Effects of tungsten on erosion–corrosion behavior of high chromium white cast iron

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Abstract

In this study, effects of tungsten on wear resistance of high chromium white cast iron with and without tungsten in erosion–corrosion condition have been investigated. At the same time, the comparison between wear resistance of this grade of cast iron and low alloy steels with various contents of Cr which are used in industrial condition (in Sarcheshme Company, the greatest copper production company in the Middle East and with more than 4000 years historical cupper production background) was studied, while, copper concentrates have used for erosion particles. Results show that, because of higher hardness of matrix due to the tungsten, the wear resistance of high chromium cast iron increases. In addition to that, combine cutting and deformation wear mechanism and spalling mechanism were attributed in high chromium cast iron and low alloy steels, respectively. Subsequently, pitting mechanism in corrosion aspect was recognized because of inhomogeneity in chemical composition and sulfide inclusions content. Finally, the combine effects of erosion and corrosion (synergetic effect) were recognized in the high chromium white iron in industrial condition for the damaged samples.

1. Introduction

Wear has been defined as the material removal from solid surfaces, which may cause failure of industrial components [1]. Likewise, erosion is loss of material resulting from a repeated impact from a stream of particles. High chromium white cast iron alloys are commonly used for wear resistant application in the mining and materials industry [2]. According to the demands in upgrading the productivity and the quality of products, as well as the pursuit of optimum economy, grinding ball is now being compelled to shift from high chromium white cast iron to new type of materials with improved performance.

It has been defined previously that the good wear resistance of high chromium white cast iron is due to the presence of hard chromium carbides embedded in the matrix of martensite or austenite (in abrasive condition). In this regard, during high stress abrasion wear, retain austenite has important roll on wear resistance of high chromium white iron as result of strain induced martensite [3–6]. Nevertheless, in erosive condition, the matrix hardness is a critical parameter on wear resistivity of these alloys. Subsequently, among several kinds of chromium carbides recognized in Fe–Cr–C ternary system, M_7C_3 is predominant for the composition range of high chromium cast iron.

Generally, carbides in the microstructure, depending on their type, morphology and volume fraction, provided the hardness, which is required for applications without degradation [3–8]. Basically, the Fe–Cr carbides can be abbreviated as follows: $(Fe,Cr)_{23}C_6$ as $M_{23}C_6$ or K_1 carbide, $(Fe,Cr)_7C_3$ as M_7C_3 or K_2 carbide and $(Fe,Cr)_3C$ as M_3C or K_c carbide [9,17].

On the other hand, the matrix can also be varied by conventional heat treatments such as austenizing and air-quenching particularly hard matrix can be obtained due to the precipitation of numerous fine secondary carbides and transformation of the matrix from austenite to martensite.

In this regard, the $M_{23}C_6$ carbides will precipitate when the chromium content is higher than 25% [19,23]. Also, previous

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investigations show that secondary carbides play an important role in determining wear resistance of high chromium white cast iron [10–13]. So far, tungsten, which is added to steels generally for alloying purposes, is also a strong carbide forming element similar to chromium, niobium, molybdenum and vanadium. Alternatively, addition of the tungsten to high chromium white cast iron leads to the formation of M_6C (upper than 10% W) that crystallizes in a finely dispersed form as eutectic in the final stage of solidification [14].

Finally, there is not any information available concerning the influence of tungsten on the erosion–corrosion wear properties or how much of this element should be combined with high chromium white cast iron to obtain optimum erosion–corrosion properties. Alternatively, alloys selection for this investigation was based on a work which has been down in solidification mechanism and heat treatment of high chromium white iron with tungsten [15]. The previous work suggested that martensitic white irons with tungsten would be the most promising family of alloys to be studied. In this study, the multi-alloyed white cast iron, which consists of special hard chromium and tungsten and heat treated tough matrix, has been developed and used particularly in erosion–corrosion condition on grinding ball of the Sarcheshme Company, which is the largest copper production company in the Middle East. Through the test results, the multi-alloyed grinding ball has very good erosion–corrosion resistance because of their high quality and long term service life.

2. Material and experimental procedures

Initial charge materials were steel scrap. [75% W]$_{Fe}$ ferroalloys, were added to a slag-free molten iron so as to minimize the oxidation loss and the slag formation. After removal of any dross and slag, the melt was poured into a CO_2 sand mold, which was contacted with a graphite plate. Chemical analyses were
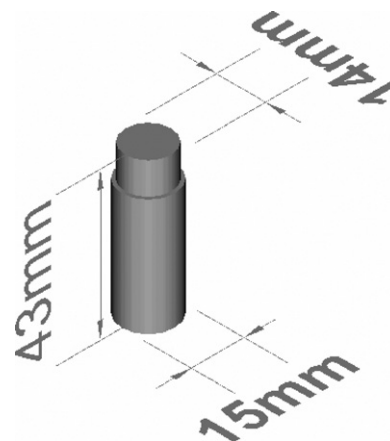

Fig. 1. Schematic graph of the wear test specimen.

undertaken by spectrometry from chill samples obtained during casting of each ingot, and the results are shown in Table 1. Subsequently, the specimens were prepared in cylindrical shape with 43 mm high and 15 mm diameter by electrical discharge machining (EDM). Fig. 1 shows the wear test specimen schematically. After that, samples were heat treated in an electrical furnace at 1000 °C for 2.5 h followed by cooling to room temperature in air cool condition. Likewise, the temperature was chosen by reference to previous work in high chromium white cast iron containing tungsten [15].

Subsequent to casting and heat treating, the specimens were mounted in epoxy and polished using conventional metallographic polishing techniques and etched with Murokami and Vilela reagent. Afterwards, standard optical microscopy observation was performed to examine morphologies of the phases present in the as cast and heat treated of the high chromium white iron. After heat treatment, erosion–corrosion wear test was performed at 600 h. Fig. 2 shows the wear test sample holder.

Table 1
Chemical composition of high chromium white iron and low alloy steel, which are used for erosion–corrosion test

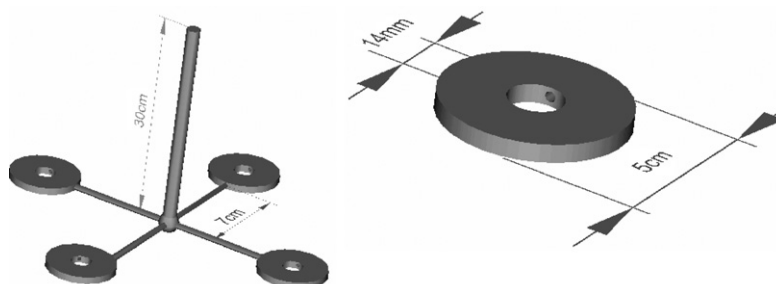| Specimen number	Fe	C	Si	Mn	P	S	Cu	Cr	W	Ni	Mo
1	Base	3.030	0.760	0.280	0.029	0.054	0.370	28.840	–	0.440	–
2	Base	3.050	0.710	0.280	0.028	0.052	0.350	28.210	0.500	0.340	–
3	Base	3.120	0.680	0.260	0.015	0.024	0.330	27.750	–	0.400	–
4	Base	3.010	0.670	0.027	0.014	0.021	0.280	27.120	2.500	0.300	–
5	Base	0.7020	0.7310	0.8970	0.0105	0.0424	0.088	3.86	–	0.8170	0.5150
6	Base	0.6080	1.1800	1.4600	0.0110	0.0171	0.1520	0.7610	–	1.4100	0.5450

Fig. 2. Schematic graph of the wear test specimen holder.

A variable speed motor controls the rate of rotation. The wear parameters were selected from the work condition in the mentioned company, the parameters were chosen to simulate the real conditions as much as possible. The erosive materials were selected as chalcosite (79.9% Cu) and chalcopyrite (34.6% Cu). The minerals grain size was 200 meshes in irregular shape. The range of pH has been set between 11.4 and 11.7. In addition to that, the amount of wear was determined by measuring weight loss with 0.001 accuracy. In order to drive erosion–corrosion wear mechanism, the specimens worn parts have been studied by the scanning electron microscopy (SEM) and the stereomicroscopy after each test.

3. Result and discussion

3.1. As cast condition

Fig. 3 shows the as cast structure of high chromium white iron. Usually, the as cast structure of Fe–Cr–C alloy usually consists of eutectic austenite and M_7C_3 dendrites [16,17]. The carbon, which is needed for the carbide formation, is easily removed from the melt on consequence of its high diffusivity. Fe–Cr–C–W alloys also contain various amounts of WC carbides in the matrix domain, in which the total amount of eutectic carbides increases with increase in W content, consequently. However, the amount of such increases is not distinguishable, quantitatively, but as we will see in the following sections, it is recognizable qualitatively by microhardness testing method. Moreover, two types of carbides exist in the high chromium white iron: hexagonal and eutectic carbides. It is shown that, between liquidus and solidus lines, hexagonal carbides can be formed. These carbides are hollow [18–21]. Meanwhile, the structure adjacent to the hexagonal carbides consists of finer carbides, which is due to higher cooling rate in the formation process of such carbides. Fig. 4 shows the hexagonal carbide in the high chromium white iron. Likewise, during eutectic solidification the M_7C_3 carbide that growing along the austenite, can absorb carbon from its surroundings and a narrow area at the austenite/carbide region becomes empty of carbon. Alter-
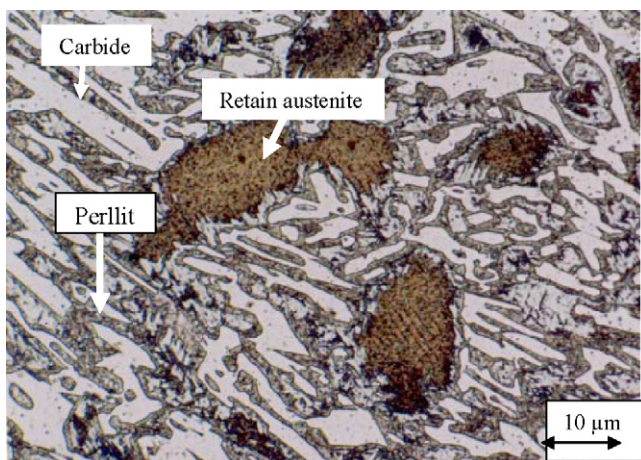

Fig. 3. As cast structure of high chromium white iron.
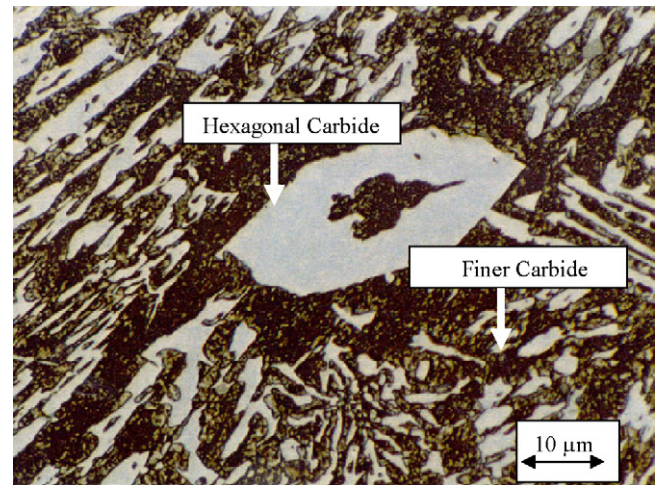

Fig. 4. Hexagonal carbide in the high chromium white iron.

natively, the lack of carbon in these areas increases the MS temperature and as a result, martensite transformation will be facilitated during subsequent cooling down. Furthermore, it is usual to find eutectic M_7C_3 carbides surrounded by laths of martensite.

3.2. Solid-state transformation

Solid-state transformation temperature, especially with the addition of Cr and W, changes remarkably with the supersaturation degree of solute elements in austenite [15]. This causes a destabilizing treatment of austenite as a standard heat treatment of high chromium white cast iron to raise the martensitic transformation temperature owing to the precipitation of supersaturated elements [22]. The consequence of such a treatment is formation of $M_{23}C_6$ precipitates, in the primary phase projection and the isothermal section of Fe–Cr–C, during the destabilization treatment according to ternary phase diagrams [23]. However, further to the formation of $M_{23}C_6$ carbides in the high chromium white iron, chromium depletion in the matrix occurs and the formation of martensite is probable. It should also be mentioned that due to the existence of tungsten in the chemical composition, the martensite formation is more expectable. However, retain austenite as a metastable phase at room temperature is inevitable but as the amount of alloying elements, particularly molybdenum and nickel are not distinguishable, these amounts would not be remarkable, in contrast, carbon that lowers the martensite start temperature (M_s) at temperatures below room temperature is remarkable one.

3.3. Microhardness

Table 2 shows the microhardness results of investigated alloys after being mentioned in heat treatment process. Microhardness of the matrix in the different samples was measured on metallographic samples lightly etched with Vilella's reagent. About 15 measurements for each sample were undertaken. As it is recognizable, the matrix microhardness of high chromium white iron containing 2.5% tungsten is the highest, which is due to the

Table 2
Matrix microhardness of high chromium white iron after heat treatment

	Specimen 1	Specimen 2	Specimen 3	Specimen 4
Matrix microhardness	790 HV	832 HV	803 HV	895 HV

higher tungsten in the matrix. Also, the matrix microhardness of specimen numbered 3 is higher than the matrix microhardness of specimen numbered 1 due to the higher carbon content—that causes higher secondary carbide content in the matrix in this alloy.

3.4. Wear characteristic

Weight losses have been considered for determining wear resistivity. As shown in Fig. 5, the weight loss increases with decreasing tungsten content. These results were obtained after 600 h wear test at the speed of 80 rpm. Moreover, erosion–corrosion wear of the matrix parts becomes less with a larger volume percentage of eutectic M_7C_3 and $M_{23}C_6$ – that is caused by the increase in tungsten content – as shown in Fig. 5. Meanwhile, it might also be observed in the mentioned figure that the erosion–corrosion resistance intensifies with increase in the tungsten content. Furthermore, the increase in hardness due to tungsten addition is a strong evidence for higher wear resistancy. This phenomenon is achieved due to the reinforcement of austenite by dissolved tungsten, which has contributed to the matrix strengthening by solid solution. Additionally, the wear resistance of specimen numbered 3 is higher than the wear resistance of specimen numbered 1 which is due to the higher carbon content in specimen numbered 3. Generally, higher carbon content results in higher wear resistancy as well as lower toughness. Furthermore, as depicted in Fig. 6, the wear resistance of high chromium white iron containing tungsten (especially 2.5%) is much higher than that of low alloy steel. Eventually, this phenomenon refers to lower carbides content in such alloys, which in turn is the direct consequence of lower chromium content.

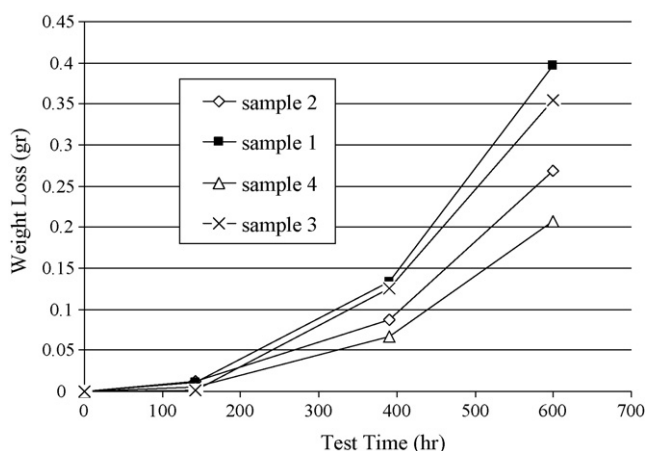Alternatively, Fig. 7 shows the SEM micrograph of high chromium white iron specimen after the same wear test.
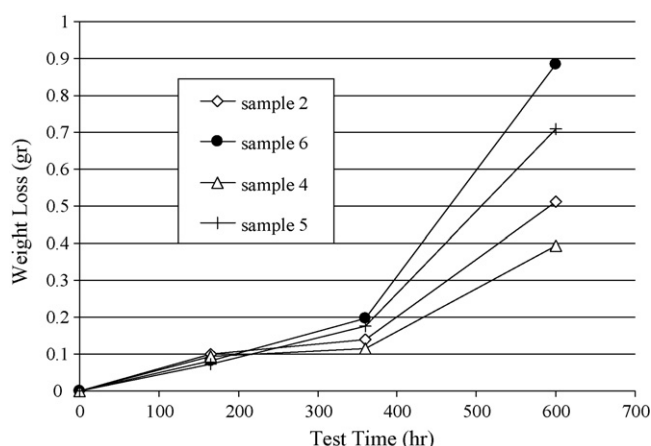

Fig. 6. Weight loss of the specimens as a function of test time for high chromium white iron and low alloys steels samples.

Eventually, cutting mechanism in erosion condition is mainly recognized in the specimen; at the same time, deformation mechanism occurs in part of the specimen. Since the particle impingement angle is smaller than 90 °C, therefore, the cutting mechanism mainly covers the specimen and is the main mechanism of degradation for such alloy. Whereas, deformation mechanism is also expectable as previously demonstrated by Suh [24]. Moreover, the stereomicrographs, which have been obtained from low alloy steels, are shown in Figs. 8 and 9. As can be seen from these micrographs, spalling mechanism can be recognized in low alloy steel specimens and subsequently this mechanism refers to the lower wear resistance in these alloys, which in turn is the result of small carbide content due to the low chromium content.

3.5. Corrosion behavior

Fig. 10 shows SEM micrograph of high chromium white iron sample with 2.5% tungsten. As depicted in this figure, in the corrosion aspect, pitting mechanism is the prevalent mechanism. However, with the existence of inhomogeneity in chemical composition and sulfide inclusion in the specimen, pitting mech-

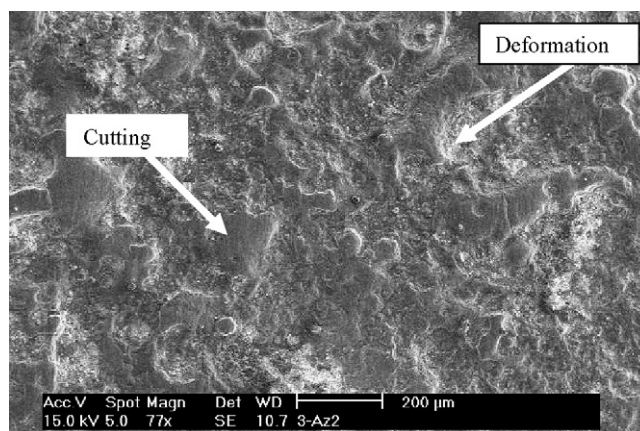Fig. 5. Weight loss of the specimens as a function of test time for high chromium white iron.

Fig. 7. SEM micrograph of high chromium white iron containing 2.5% tungsten after wear test (specimen 3).

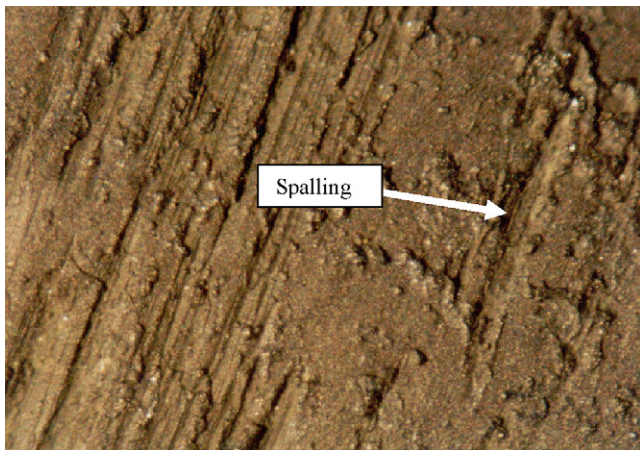Fig. 8. Stereomicrograph of the low alloy steel containing 0.76% Cr (specimen 6) (70×).

Fig. 9. Stereomicrograph of the low alloy steel containing 3.86% Cr (specimen 5) (70×).

anism is predictable. As a matter of fact, due to the carbide formation—which has chemical composition far from the chemical composition of the matrix, inhomogeneity is more common mechanism in the high chromium specimen. Likewise, because of higher chromium content of carbide (more that 30% in high chromium white iron) with respect to the matrix, the carbide will
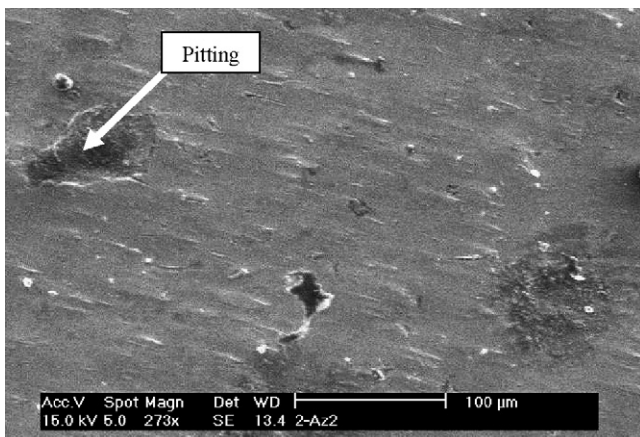

Fig. 10. SEM micrograph of high chromium white iron with 2.5% tungsten.

resist against the corrosion and acts as cathode while the matrix becomes anode and the corrosion mechanism will propagate consequently. Meanwhile, sulfide inclusions are common inclusions in the white cast iron and alternatively, the areas around these inclusions are very suitable locations for corrosion initiation and propagation as a result of the inhomogeneity in these locations.

In addition to the mentioned reasons for the corrosion mechanism, erosion and spalling increase the prevalent locations of pitting mechanism by means of increase in dead zone. Therefore, the corrosion will also attribute to erosion mechanism. Finally, the combination of erosion and corrosion is responsible for the damage aspect, so both effects must be taken into account in order to be applicable in industrial conditions.

4. Conclusions

Of the results obtained under the experimental conditions of this study the following conclusions can be drawn:

(1) In the high chromium white iron, tungsten increases the matrix hardness of these alloys.
(2) Tungsten increases the wear resistance of high chromium white iron and this increase is intensified by increase in tungsten content.
(3) The wear resistance of high chromium white irons is higher than low chromium steels. Similarly, this phenomenon has been related to the existence of M_7C_3 and $M_{23}C_6$ carbides in the high chromium white iron samples, which cannot be found in steel sample situation.
(4) With increasing the wear time, the wear will be increased, and this phenomenon can be attributed to the synergetic effect between erosion and corrosion.
(5) In this investigation, the cutting and deformation mode in the erosion aspect and the pitting mode in the corrosion aspect are recognized.

Acknowledgments

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