Microstructural Investigation on Heat Treatment of Hypoeutectic High Chromium White Cast Irons

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Abstract: High chromium white cast irons (HCWCI) are widely used as abrasion resistant materials in cement manufacturing, mineral processing and slurry pumping industries. Their high resistance to wear in these demanding situations stems from the presence of hard eutectic (Cr,Fe)7C3 carbides in their microstructures. In this context, the properties of hypoeutectic iron of HCWCI containing 25 wt. %Cr-2.5 wt. %C were investigated after destabilisation heat treatments, cooling (slow and fast cooling) to ambient temperatures, their influence on the microstructure was investigated. For characterization of the hypoeutectic iron of HCWCI, several experimental tests were performed using the following laboratory equipment: light optical microscope, scanning electron microscope. The amount of retained austenite also depends on the alloying additions in the melt during melting processes, destabilisation temperatures, soaking time and the cooling rates during heat treatment processes.

1. Introduction

High chromium white cast irons (HCWCI) are known as abrasion resistant cast irons and represent one of the most complex microcomposite systems among engineering materials available to wear-resistance applications. Their range of mechanical properties and wear properties provide a broad scope of options in meeting the challenges of a particular environment [1], [2], [3]. The invention of HCWCI was considered a breakthrough [4]. HCWCI are well known ferrous based alloys containing between 11 - 30%Cr and 1.8 - 3.6%C. Some other elements, such as Mo, Mn, Cu, Ni, etc. may be added as alloying elements to improve hardenability [5], [6], [7], [8].

The mechanical properties and wear resistance of these irons depend on the type, hardness, morphology, distribution, volume fraction and orientation of the eutectic and precipitated carbides within their microstructures, and on the nature of the matrix supporting these hard and brittle carbides [9]. High chromium irons are an important class of wear resistance materials currently used in a variety of applications where stability in an aggressive environment is a principal requirement, including the mining and mineral processing, cement production, slurry pumping and pulp, and paper industries [10], [11], [12], [13].

HCWCI can fill in the gap between the low toughness and/or good abrasion-resistance Ni-Hard and the higher toughness and/or lower abrasion resistance high manganese steels [14], [15], [16], [17]. The abrasion resistance of HCWCI is 20 - 25 times better than low carbon steels when the abrasion particles, such as quartz and garnet
particles are softer than the carbides. In wear applications that do not involve corrosion, for example, roller and tables in coal pulverizing or in dry ball mills, the most popular alloys are based on chromium levels of 18 - 22% Cr. In wet wear applications where combined abrasion and corrosion resistance are needed, for example slurry pumping in extraction processes, grades containing 25 - 30% Cr are preferred. The high chromium irons containing 30 - 40% Cr with lower levels of 1.5 - 2.4% C have ferritic matrix structures [10], [11].

These three classes of high chromium irons have similar crystallization rules and structures. The as-cast structure contains large amounts of chromium-rich carbides [(Cr,Fe)-C\textsubscript{3} /or M\textsubscript{7}C\textsubscript{3}, where M is a metal, such Cr or Fe] that makes irons very hard and brittle, and difficult to machine [18], [19]. Compared with hypoeutectic alloys, hypereutectic alloys have more carbide volume fractions (CVF) of hard and wear-resistant (Cr,Fe)-C\textsubscript{3} carbides, and are often the preferred alloys for many hardfacing applications. However, hypereutectic alloys are generally not favoured for casting technique, due to high scrap and rejection rates which are mainly caused by coarser and larger primary (Cr,Fe)-C\textsubscript{3} carbides [20], [11].

The metastable Fe-Cr-C liquidus surface is shown FIGURE . In FIGURE , line U\textsubscript{1} - U\textsubscript{2} indicates a eutectic valley, i.e. eutectic region. The left side in FIGURE indicates a γ-Fe or δ-Fe phase fields and is a hypoeutectic region, while the right side indicates hypereutectic region consisting of M\textsubscript{7}C\textsubscript{3} or M\textsubscript{3}C phase field [20], [19], [21].

The carbide types known to be present in the Fe-Cr-C alloys are M\textsubscript{3}C, M\textsubscript{7}C\textsubscript{3}, M\textsubscript{23}C\textsubscript{6} and M\textsubscript{6}C, with increasing M/C ratio. Some researchers showed that the excellent abrasive wear resistance of the Fe-Cr-C alloy was gained when the high volume fraction of M\textsubscript{7}C\textsubscript{3} carbides in the austenitic microstructure was achieved [21], [10]. Such microstructures can be observed in hypoeutectic, eutectic, and hypereutectic compositions with the ratio Cr/C = 5 – 8 [21], [12]. The type and morphology of the eutectic carbides in high chromium irons depends upon both chemical composition and solidification rate [21], [11].

Tempering heat treatment after destabilisation is highly recommended. Tempering in the range between 450 - 650°C for 4 hours is to reduce the amount of the retained austenite in the matrix and the residual stress after quenching. [11]. Castings can be put into service in the hardened (as cooled) condition without further tempering or subcritical heat treatments. However, tempering in the range of 200 - 230°C for 2 - 4 hours is recommended to restore some toughness in the martensitic matrix and to further relieve residual stresses [21].

This paper is aimed at the study of the effect of different heat treatment processes on the matrix structures, and carbides of hypoeutectic HCWCI by the means of light optical microscope, scanning electron microscope.

2. Experiment
2.1. Preparation of test Specimens
The charge materials for the test specimens were melted and heated up to 1500°C using a high frequency industrial induction furnace. Each melt was poured from 1380 - 1390°C into a special chemical bonded sand moulds as shown in Figure 1 [23].
The as-cast and heat-treated samples were randomly sectioned, and were further reduced to smaller sizes using an Electric Discharge Machine (EDM) machine. The composition of the molten metal prior to pouring was performed using chill-cast moulds after the melt was fully liquid and are given in Table.1. A specimen from each heat in as-cast condition and heat-treated samples were examined.

2.2. Heat treatment processes
Programmable electrical resistance heat treatment furnace was used for different heat treatments of the experimental irons.

2.3. Sample chemical composition
Casting coupons were grounded flat with 60 grit grinding paper. The optical emission spectrometer “Specromaxx spectrometer” were standardized and calibrated, and analysis of actual casting coupons performed. Averages of three readings were taken for each result.

2.4. Microstructure measurement
Casting coupons were mounted in an epoxy resin and were metallographically prepared to 1µm finish. The as-polished samples were etched with Beraha’s reagent to reveal the microstructures. Eutectic and other carbides (primary and or secondary) were selective etched with Murakami (which colours the eutectic M₇C₃ carbides) and Groesbeck reagents (which revealed the secondary carbides, especially Cr₇Fe₆C₃).

Table 1. Chemical composition of specimens

| Elements | As-Cast | A   | B   | C   |
|----------|---------|-----|-----|-----|
| %C       | 2.5     | 2.69| 2.64| 2.64|
| %Si      | 0.6     | 0.47| 0.46| 0.46|
| %Mn      | 0.68    | 0.78| 0.76| 0.76|
| %Cr      | 24.09   | 23.02| 23.43| 23.43|
| %Fe      | bal.    | bal.| bal.| bal. |
Table 2. The heat treatment schedule

| C.I.D. | H.T.S | H.T.P       |
|--------|-------|-------------|
| A      | 950°C x (28.8Ks) + 680°C x (36Ks) | Annealed   |
| B      | 950°C x (28.8Ks) + 680°C x (36Ks) + 1020°C x (12Ks) + 700°C x (54Ks) | Hardened and first temper |
| C      | 950°C x (28.8Ks) + 680°C x (36Ks) + 1020°C x (12Ks) + 700°C x (54Ks) + 250°C x (35.1Ks) | Second Tempered |

C. I.D., casting identity, H.T.S., heat treatment schedule and H.T. P., heat treatment process

Microstructures were examined with an optical Olympus System Microscope (OSM BX51) and a Zeiss EVO® MA15 SEM. The OSM BX51 is equipped with Image Analyser. Micrographs were taken at 10, 20 and 50X magnifications. Volume fraction of the carbides was determined using point counting from the optical micrographs. An average of five readings was reported.

The Zeiss EVO® MA15 SEM equipped with a Bruker energy dispersive X-ray (EDS) spectrometer. The images were captured at 10 and 2µm magnifications in backscattered electron mode and EDS were used to map elemental compositions.

3. Results and discussion

3.1. Chemical composition analysis

Solidification begun with the formation of austenite dendrites and as the remaining liquid reaches the eutectic composition. It forms a mixture of austenite/carbide within the interdendritic regions, the eutectic carbides develop and grow in the preferred crystallographic direction [1], [7].

3.2. Microstructure analysis

3.2.1. As-cast conditions

Hypoeutectic iron solidify as primary austenite dendrites followed by a eutectic of austenite and (Cr,Fe)$_7$C$_3$ carbides. On subsequent cooling, austenite may be largely retained or may full or partially transform to ferrite plus carbides, e.g. pearlite, and/or martensite [25], [26]. In the as-cast alloy, primary austenite is considered thermodynamically unstable because of its supersaturation by carbon and alloying elements, i.e. chromium. Thus, austenite is prone to carbides precipitation that may change its stability to phase transformation [27].

Microstructures of hypoeutectic iron in as-cast conditions are shown in Figure 2. The iron consists of large austenite dendrites as shown in Figure 3 (a) along with a eutectic mixture of (Cr,Fe)$_7$C$_3$ carbide/austenite [21], [25].

In addition, the structure shows a dark-brown martensitic layer surrounding the eutectic (Cr,Fe)$_7$C$_3$ carbides (outlined in Figure 3 (a)). Murakami and Groesbeck reagents colour eutectic (Cr,Fe)$_7$C$_3$ and reveal secondary (Cr,Fe)$_{23}C_6$ carbides as shown in Figure 3 (b) and (c), respectively. The identified phases in as-cast conditions of hypoeutectic iron agreed with the predicted phases by the Fe-rich corner of the Fe-Cr-Cr phase diagram [26], [25].
3.2.2. Fully annealed

During destabilisation treatment, precipitation of secondary \((\text{Cr,Fe})_2\text{C}_6\) carbides took place. The number and size of secondary carbides are a function of temperature, soaking time and chemical composition. Eutectic \((\text{Cr,Fe})_7\text{C}_3\) carbides are generally unaffected by the destabilisation heat treatment [26], [25], [28]. It contains sufficient concentration of carbon and chromium to allow transformation of austenite to either martensite/or pearlite [25], [24]. As a rule, high chromium cast irons are subjected to destabilizing heat treatment to increase wear performance or improve the machinability [21], [29].

During destabilizing heat treatment, primary austenite decomposes with the subsequent precipitation of secondary carbides. Due to austenite phase depletion of carbon and chromium, and subsequent precipitation of secondary carbides within the ferrous matrix. The Mₜ-temperature is raised, affecting the appearance of either martensite and/or pearlite in matrix [11] [28] [30], [31]. Full annealing has caused significant modifications to the microstructure of as-cast alloy as shown in Figure 3.

Microstructures of fully annealed alloy consists of large ferritic grains, eutectic carbide islands and pearlitic matrix. The large ferritic grains could also compromise the mechanical properties especially hardness since it is directly proportional to the tensile strength. A closer examination of the ferritic grains reveals a massive precipitation of secondary carbides, which have been formed either during 950°C or during 680°C [21], [19], [22].

Fully annealed specimen shows that destabilisation at 950°C (28.8Ks) and 680°C (36Ks) changed the as-cast austenite matrix to full pearlite matrix as shown in Figure 4. In addition, fully annealed micrograph also showed unchanged eutectic carbides (white in colour), while pearlite matrix is dark-brown and greyish in colour as shown in Figure 4 (a). Small white precipitates within the pearlite matrix are secondary carbides.
3.2.3. Hardened and temper at higher temperatures

Microstructures of hardened and tempered at high temperatures are shown in Figure 5. It is observed that hypoeutectic iron obtained a microstructure containing a eutectic \((\text{Cr,Fe})_7\text{C}_3\) carbides (white in colour) embedded in tempered martensitic matrix (dark in colour). Fine secondary \((\text{Cr,Fe})_{23}\text{C}_6\) carbides are uniform in size and homogeneously distributed within the matrix. Secondary carbides are localized in the austenitic grains, where netted eutectic carbides are essentially unchanged after the heat treatment [21], [31], [20].

3.2.4. Temper at low temperatures

Tempering at lower temperature micrographs are shown in Figure 6. There were no significant microstructural changes observed. The only noticeable effect is the greater uniformity in the etching response, especially with Beraha’s reagent.

Red and maroon sections as shown in Figure 7 in the corresponding micrographs shows a ferrous matrix in as-cast and eutectic \((\text{Cr,Fe})_7\text{C}_3\) carbides in heat treated casting specimens. The limitation of the image analysis is the ability to get good contrast and the ease of not detecting some of the minute phases that could be contributing to mechanical properties, hence the need for the empirical equation to verify the measured CVF.
For instance, secondary \((\text{Cr,Fe})_2\text{C}_6\) carbides precipitates are very small and difficult to colour entirely during image analysis. While, using Equation 1 gives total estimated carbides contents of eutectic \((\text{Cr,Fe})_7\text{C}_3\) and secondary \((\text{Cr,Fe})_2\text{C}_6\) carbides of high chromium irons. Thus, CVF using Equation 1 will give accurate results compared to image analysis and will be the best tool to measure the total volume fraction of carbides in high chromium cast irons.

![FIGURE 6. Tempered at lower temper micrographs](image)

![FIGURE 7. Image analysis at different casting conditions micrographs](image)

![FIGURE 8. CVF from image analysis and CVF using CVF empirical formula from actual chemical analysis](image)
3.3. Scanning electron microscope analysis

3.3.1. As-cast conditions

Figure 9 shows scanning electron microscopy (SEM) micrographs of hypoeutectic iron in as-cast condition at different magnifications. In the scanning electron micrographs, it can be seen that the eutectic (Cr,Fe)_7C_3 carbides are surrounded by a narrow region in which austenite has transformed to martensite at higher magnification, i.e. 2µm. The martensite layer is dark-brown in colour when detected by light optical microscope as shown in Figure 9 (a). The major morphological features at higher magnification are shown in Figure 9 (b). Thus, large eutectic carbides islands are surrounded by the martensite layer [25].

3.3.2. Fully annealed

Figure 10 shows the prolonged duration of fully annealed alloy, dramatically alters the as-cast matrix observed in Figure 9. Figure 10 shows that the microstructure of the as-cast matrix has been extensively replaced by new phases, i.e. pearlitic matrix. Eutectic (Cr,Fe)_7C_3 carbides islands and secondary (Cr,Fe)_{23}C_6 carbides precipitates are detected. Secondary carbides are within the pearlitic matrix and clearly visible at higher magnification.

3.3.3. Hardened and tempered at higher temperatures

Figure 11 shows the micrographs of hardened and tempered at higher temperatures of the iron. The pearlitic matrix has been altered by quenching and temper at higher temperatures to tempered martensite matrix. The micrographs in Figure 11 consist of eutectic (Cr,Fe)_7C_3 carbides islands, secondary (Cr,Fe)_{23}C_6 carbides precipitates within tempered martensite. While, retained austenite was detected in lower and higher magnification.

3.3.4. Tempered at lower temperatures

Micrographs of iron tempered at lower temperatures are shown in FIGURE 12. The micrographs are similar to those in FIGURE 1. Martensitic matrix with small quantities of retained austenite was detected at both lower and higher magnifications. Eutectic (Cr,Fe)_7C_3 carbides islands were detected in both lower and higher magnification, while secondary (Cr,Fe)_{23}C_6 carbides precipitates (within martensite matrix) were clearly detected at higher magnification.
4. Conclusion
Microstructure predominately shows eutectic \((\text{Cr,Fe})_7\text{C}_3\) and secondary \((\text{Cr,Fe})_{23}\text{C}_6\) carbides in as-cast and in heat treated 25\%Cr-2.5\%C irons of hypoeutectic composition of HCWCI. Machinability of 25\%Cr-2.5\%C iron can be improved by destabilisation temperature at 950\°C (28.8Ks) and pearlitized at 680\°C (36Ks), and for both processes furnace cooling is performed.

Destabilisation temperature at 1020\°C (12Ks) and FAC, and temper at higher temperatures 700\°C (54Ks) increased the macrohardness of 25\%Cr-2.5\%C iron from the as-cast condition of about 539 up to about 726HV (30kgf/15s).

During full annealing and hardening heat treatment processes, the ferrous matrix is altered onto pearlitic and/or martensitic matrix with small amounts of retained austenite depending on the cooling rate of the hypoeutectic iron of HCWCI alloy.

Tempering at lower temperatures, i.e. at 250\°C (35.1Ks), relieves residual stress by decreasing macrohardness of about 707 from 726HV (30kgf/15s). Hardness measurements showed that higher retained austenite gives lower hardness, whereas higher martensite with and lower retained austenite gives higher hardness. Higher amounts of pearlite are detrimental to hardness.

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