempos cortos durante la desestabilización de los rodillos de molinos de carbón.

1. Introduction

The microstructure of high chromium white cast iron is comprised of eutectic carbides. Additionally, there is a metallic matrix comprised of secondary chromium carbides, martensite, austenite and in some cases ferrite, after heat treatment. Eutectic carbides are formed during solidification. They do not undergo further transformation during solidification. Only the matrix can be altered. Three factors generate different microstructures in the matrix: thermal cycle, material’s chemical composition and the initial alloy state (as-cast or annealed). This affects the hardness and wear resistance of the material.

A high chromium white cast iron (II D ASTM A532-10) is commonly used to manufacture the coal grinders. As-cast alloys have excellent wear resistance after destabilization treatment. Consequently, the literature only provides information about as-cast material. This research objective studies the wear of annealed II D alloy after destabilization treatment. A comparison of the wear results on the II D
alloy, between the initial as-cast and annealed states.

This work consists of analyzing two groups of samples. Both contain 22% chromium and 3% carbon. One is a raw outcome from the casting process. The other underwent an annealing thermal treatment. Destabilization was performed applying different treatment times and temperature. An initial microstructural analysis was performed. The influence of annealing on the wear resistance was observed. Hardness measurements and secondary carbides quantification were performed. The values found were proportional to the wear resistance results, in accordance with other studies [1-6].

After destabilization treatment, the results show wear behavior differences in the II D alloy, as-cast and annealed.

2. Bibliographic review

2.1. High-chromium white cast iron characteristics

High-chromium white cast irons are ferrous alloys containing 11-30% Cr and 1.8-3.6% C along with variable amounts of molybdenum, manganese, copper and nickel [1]. The standard procedure most commonly used for the classification of this kind of cast iron alloy is ASTM A532-10 (2014). The microstructure of a white cast iron is the result of the chemical composition, the heat extraction rate during solidification and the rate of cooling after solidification [7-9]. Generally, at the end of the solidification, the high-chromium white cast iron is composed of a primary phase (austenite dendrite) and a eutectic compound \([\text{M}, \text{C}]_\text{C}\). The carbides of the eutectic compound do not transform during subsequent cooling [10]. On the other hand, the austenite (both from dendrites and the eutectic compound), which is rich in carbon and chromium, can be quenched smoothly and has a high martensite start temperature \([M_s]\) and final temperature \([M_f]\) in the transformation process. The transformations during cooling are dependent on the rate of cooling in the mold and the chemical composition of the cast iron [2, 3]. High-chromium white cast irons, in the working state, generally have a high volumetric fraction of carbides (10-30%) and a metallic matrix that is constituted of different proportions (depending on the history of thermal treatment) of austenite, secondary carbides and martensite. The high fractions of carbides provide higher hardness and, in general, higher wear resistance, which is why these materials are used in the mining and cement industries. Furthermore, the possibility of obtaining complex parts (due to the cast process) makes this material economically competitive when compared to other machined components [4, 5, 11, 12].

2.2. Heat treatment

The annealing of high-chromium white cast iron alloys is conducted when it is necessary to machine the pieces before destabilization. This treatment is applied to obtain a soft matrix with the maximum amount of ferrite after solidification, creating excellent conditions for machining. The decomposition of austenite into ferrite and carbides is a phenomenon that occurs at, approximately, 700-750°C [1]. To obtain a complete transformation of austenite into ferrite it takes approximately 6 hours.

Moreover, the destabilization is carried out when the amount of retained austenite needs to be reduced (increase in the amount of martensite), which leads to higher hardness and better wear resistance. This treatment is equivalent to the quenching of steels, but with a higher soaking time [1].

The austenite destabilization involves the precipitation of secondary carbides leading to an increase in \(M_s\) and \(M_f\) and therefore to a decrease in the amount of austenite retained in the material [6].

2.3. Destabilization phenomena

The precipitation of secondary carbides is dependent on the alloy composition and the destabilization temperature. The precipitated carbides can be \(M_xC_y\) and/or \(M_yC_z\). In high-chromium white cast iron alloys the precipitation occurs from the center to the peripheries of the dendrite.

The increase in the volumetric fraction of precipitated carbides over time results in a reduction of the carbon dissolved in austenite and an increase in the \(M_s\) and \(M_f\) temperatures, which reduces the amount of austenite retained after cooling [13].

2.4. Wear characteristics of high-chromium white cast iron

High chromium white cast iron alloys have a relatively good wear resistance when compared to other metallic materials, but the level of resistance varies according to the type of matrix microstructure and the volumetric fraction of the primary carbides in the alloy [14-16]. Thus, it is important to study the influence of these micro-constituents on the wear resistance. Depending on the type of microstructure and abrasive wear tests that are used, the results can differ. The available literature recommends the dry sand rubber wheel abrasion test (according to the ASTM G65-04 Standard). This reportedly best reproduces the coal grinding roll under track conditions, since the test operates under low tension and simulates the attrition action and abrasive particles present during the relative movement between the distinct surfaces [17].

3. Experimental procedure

To extend our knowledge on the influence of the matrix microstructure on the wear resistance of II D high-chromium white cast iron alloy (ASTM A532-10), the tests were carried out in different thermal environments. Then, after the test, a comparison of the different material properties obtained was performed.
3.1. Sample preparation

The samples, blocks of IID alloy (containing 22% chromium and 3% carbon), were casted in an induction furnace, according to the ASTM A532-10 (2014) standard. To obtain the test specimens with dimensions required for the wear test (75 x 25 x 12.5 mm) the blocks were further cut by water-jet machining. To study the heat treatment effects, two groups of samples were destabilized (for 0.5, 1.0, 2.0, 4.0 and 6.0 hours and at 900, 950, 1000, 1050, and 1100°C, respectively), giving a total set of 50 experiments. For destabilization, the temperatures and times from 4 hours are usually used for these alloys [1]. Shorter times 1 and 2 hours have been used by other authors, too [3]. Treatments with less than 1 hour do not yet appear in the literature.

Each experiment yielded three samples for data collection and subsequent analysis. The first group of samples was composed of as-cast test specimens and the second, of annealed samples, at 700°C for 6 hours. After the destabilizing treatment, a tempering treatment at 200°C for 2 hours was applied to relieve stress, followed by air cooling of all specimens.

3.2. Chemical composition analysis and microstructure

The determination of the total chemical composition of the IID alloy (containing 22% Cr and 3% C) was carried out with an emission spectrophotometer according to the IT 7433 standard. The characterization of the microstructure components was performed using optical NEOPHOT 30 – CARL ZEISS and electronic microscope mod. 810-PHILLIPS. To determine the fraction of the primary and secondary carbides, images were obtained with a scanning electron 810-PHILLIPS at a BSE magnification of 200x and 6000x respectively and analyzed in IMAGO Software.

3.3. Hardness measurements

Rockwell C hardness from the test specimens were measured before their preparation for the metallographic analysis. Rockwell C measurements were carried out using a bench durometer according to the specifications of the ABNT-NBR 6671 standard. The test was performed with a pre-load of 10 kgf and an end load of 150 kgf. For the microhardness tests the specimens were polished and chemically etched. The measurements were taken with a Shimadzu HMV microdurometer with a load of 100g (HV 0.1). In hardness and microhardness tests the load was applied for 15 seconds.

3.4. XRD

To quantify the retained austenite, an X-ray diffraction (XRD) analysis was performed in Philips PW1710 equipment, with a scan velocity of 0.4 degrees per minute and using a chromium beam with $\lambda = 1.788965$. This result and the carbides volumetric fraction were used to calculate the amount of austenite retained according to ASTM E975 standard.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Chemical Composition (mass%)</th>
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<tbody>
<tr>
<td>ASTMA532</td>
<td>C  2.0 to 3.2  Si  1.0 max  Mn  0.5 to 1.5  Mo  1.0 to 2.0  Ni  1.5 max  Cr  18.0 to 23.0  Cu  1.2 max</td>
</tr>
<tr>
<td>As-Cast</td>
<td>C  2.98  Si  0.71  Mn  0.75  Mo  1.90  Ni  0.35  Cr  21.22  Cu  0.06</td>
</tr>
</tbody>
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3.5. Wear experiments

Dry sand rubber wheel tests were conducted and calculated according to procedure A of the ASTM G65-04 (2010) standard for high wear resistance materials, applying a load of 130 N and 6000 spins. The equipment was manufactured in accordance with ASTM G65-04 (2010) for the tests.

The retained austenite, secondary carbides and wear test were carried out exclusively in the time and temperature levels that showed the highest hardness.

4. Results and discussion

4.1. Chemical analysis

Chemical composition of the alloy specimens are shown in Table 1. Also the composition recommended by the ASTM A532 standard for IID alloy high-chromium white cast iron is shown.

The data in Table 1 indicates that the chemical composition of the test specimens of the alloy IID meet the recommended standard composition. Based on the results it can be seen that the alloy under study is hypoeutectic, with approximately 30 percent of primary eutectic carbides do type $M_7C_3$. 
Figure 1 SEM micrographs of II D alloy: (a) as-cast state and (b) after thermal treatment
Figure 2 (b) illustrates that at temperatures lower than 1050°C the hardness initially decreases and then increases over time. At a temperature of 1100°C the results show a decrease in hardness over time. Based on the analysis of the graphs (a) and (b), in Figure 2, it is clear that the most effective destabilization time for the alloy is 6 hours (at 1000°C).

Figure 3 reveals hardness changes when increasing the temperature and the effect of time for the high-chromium white cast iron alloy in the initial annealed state [6 h at 700°C]. Figure 3 (a) illustrates that, similar to the as-cast state, the hardness initially increases and then decreases when the temperature is increased, resulting in a hardness peak (65 HRC) at 1050°C after 0.5 hours.

**4.2. Heat treatment**

After destabilization treatment, hardness measurement were performed on both two groups, to determine the temperature that provides the highest wear resistance values in each initial states. Figures 2 and 3 show the trends in the hardness behavior. Similar results are shown in other works [3, 5, 18, 19].

Figure 2 shows the changes in the hardness when increasing the temperature and the effect of treatment time for the high-chromium white cast iron alloy in the initial as-cast state.

Figure 2 (a) shows that the increase of temperature also increases the hardness. However, after the temperature reaches a certain value, it was observed that the hardness starts to decrease. The maximum hardness peak (63 HRC) was reached at 1000°C after 6 hours. This value is similar to the literature [18-20].

Figure 3 (b) shows that the hardness peak occurs at 0.5 hours of destabilization time for every time period analyzed. To obtain Figures 3(a) and (b) the treatments were applied twice (1050°C for 0.5 h) to observe the respective hardness peaks that occur. Thus, the temperature of 1050°C and the time of 0.5 hours were used in the subsequent analysis.

By comparing Figures 2 and 3, it can be observed that samples that were initially annealed prior to destabilization (heat treatment) have presented higher hardness values at lower treatment times. Samples of as-cast state...
reached higher hardness values with longer treatment times, but not as high as those of the samples that were previously annealed. As the samples previously annealed and destabilized for times of 0.5 hour and temperature of 1050°C showed better hardness, the treatments were made two times, both results are in Figures 3 (a) and (b) too.

4.3. Mechanical microstructural and tribological properties

Figure 4 shows the matrix microhardness behavior against a temperature variation (a) and a time variation (b) for the alloy in the as-cast initial state. In (a), the microhardness and the amount of secondary carbides in the matrix increase with temperature up to 1000°C, after which both properties decrease. In (b), there is an increase in the amount of secondary carbides over time, at 1000°C. This could be a consequence of the carbon’s super-saturation.

Figure 5 show the matrix microhardness behavior against a temperature variation (a) and a time variation (b) for the alloy in the annealed initial state. In (a), the amount of secondary carbides reaches its maximum at 1050°C, then decreases within the temperature range from 1050°C to 1100°C. This is probably a consequence of the increase in solubility of the carbon and chromium in the austenite. However, the reason for the increase from 900°C to 1050°C is not clear.

In Figure 5 (b), the amount of carbides decreases over time, at 1050°C. The maximum is reached after 0.5 hours. These aspects are not discussed in the literature. Nevertheless, it is believed that before annealing, precipitation and coalescence of secondary carbides takes place during destabilization. This would explain the best results being obtained with shorter times when samples in the annealed initial state were tested.

Since the amount of primary or eutectic carbides is not changed by heat treatment, the evolution of hardness over time depends only on the matrix constituents. Therefore, a correlation between the hardness of the alloy and the matrix microhardness exists, as can be seen in the data in Figures 4 and 5. The hardness of the alloy and matrix microhardness curves present the same tendencies.

The relation between the volumetric fraction of the secondary carbides, retained austenite and the temperature, for both initial states (as-cast and annealed), are shown in Figure 6. Nevertheless, Figure 7 compares the volumetric fraction of the secondary carbides, retained austenite against the soaking time, for the two initial states (as-cast and annealed). Comparatively, Figures 6 and 7 demonstrate that the tendencies observed for these properties also occur for the hardness values of the alloy.

Figure 6 (a) reports the as-cast sample and it shows that the volumetric fraction of secondary carbides remained approximately constant with a temperature up to 1000°C.
At higher temperatures the secondary carbides fraction decreases. It is probably because their solubility increases and they start to dissolve, leading to a decrease in hardness, in volumetric fraction of secondary carbides, and an increase in the amount of austenite retained in the alloy.

Figure 6 (b), on the other hand, reports annealed alloy and an increase in the secondary carbides fraction can be observed up to 1050°C. At higher temperatures this fraction starts to decrease. This proves, also, that the retained austenite increases as the secondary carbides fraction decreases.

The as-cast initial state Figure 7 (a) shows that the volumetric fraction of secondary carbides remains approximately constant in the first 4 hours. After which a slight increase in the secondary carbides fraction can be observed. The amount of austenite retained decreases over time, too.

The annealed samples in Figure 7 (b), the volumetric fraction of secondary carbides decreases as the soaking time gets longer. After 0.5 hour, there is an increase in the amount of austenite retained. This could be due to the dissolution of secondary carbides in the matrix, since the secondary carbides begin to precipitate during annealing. This phenomenon can explain the decrease in the hardness of the alloy.

Finally, to identify the relationship between all of the previously described properties and wear resistance, tests were conducted on three samples in the as-cast initial state and on three samples in the annealed initial state. The former destabilized at 950, 1000 and 1050°C for 6 hours in each case. The later destabilized at 1000, 1050 and 1100°C for 0.5 hour in each case.

These cycles were chosen because they provide conditions which lead to optimum property values for this alloy (containing 22% chromium and 3% carbon), in both initial states. The average values for the mass loss in the wear tests are shown in Figure 8.

Figure 8 shows that the treatments with higher wear resistance (the lower mass loss) were obtained from as-cast samples at 1000°C, for 6 hours and from annealed samples at 1050°C, for 0.5 hour. Furthermore, it can be observed that the highest wear resistance occurred when the alloy hardness, matrix microhardness, volumetric fraction and the amount of secondary carbides all reached their maximum values, yet the amount of austenite was minimum.

The correlation made in this research between the alloy wear resistance and its other properties contradict what it is being applied by the metallurgical industry nowadays.
6. Acknowledgements

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7. References