Journal of Materials and Manufacturing (2022) 1: 23-30

Journal of Materials and Manufacturing

Influences of Cr on the microstructural, wear and mechanical performance of high-chromium white cast iron grinding balls

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Abstract

High-alloyed white cast irons are widely used by casting methods to produce grinding balls used in the cement and mining industry. Balls produced in this class are in the high chromium white cast iron class, and the chromium content in this material has a significant effect. This study on improving quality and competitive conditions in ball production aimed to obtain balls with the same mechanical properties and to investigate their performance by reducing the Cr ratio of the sample with 17-19% chromium (Cr) content. In this context, studies have been carried out by reducing the amount of Cr in the ball by performing oil-quenching heat treatment instead of the air-cooling system used within the company. The samples' wear amount, hardness, toughness and microstructure were evaluated by reducing the Cr content. Since reducing Cr atoms cause the carbide phases in the balls to decrease and the martensite ratio to increase, materials with the same wear resistance have been obtained. The same mechanical properties as the existing mass-produced balls with a Cr content of 17-19% were determined by reducing the Cr content to 10%. As a result, a significant reduction in raw material cost has been demonstrated by producing balls with the same mechanical properties suitable for working conditions.

Keywords: High chromium White cast iron; Effect of chromium; Wear resistance; Microstructure; Hardness

1. Introduction

High Chromium White Cast Irons (HCCIs) are iron-based alloys containing 11-30% chromium and 1.8-3.6% by weight carbon, sometimes with added Mo, Mg, Cu and Ni as additional alloying elements [1]. HCCI, first patented in 1917, was found to be less brittle, with excellent resistance to wear and corrosion, compared to unalloyed white irons [2]. In research conducted in the laboratory of the Electro Metallurgical Company since 1920, alloys containing 15-35% chromium and 1.5-3% carbon by weight were developed and used by Frederick Becket in high-temperature applications and to reduce the maintenance of grinding (crushing) equipment. Later, it was understood that the properties of HCCIs depend on the chromium carbides and the matrix. In 1962, Bradley and Foster Ltd. investigated the effects of alloy additions and heat treatment on the working life of HCCIs containing various chromium and carbon [3]. Most researchers have focused on either strengthening the matrix by destabilizing it or improving wear resistance with alloy additions [4]. A common way to increase hardness and wear resistance is to add carbide-forming elements that change the alloy’s stoichiometry, shape, distribution and volume content. Elements such as Ti, W, V and higher Cr in amounts up to 12% by weight increase the carbide volume fraction in the structure and cause primary carbides formation [5-7]. Most cast irons contain nickel, molybdenum, copper or combinations of these alloying elements. Elements such as chromium, boron, titanium and vanadium form strong carbides [8-10]. After the chromium element solidifies,

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DOI: 10.5281/zenodo.7107351
Received: 04 August 2022, Revised: 15 August 2022 and Accepted: 19 September 2022

it forms carbide instead of graphite. The gradual increase in the addition of Cr and C alloys affects the carbide precipitation, increasing the hardness of the materials under different heat treatment conditions. However, the additions of these elements can represent a significant cost increase due to the high amount required [11]. The microstructure of these alloys usually consists of an austenite matrix or its transformation products from hard primary or eutectic carbides. The presence of primary and eutectic M_7C_3 carbides with an austenitic matrix or heat treated martensitic matrix in the casting condition leads to high hardness and excellent wear resistance. While martensitic phases are thought to have a positive effect on wear resistance, pearlitic/ferritic morphologies generally increase wear loss [12-15]. In addition, $M_{23}C_6$, M_7C_3, and M_3C type carbides can be formed in HCCIs depending on the alloy composition and heat treatment condition [16-18]. Different critical and subcritical heat treatments alter the initial casting microstructure of HCCIs and lead to varying degrees of secondary carbide precipitation. Zhang et al., 2001 confirmed the formation of secondary carbide particles after subcritical heat treatments of two chromium cast irons with different Cr content [19]. Powell and Bee, 1996 reported that 18% Cr white iron was 1273K, and square prism $M_{23}C_6$ particles precipitated in the austenitic matrix after a short time of destabilization. After 4 hours at the same temperature, a mixture of $M_{23}C_6$ and M_7C_3 was formed. They also noted the formation of secondary carbide particles at the lower grain boundaries during the solidification stage [20]. The size and volume of M_7C_3 type carbides increased with increasing temperature in high chromium alloys [21]. Wiengmoon and Chairuangsri, 2005 destabilization process was applied to cast iron containing 30% Cr and 2-3% C by weight in the range of 900-1100°C for 2-8 hours. Subsequently, air-cooling was carried out at room temperature. They determined the volume fraction of secondary carbide in the martensite matrix and $M_{23}C_6$ in the eutectic carbides [22]. Zhou et al., 2015 optimized the optimal heat treatment process applied to Cr26 HCCI. The optimum heat treatment step was determined by quenching at 1000 °C for 2 hours followed by a 2-hour tempering at 400 °C. The hardness of HCCIs is related to the precipitation and re-dissolution of carbides secondary to the heat treatment process [23]. Carrillo et al., 2017 reported that the carbide volume fraction increased with the addition of tungsten to 17% Cr white cast iron, and W_6C carbide was detected for contents above 4%. In addition, tungsten did not affect the secondary carbide precipitation process [24]. Pourasiabi and Gates, 2021 investigated the effect of niobium carbide (NbC) macro addition on the hardness, microstructure, and high tensile wear performance of high chromium white cast irons quantitatively and qualitatively. Abrasive wear resistance evaluated using the ball mill wear test showed improvement of up to 11.4% by volume and 7% by volume in basalt and quartzite, respectively, with NbC [25]. For this reason, the production of HCCIs is used in the cement and mining industries in grinding mill balls, various linings, gears, various conveyors, grader blades, various pumps, discs and piston ring due to its unmatched wear resistance [25-29].

In this study, since the existing cooling system is carried out with air hardening after heat treatment, homogeneous cooling cannot be achieved, causing severe wear and deformation problems in the working conditions of the balls. Especially in the preliminary studies, it was planned to reduce the amount of chromium, increase the quality and reduce the cost by homogeneous cooling (in oil).

2. Materials and Methods

In this study, white cast irons were prepared following the chemical analyses given in Table 1. Chromium element was added in varying proportions between 17-19% and 8-10% by weight. It consists of 430 stainless steel, pig carbon, exposed steel and ferrochrome as charging materials. The melting process was carried out in an Eges brand induction furnace with 6 tons/hour capacity. After the materials were melted, their analysis was checked with an OBLF GS 1000 II brand spectrometer. A 90 mm diameter ball model was connected to the HWS SINTO HSP-3 fully automatic horizontal molding line, and casting processes were carried out (Fig.1.). Then, samples were separated from both their sands and their connections with each other. Afterwards, the samples are subjected to surface cleaning.

Table 1. Chemical analysis parameters of high chromium white cast iron (% by weight) and raw material amounts

Sample number	Diameter (mm) Ø	C%	Si%	Mn%	Cr%	430 Stainless steel	Pig carbon	Exposed steel	Ferrochrome
1	90	2.05	0.816	0.652	9.25	80	2	18	0
2	90	2.1	0.756	0.712	10.42	82	2	16	0
3	90	2.02	0.788	0.641	11.56	84	2	14	0
4	90	2.08	0.794	0.641	12.33	86	2	12	0
Standard 5 (Ref.)	90	2.25	0.701	0.4-1	17-19	93.2	1.8	0	5

Fig. 1. HWS SINTO HSP-3 horizontal molding line [30]

The obtained samples were subjected to heat treatment in a fully automatic, computer-controlled LOCHER brand (700 kg/hour) heat treatment furnace working with natural gas by increasing the austenitization process to 900°C and keeping them for 4 hours. After austenitization, 1, 2, 3 and 4 samples were oil quenched into the oil bath at 70°C. However, the standard 5 sample, whose mass production continues, is cooled with air after heat treatment. After heat treatment, stress relief annealing was applied to the samples at 280°C for 3 hours. Marquench 875 supplied by Petrofer Industrial oils was used as quenching oil. This product is a high-performance, high-viscosity hot bath oil with an increased cooling rate with a short vapour phase. It is used successfully in the hardening process by reducing the distortion, especially in the cementation and tempered steel parts, which are at risk of distortion.

In order to examine the microstructural characterization of the samples, they were first cut into 12.5 mm cubes with a Struers Labatom 5 cutting device. Since the samples are in sizes that can be easily held by a hand, there was no need for mounting. In this context, the samples are grinded 120, 320 and 1000 grid. sandpaper under water. Then, the surfaces were polished by applying a polishing process for 5 minutes with a maximum of 6 µ polycarbonate diamond suspension. The samples were etched with 3% Nitric acid and 97% Ethyl alcohol solution for approximately room temperature. Microstructure images of all etched samples were examined with a Nikon Eclipse MA 100 optical microscope.

Wear tests were carried out using a laboratory scale wear mill (drum) measuring Ø55 mm x L:700 mm. In the wear tests, the measurement is started when there is no sample in the prototype mill. Then in the tests performed for each sample group, tumbling is performed at 6300-18900-31500-44100-56700 revolutions (90-270-450-630-810 min.) and 90 mm diameter balls are filled with the heaviest conditions, they were eroded by hitting each other. Wear drum rotation speed was 70 rpm, and ball measurements were made at a 30% ball fill rate. The Mergo GmBH brand Minor 69 type Rockwell device characterised hardness values according to ASTM E18-98 standard. Each sample was tested under a preload load of 10 kgf and the main load of 150 kgf

[31]. Impact strengths were determined by lifting the samples to a height of 7 meters using a conveyor elevator and releasing them onto a steel plate. The test was terminated if there was no breakage up to 10000 cycles, which is the minimum accepted value for the toughness/impact strength of the ball in the drop tests [31].

3. Results and Discussions

3.1. Microstructure Analyzes

Analysis of the samples is shown in Figure 1. The primary purpose of microstructural analysis; is the fragmentation of martensite phases into small islets and arranging them side by side in a specific order. It is undesirable for the primary carbide phases to be in long lines. For this reason, the martensite phases in the 1st test sample remained combined despite the heat treatment, the primary carbides were not homogeneously dispersed in a linear state, and the martensite phases were not homogeneously dissolved. These undesirable phases in the microstructure caused breakage under operating conditions. Approximately 77.4% martensite and 22.6% primary carbide were detected in these samples (Figure 1-a). In sample 2, heat treatment fragmented martensite phases into islets, and primary carbides have a reticulated structure. This reticulated structure has contributed to the adhesion of the ball tissue to each other and prevents the part from breaking or wearing away from the main structure. In addition, it was observed that the martensite phases were homogeneously distributed. Approximately 76.6% martensite and 23.4% primary carbide were detected (Figure 2-b). In samples 3 and 4, phase distribution with a similar microstructure to sample 2 was obtained. While approximately 75% martensite and 25% primary carbide were detected in sample 3, approximately 77.3% martensite and 22.7% primary carbide were detected in sample number 4 (Figure 3-c and Figure 4-d). On the other hand, approximately 77% martensite and 33% primary carbide were detected in standard 5 serially produced balls (Figure 5-e).

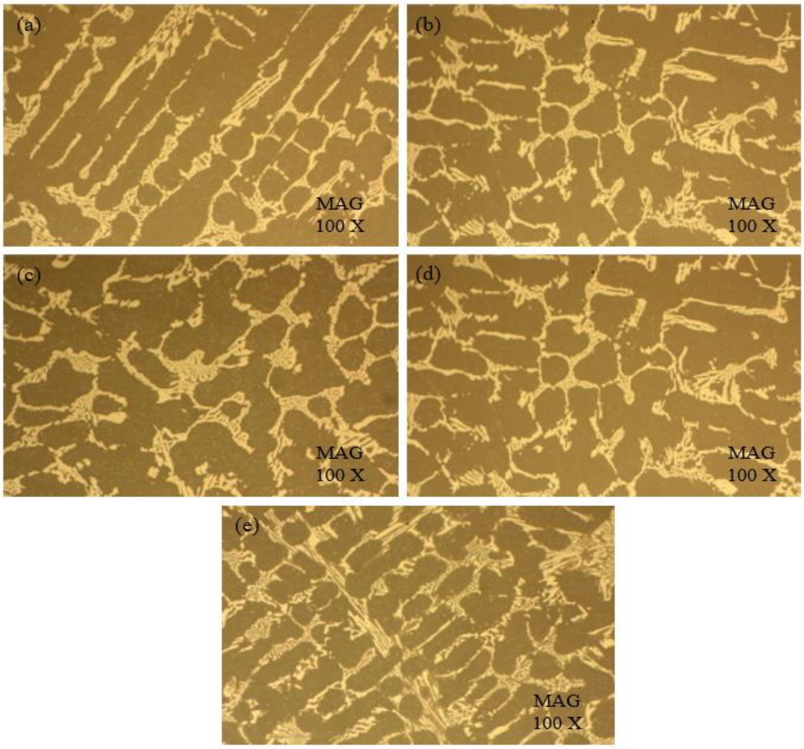

Fig. 2. Microstructure images of samples (a) %9; (b) %10; (c) %11; (d) %12; (e) %17-19

3.2. Wear tests

The wear data obtained during the tumbling processes provide guiding data in the evaluation of the wear performance of the balls. In actual mill conditions, the interaction between the balls decreases with increasing the raw material used for grinding. There will inevitable be a decrease in the amount of wear. As the number of tumble cycles increases to a specific value, the wear values also increase. Since less wear occurs afterwards, the slope of the wear curve in the graph shows a horizontal trend. Due to the inhomogeneity of the martensite phase in the wear tests, it was observed that the wear loss was higher when the chromium ratio was reduced to 9-10%. This is due to the inhomogeneity of the martensite phase in the structure. A material with the same wear resistance has been obtained since the reduction of the chromium content will lead to a decrease in the wear-resistant carbide phases in the material, an increase in the martensite ratio, and a lower carbon ratio than the current productions. As a result, reducing the chromium content to 9% harmed wear resistance. It is seen that the wear tendencies of 2-3-4-5 samples are almost the same. For this reason, it is ensured that balls no. 2 are used instead of balls no. 5, which are produced as standard in the factory, with the cooling process by quenching in oil after heat treatment.

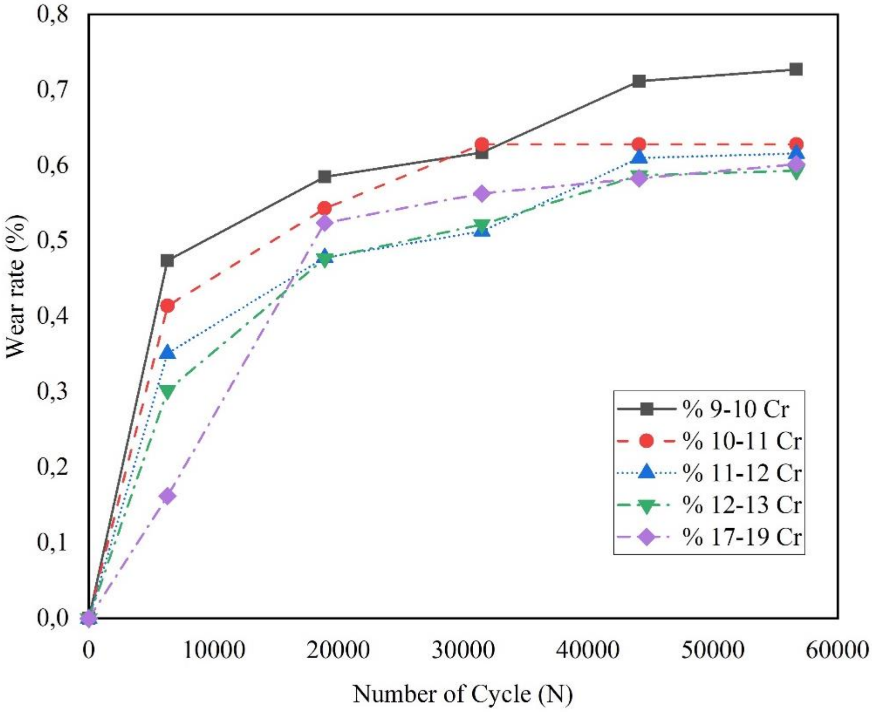

Fig. 3. Wear-cycle number of chromium ratios

3.3. Hardness and Impact (Drop) Tests

The measured macro hardness values at different chromium ratios are reported in Figure 3. The results obtained from the hardness measurements of the samples are very close. Microstructural property such as size, morphology and distribution of various phases in the structure play an important role in determining the hardness of white cast irons. Generally, the more acceptable grain size and homogeneous distribution of hard particles cause high hardness values of the materials. For this reason, 9-10% chromium has a lower hardness value than other samples.

As a result of the impact (drop) tests performed on the balls, there was deformation on the surfaces of samples 1, 2, 3 and 4, but the balls were not broken. However, it was observed that the standard samples numbered 5, whose mass production continues, were divided into two after the impact (drop) tests and were broken at the number of falls of 1553.

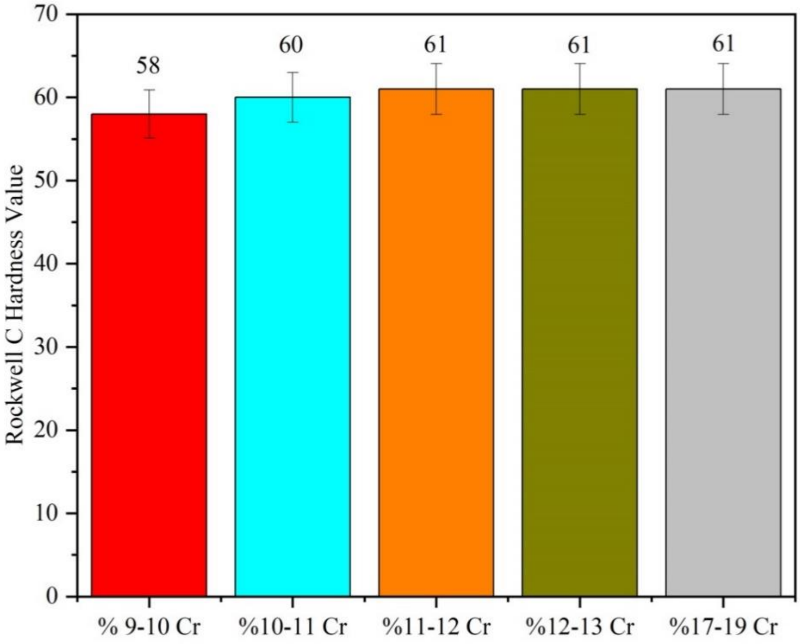

Fig. 4. Hardness values of samples

3.4. Cost Analysis

Table 2 shows the raw material cost comparison of the samples. Reducing the cost of raw material usage is inevitable by reducing the chromium content of the mass-produced standard sample. The desired properties were obtained by reducing the chromium ratio to 10%, and the raw material was compared with the standard produced sample. In 1-ton melting, cost advantage of $144.39 was achieved over raw material alone [25]. These results may vary as they are calculated over the dollar rate.

Table 2. Raw material cost comparison [25]

Raw materials	Charge amount of 17% Cr ball	Charge amount of 10% Cr ball	Price($\frac{kg}{\$}$)	Charge amount of 17% Cr ball	Charge amount of 10% Cr ball
430 Stainless steel	945.17	684.262	0.956	903.582	654.1545
Exposed steel	-	293.25	0.6411	-	188
Ferrochrome	37.807	-	2.3	86.956	-
Pig carbon	17.01	22.48	0.73	12.4173	16.4104
Total	1000	1000	4.6271	1002.96	858.57

4. Conclusion

In this study, detailed research was carried out to analyse the wear resistance, hardness and microstructures and to make sense of the cost comparison by applying the oil cooling process after heat treatment on the reduction of Cr% content of 17-19% 90 mm diameter balls produced in the current series (standard). The obtained results can be summarized as follows:

- By reducing the ratio from 17% to 10-11-12%, very little difference was obtained in the same hardness and wear rates. Due to the inhomogeneity of the martensite phase in the balls with 9% Cr, it was observed that the hardness value and the amount of wear were high. There was no improvement in the wear resistance and hardness of the 9% Cr samples.
- By reducing the Cr ratio, the impact resistance of the samples can be improved.
- Oil quenching showed better wear resistance than air cooling.
- By reducing the amount of Cr from 17% to 10-12% by weight, primary carbides decreased while the martensite phase increased; however, balls with the same microstructure were obtained by the homogeneous distribution of the martensite phases in the structure.
- Raw material cost is reduced by decreasing the Cr ratio. In 1-ton melting, cost advantage of $144.39 was achieved in raw material alone.

Based on these results, it has been determined that a revision should be made in the quenching process of the balls in order to ensure standardization in the development process of the existing products, and the selection of the quenching process in oil instead of air has significant results in increasing the quality of the balls.

Acknowledgments

We would like to thank Işıklar Holding Çemaş for its support to this study.

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