XRD Investigation on Heat Treatment of High Chrome White Cast Irons

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Abstract: 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 structure and hardness was investigated using X-ray diffraction (XRD), element distribution analysis and hardness tests. The experimental results show that appropriate heat treatments contribute to a significant improvement on the mechanical properties of selected alloy of HCWCI. The results are discussed in terms of the change in austenite phase at the different destabilisation heat treatment temperatures.

Keywords: white cast irons, high chrome white cast irons, heat treatment, XRD investigation

1. Introduction

The abrasive wear of materials is of technical and economic importance. It has recognised as one of the potential serious problems facing the operators of many types of plants and machinery. Several industrial surveys have indicated that wear by abrasion can be responsible for more than 50% of unscheduled stoppages [1]. In view of this, newer materials that may adequately function in wear prone environments have been developed [2]. In the course of the development of wear-abrasion resistant materials, a better combination of toughness and hardness is a concerned problem all the times [1].

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 [3] [1]. The invention of HCWCI was considered a breakthrough [4], [5]. HCWCI are well known ferrous based alloys containing between 11 - 30%Cr and 1.8 - 3.6%C (all concentrations are given in wt. %). Some other elements, such as Mo, Mn, Cu, Ni, etc. may be added as alloying elements to improve hardenability [6], [7].

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)7C3 or M7C3, where M is a metal, such Cr or Fe] that makes irons very hard and brittle, and difficult to machine [8], [9], [10]. Compared with hypoeutectic alloys, hypereutectic alloys have more carbide volume fractions (CVF) of hard and wear-resistant (Cr,Fe)7C3 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)7C3 carbides [11], [12].

There is an optimum austenitizing temperature to achieve maximum hardness, which varies for each composition. The austenitizing temperature determines the amount of carbon that remains in...
solution in the austenite matrix as shown in references [13], [14], [15]. Higher temperature increases the stability of austenite, and the higher retained austenite content reduces hardness. Lower temperatures result in low-carbon martensite reducing both hardness and abrasion resistance [13].

The holding period is called “destabilisation”, since it allows carbon and chromium in the austenite matrix to come out of solution as precipitates of secondary carbide. This lowers the alloy content of the austenite and raising the M_S-temperature. Thus, it enables the austenite to transform to martensite on forced air-cooling (FAC) [1], [16]. The resultant microstructure consists of eutectic M_7C_3 carbides and secondary carbides within a martensitic matrix together with some retained austenite [17].

Wang [18] examined destabilisation response of a 16%Cr-1%Mo-1%Cu cast iron. They observed two types of M_23C_6 carbides: one of cubic morphology with a specific to the matrix orientation and one of grainy morphology with no specific to the matrix orientation. The latter was mainly formed during the cooling stage of the destabilisation treatment. They also noticed a gradual transformation of M_23C_6 to M_7C_3 rods after prolonged destabilisation [19]. During the conventional destabilisation heat treatments of 10 - 25%Cr high chromium irons, the eutectic M_7C_3 carbides remain unaffected and no change in morphology occurs. Some researchers also agree that the austenitizing temperature hardly affects the carbide morphology. However, a large effect is found on the shape and size of the secondary carbides formed, and on the relative fractions of austenite and martensite [20] [21].

This paper is aimed at the study of the effect of different heat treatment processes on the matrix structures, secondary carbides and hardenability behaviour of hypoeutectic HCWCI by the means of X-ray diffraction (XRD) and hardness analysis.

2. Experimental procedure

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[22].

![Figure 1. Ametex casting design nett and gross weight casting](image)

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 using chill-cast moulds were given in Table 1. Chemical composition of specimens Specimen from each heat in as-cast condition and heat-treated samples was examined [5].

Programmable electrical resistance heat treatment furnace was used for different heat treatments of the experimental irons. The shows the heat treatment schedules, i.e. fully annealed, hardened and double tempered, respectively.

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.
2.2. **Hardness Measurement**

Hardness of casting coupons was measured at room temperature using Brinell and Vickers testing device. Loads of 750kg for Brinell and 30kg for Vickers were used. Ten and five random measurements for Vickers and Brinell were performed, respectively.

2.3. **X-ray Diffraction Measurement**

XRD analysis was performed on a Bruker D8 Advance X-ray diffractometer, using a Co X-ray source. The scans were done from 40 - 100° 2-theta in Bragg-Brentano (theta-2theta) geometry with a step size of 0.2° 2-theta. The Rietveld refinement was done in Topas, using data from the ICSD database.

| 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 1.** Chemical composition of specimens

| 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 Temper |

**Table 2.** The heat treatment schedule

3. **Results and discussion**

3.1 **Chemical Composition Analysis**

The properties of HCWCI are critically dependent on their composition, such as carbon, chromium and alloying element contents. Amounts of carbon and chromium contents suggest hypoeutectic iron of HCWCI alloy [23], [20]. 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.

3.2. **X-ray Diffraction Analysis**

3.2.1. **As-cast conditions**

The XRD pattern of as-cast hypoeutectic iron is shown in **Figure 2**. The crystalline phases were retained austenite, martensite, eutectic (Cr,Fe)\(_2\)C\(_3\) and secondary (Cr,Fe)\(_2\)C\(_6\) carbide. Austenite peaks (53.19%) in as-cast alloy are the highest compared to other iron specimens, i.e. heat-treated specimens. Peaks of austenite and eutectic (Cr,Fe)\(_2\)C\(_3\) carbides are present in all casting specimens. This is due to the hypoeutectic iron solidification path [21].

XRD examination, as shown in, verifies the limited, yet not negligible, presence of martensite phase (19.85%). Eutectic (Cr,Fe)\(_2\)C\(_3\) and secondary (Cr,Fe)\(_2\)C\(_6\) carbides, as measured by XRD are about 19.74 and 7.22%, respectively.
3.2.2. Fully annealed

Further examination with XRD as shown in Figure 2 identified the ferritic phase but did not clarify the stoichiometry of the carbide phases. Since, it is difficult to distinguish between phases, such as (Cr,Fe)\(_3\)C, (Cr,Fe)\(_6\)C, (Cr,Fe)\(_{23}\)C\(_6\), etc., due to extensive peaks overlapping. It should also be mentioned that the possibility of martensite and/or austenite presence must not be excluded for the same identification weaknesses [23].

Figure 3. shows XRD spectrum of fully annealed casting specimen. Pearlitic phase (\(\alpha\)-Fe) (84.04\%) shows higher peak compared to other phases in the structure. The XRD spectrum for retained austenite and eutectic (Cr,Fe)\(_7\)C\(_3\) was measured as 0.08 and 15.88\%, respectively. Secondary (Cr,Fe)\(_{23}\)C\(_6\) carbides were not detected in the structure by the XRD spectrum.

3.2.3. Hardened and tempered at higher temperature

Figure 4 shows XRD spectrum for harden and tempered at higher temperature iron. Martensite phase (\(\alpha\)-Fe) has increased in concentration to 64.09\% showing higher peaks compared to other phases present in the structure. While, retained austenite was measured at lower concentration (5.23\%). By calculation based on XRD, the percentages of eutectic (Cr,Fe)\(_7\)C\(_3\) and secondary (Cr,Fe)\(_{23}\)C\(_6\) carbides are 15.62 and 15.06\%, respectively. The XRD analysis is in agreement with phases detected by light optical microscopy, since it is discussed that pearlitic will transform to tempered martensite after hardened and temper at higher temperatures.
3.2.4. Tempered at lower temperatures
XRD spectrum of iron tempered at lower temperatures is shown in Figure 5. It shows that austenite peaks (0.42%) are the lowest peaks compared to other alloys. This was due to destabilisation treatment and double tempering that was performed in irons. The destabilisation and double tempering resulted in austenitic matrix transforming into martensite matrix that was double tempered.

3.3 Element Distribution Analysis

3.3.1. As-cast conditions
Figure 6 shows Chemical mapping of As-cast micrographs. It illustrates the alloying element distribution in the iron. It shows a secondary electron image of the typical as-cast iron microstructure, i.e. an austenitic matrix and the eutectic (Cr,Fe)iC3 carbides.
The carbon and chromium distribution is shown in blue and red in colour, respectively within the iron. It can be observed that carbon and chromium are mainly combined forming the carbide phases but are also detected in lesser amounts within the ferrous matrix. On the contrary, iron as shown in in green in colour is found primarily in the ferrous matrix and in lesser amounts in the eutectic (Cr,Fe)-C₃ carbides. Agunsoye, 2012 [1] found that the partition of carbon and chromium in austenite is smaller than in chromium-rich carbides. Thus, carbon and chromium will be expelled into the surrounding area during the formation of austenite.

The smaller quantities of carbon and chromium distribution within the ferrous matrix confirms the presence of secondary (Cr,Fe)₂₃C₆ carbides in the as-cast structure. Micrographs in as-cast conditions as shown in Figure 9.

3.3.2. Fully annealed
Figure 7 shows a secondary electron image of a fully annealed iron microstructure, i.e. a pearlitic matrix, eutectic (Cr,Fe)₇C₃ and secondary (Cr,Fe)₂₃C₆ carbides precipitate. Iron distribution is primarily within ferrous matrix. While, carbon and chromium distribution shows an improvement (improved contrast) in concentration in the ferrous matrix compared to as-cast structures. Precipitation of secondary carbides during destabilisation and pearlitizing treatment resulted in an improvement in carbon and chromium distribution within the ferrous matrix. Thus, it indicates that in as-cast structure the volume of secondary (Cr,Fe)₂₃C₆ carbides is minimal compared to fully annealed alloys and confirming the precipitation of secondary within ferrous matrix.

3.3.3. Hardened and tempered at higher temperatures
Figure 9 shows secondary electron image of hardened and tempered iron at higher temperatures. They consist of tempered martensite, eutectic (Cr,Fe)₇C₃ and secondary (Cr,Fe)₂₃C₆ carbides, with small amounts of retained austenite detected by XRD. Secondary carbides are within the tempered martensitic matrix.

Carbon and chromium distribution shows higher concentration compared to as-cast and fully annealed alloys. Thus, precipitation of secondary carbides in higher quantities was induced by higher tempering temperatures and prolonged soaking time. Iron distribution is primarily within ferrous matrix as shown in the previous element distribution micrographs in as-cast and fully annealed casting specimen.

3.3.4. Tempered at lower temperatures
Figure 9 shows scanning electron micrographs of tempered iron at lower temperature. The micrograph is similar to harden and tempered at higher temperatures. The microstructure consists of tempered martensite, eutectic (Cr,Fe)₇C₃ and secondary (Cr,Fe)₂₃C₆ carbides, with small amounts of retained austenite detected by XRD. Secondary carbides are within the tempered martensitic matrix.

Carbon and chromium distributions are primarily within eutectic carbides and at ferrous matrix. In the ferrous matrix, compared to other casting specimens, it showed higher contrast, which confirms the uniform distribution, which was due to temper at lower temperatures and no transformation is expected at these temperatures. Iron distribution is primarily within ferrous matrix as explained previously.
3.4. Hardness Measurement

Figure 10 shows bulk hardness measurements of hypoeutectic irons in as-cast and heat-treated conditions. The major effects on hardness were the differences in destabilization temperatures, soaking time and cooling rates of the experimental alloys. A decrease in hardness of fully annealed specimen from 539HV to 325 HV of as-cast samples was due to austenite transformation to pearlite. Pearlite in high chromium cast iron improves machinability but adversely affect hardness and strength [24].

In contrast, an increase was observed from fully annealed casting specimen to harden and temper at higher temperatures, i.e. from 325HV to 726HV, respectively. The increased in hardness was due to austenite matrix transforming to martensitic matrix and an increase in volume fraction of carbides induced by secondary (Cr,Fe)\textsubscript{23}C\textsubscript{6} carbide precipitates within tempered martensitic matrix.

Tempering at lower temperatures resulted in similar microstructure to harden and temper at higher temperatures. The hardness measurement decreases slightly from 726HV to 707HV. This was due to stress relieve after destabilisation temperatures and tempering at higher temperatures as reported previously [24].

The change in hardness induced by various heat treatment processes is complicated because many factors are involved, such as the volume fraction of secondary carbide, their distribution and sizes, the different properties of martensite formed, and the amount of the retained austenite at a particular temperature. The precipitation of the secondary carbides is a hardening effect for the dendritic regions [25].
It is noticeable that, besides high chromium white cast iron, high manganese steel is another alloy widely used in crushing and grinding processes [26], [27], where the mechanical components are under severe conditions of combined high abrasion and impact [28].

4. Conclusion

- Microstructure predominately shows eutectic (Cr,Fe)\textsubscript{7}C\textsubscript{3} and secondary (Cr,Fe)\textsubscript{23}C\textsubscript{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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