# MME SEE CONGRESS 2023

5th Metallurgical & Materials Engineering
Congress of South-East Europe
Trebinje, Bosnia and Herzegovina
7-10th June 2023

# CONGRESS PROCEEDINGS

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# CONGRESS PROCEEDINGS

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# MICROSTRUCTURE DEVELOPMENT DURING HEAT TREATMENT OF HIGH CHROMIUM WHITE CAST IRON

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Even though it has been in use for a very long time, the high chromium white cast iron (HCWCI) still triggers scientists due to its outstanding wear resistance. Besides its well-known as-cast usage, it can be used as a coating material, as well. HCWCI owes this feature due to the presence of carbides in microstructure, which depends on the composition and heat treatment regime. This investigation was conducted on two HCWCI alloys, where in addition to chromium, the second important alloying element is molybdenum (Mo). Apart from other alloying elements, HCWCI_1 is alloyed with 24.48% Cr and 1.32% Mo, while HCWCI_2 contains 14.11% Cr and 2.47% Mo. The comprehensive microstructural characterization was carried out on as-cast samples and samples obtained after quenching (at -196ºC) and/or quenching followed by tempering (at 250ºC). Important microstructure indicators are: the stability of austenite, the ratio of micro-constituents (especially different types of carbides), as well as their arrangement and morphology, so they are revealed and discussed in relation to the influencing mechanical properties.

**Keywords:** wearing; carbides; molybdenum; eutectic; austenite.

## Introduction

White cast iron with high chromium content, also known as high chromium white iron (HCWCI), is a type of white cast iron that contains a significant amount of chromium in addition to carbon. The chromium content can range from 11% to 35%, which gives it a high level of wear resistance, corrosion resistance, and toughness [1, 2, 3, 4]. HCWCI is often used in applications that require exceptional wear resistance, such as mining equipment, oil drilling bits, rail track components, and power generation industries. It is used in a variety of components, such as grinding balls, mill liners, crusher parts, and pumps.

The high chromium content in HCWCI creates as-cast hard and wear-resistant microstructure that is composed of carbides, and other microconstituents (austenite, pearlite, martensite and bainite) depending on the exact chemical composition, the ratio of main alloying elements, and temper state [5, 6]. The carbides, which are primarily made up of chromium, are dispersed throughout the matrix of the material, giving it high resistance to abrasive wear [7, 8, 9, 10]. The martensite, which forms during the cooling process, provides the material with high tensile strength and toughness [11]. One of the most important characteristics of HCWCI is its corrosion resistance. The chromium in the material protects it from corrosion in aggressive environments. However, like other types of white cast iron, HCWCI is also brittle and can be difficult to work with. It can be prone to cracking during manufacturing or when subjected to impact or shock loading. To improve the mechanical properties of white cast iron, it must be subjected to heat-treatment to produce designed microstructure.

White cast iron with molybdenum and high chromium content is also known as high chromium-molybdenum white iron (HCMWCI). The high chromium content provides it with exceptional wear resistance, while the molybdenum content improves its toughness and corrosion resistance. However, the addition of molybdenum to the material results in the formation of a bainite, which gives it better toughness and impact resistance [12].

## Materials and methods

This investigation was conducted by metallographic examination of two HCWCI alloys. Both alloys were induction melted and cast into silicate sand molds bonded with $CO_2$. Their chemical composition is presented in Tables 1 and 2. Heat treatment was conducted in an electrical furnace prior to sample preparation for testing. Samples were examined as-cast, after quenching (heated up to 1000$^o$C/2h and cooled down to -196$^o$C), and quenching (from 1000$^o$C/2h) followed by tempering at 250$^o$C/3h.

**Table 1** Composition of the high chromium white cast iron alloy 1: HCWCI_1

| Alloy | C [%] | Cr [%] | Mo [%] | Ni [%] | Si [%] | Mn [%] | P [%] | S [%] |
|---|---|---|---|---|---|---|---|---|
| HCWCI_1 | 2.66 | 24.48 | 1.32 | 1.6 | 0.99 | 0.96 | 0.027 | 0.009 |

**Table 2** Composition of the high chromium white cast iron alloy 2: HCWCI_2

| Alloy | C [%] | Cr [%] | Mo [%] | Cu [%] | Si [%] | Mn [%] | P [%] | S [%] |
|---|---|---|---|---|---|---|---|---|
| HCWCI_2 | 3.29 | 14.11 | 2.47 | 0.94 | 0.87 | 0.93 | 0.028 | 0.003 |

The microstructure was assessed based on measuring the grain size and distribution by the linear-intercept technique, as defined in EN ISO 4499-2:2020 standard. An optical microscope equipped with the Image analysis device Leica Q5000MC was used.

For preparation, specimens were fine grinded up to 1000 paper quality, polished with alumina slurry kit, and then cleaned ultrasonically in ethanol and water. For microstructure revealing, the etching agents such as: hydrochloric acid, picric acid, nital (nitric acid in ethanol) and Murakami's reagent (potassium ferricyanide and potassium hydroxide mixture) were used, depending on the alloy temper and the aim what to reveal in microstructure.

## Results and discussion

The as-cast microstructures of both alloys consist of primary dendrites of austenite (γ) together with γ-martensite-carbide eutectic. HCWCI alloys contains several types of carbides $M_3C$, $M_7C_3$ or $M_{23}C_6$, depending on the alloy composition and heat treatment employed [11]. Figure 1 presents as-cast microstructure of both alloys at the same magnification, a) HCWCI_1 and b) HCWCI_2. Microstructure is revealed by etching in nital+picric acid. A finer and more homogenous dendritic structure is obvious in the HCWCI_2 alloy, at the same magnification, in an alloy with lower Cr, but higher Mo content. There are primary γ dendrites and eutectic, which consists of carbides and γ. According to the alloys composition and literature [12], carbides are predominantly of $M_7C_3$ type, but there can be present $Mo_2C$ carbide, typical for this alloy composition [13]. It can be revealed by selective etching, what is confirmed in Figure 2, obtained after etching in Murakami's reagent. $Mo_2C$ carbides containing Mo are present in the microstructure of the base metal. It is reported [13] that the presence of $Mo_2C$ is confirmed in all studies concerning Mo-containing alloys, and proven by XRD examinations, appearing in small patches of eutectic, just like in Figure 2.

Figure 3 a) HCWCI_1 and b) HCWCI_2 alloys, at comparable but higher magnification than in Figure 1, microstructures developed by nital+picric acid etching, shows that microstructure of HCWC_1 alloy is more like the primary phase islands surrounded by the eutectic. HCWCI_2 has a microstructure with well-pronounced dendrites.

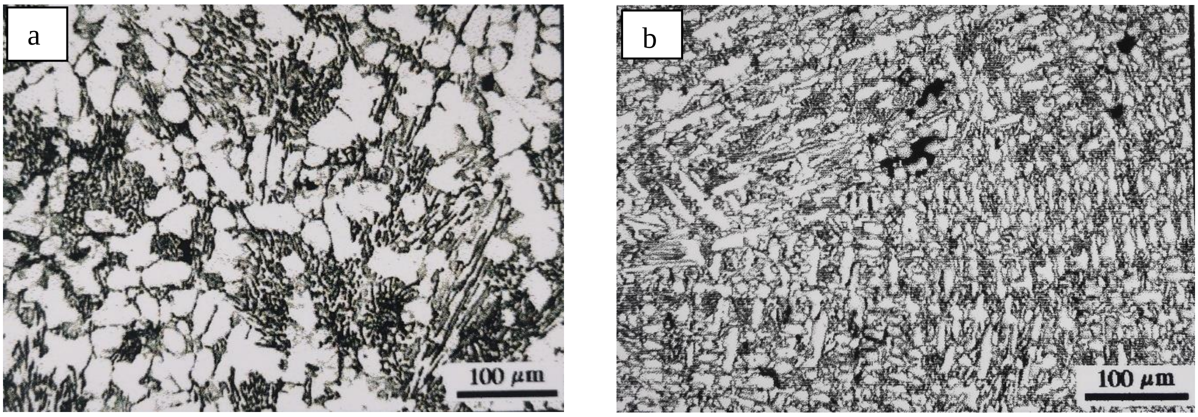


**Figure 1** As-cast microstructure of a) HCWCI_1 and b) HCWCI_2

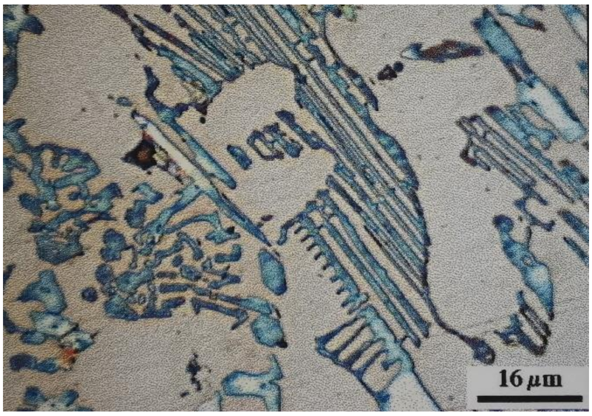


**Figure 2** As-cast microstructure of HCWCI_1, etched in Murakami's reagent

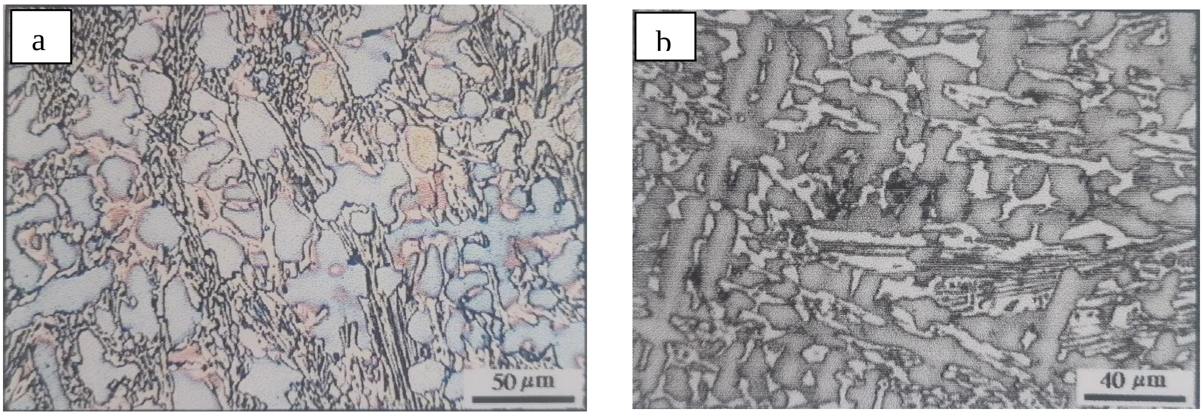


**Figure 3** As-cast microstructure of a) HCWCI_1 and b) HCWCI_2

After austenitizing heat treatment at 1000°C, quenching followed by cooling down in liquid $N_2$, there are fine precipitates of secondary carbides in the dendritic regions, the amount of γ retained in the dendrite area increased, and martensitic transformation can be noted.

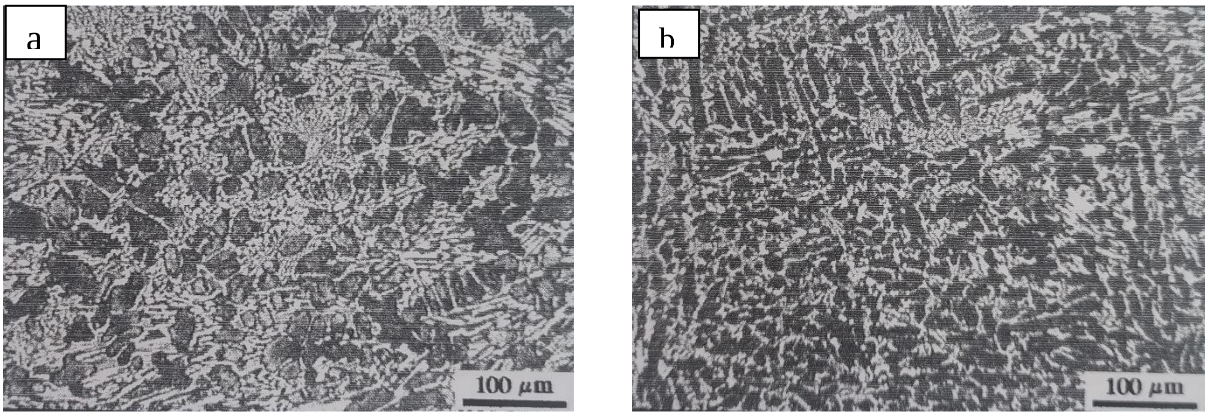


**Figure 4** Quenched and tempered Microstructure of a) HCWCI_1 and b) HCWCI_2

Similarly, after austenitizing heat treatment at 1000°C and quenching followed by a slow (atmospheric) cooling down, instead of martensitic transformation, the bainitic phase reveals, Figure 4. HCWCI_2 alloy, the one with lower Cr, but higher Mo content exhibits finer microstructure. Distribution of the austenite transformation products (martensite -M and/or bainite -B) and precipitated carbides appears to be more uniform compared to the as-cast samples.

## Conclusion

Microstructure developed during heat treatment of cast iron with molybdenum and high chromium content (HCMWI) revealed carbides as the primary microconstituent, which are formed from the high levels of chromium and molybdenum in the material. Carbides present here are mostly of $M_3C$ and $M_7C_3$ type, but also for this alloy typical $Mo_2C$ carbide. Martensite in HCMWI is formed during the cooling process from the austenitic phase. Martensite is very hard and provides the material with high tensile strength. Bainite is a microconstituent in HCMWI that forms due to the addition of molybdenum in the alloy, but at lower cooling rates than martensite and provides the material with improved toughness and ductility and for the sake of high alloy performances; this technological parameter is of high importance.

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