A Microstructural Study of Destabilised 30wt%Cr–2.3wt%C High Chromium Cast Iron

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An as-cast 30wt%Cr–2.3wt%C cast iron was destabilised in the temperature range of 900–1 100°C for times of 2–8 h, followed by air cooling to room temperature. The resultant microstructures were examined using light microscopy (LM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Volume fractions of secondary carbide within the martensite matrix and of M23C6 in eutectic carbides were determined. Vickers microhardness and Vickers microhardness of the dendritic regions were also measured. It was found that morphologies of secondary carbide were cube, plate-like shape or discrete-rod. A duplex core-shell structure was found in the eutectic carbides after destabilisation. It consists of M7C3 as a core surrounding by M23C6, while the secondary carbide in these alloys was identified as M23C6. Higher destabilisation temperatures resulted in coarser secondary carbides with comparable volume fraction, but less in counts per area. The volume fraction of M23C6 within the duplex structure was also increased when increasing destabilisation temperature and time. The results from hardness measurements revealed that the overall macrohardness of the iron was increased with increasing the destabilisation temperature up to about 770 HV (30 kgf/15 s) at 1 025°C, whereas the microhardness of the dendritic regions reached the maximum value of 800 HV (100 gf/15 s) at about 1 025°C.

KEY WORDS: high chromium cast iron; destabilisation; microstructure.

1. Introduction

High chromium cast irons are widely used as abrasion resistant materials in cement manufacturing, mineral processing and slurry pumping.1–11) Their high resistance to wear in these demanding situations stems from the presence of hard eutectic M7C3 carbides in their microstructures. Most commercial alloys are based on hypo-eutectic compositions containing between 12 and 30 wt% Cr and from 1–3 wt% C plus additions of other elements such as Mo, Ni and Cu to improve hardenability. The most popular alloys, providing cost-effective solutions to wear problems in many applications, are based on Cr levels of 18–22 wt%. Lower Cr irons containing around 12 wt% Cr have lower initial costs but can only be used for less severe wear situations such as small grinding media. The 25–30 wt% Cr alloys have been developed to provide resistance to the combined effects of abrasion and corrosion in wet grinding and in slurry transport. For all Cr irons, wear resistance, and mechanical properties in general, depend on the type, morphology and distribution of carbides, and on nature of the matrix structure.4–9)

The as-cast microstructure of the 25–30% Cr irons consists of primary austenite dendrites, eutectic austenite (partially transformed to martensite) and interdendritic eutectic M(C) carbide.9) The as cast irons posses useful resistance to abrasion under conditions which allow austenite to work harden10) but have limited fracture toughness. Improved service performance can be obtained by heat treatments and additional alloying to provide harder, more wear resistant martensitic matrix structures or to obtain austenitic matrices with improved crack propagation resistance.2,4–6–8)

Conventional heat treatment involves heating castings to and holding at 950–1 050°C, followed by air cooling and tempering. 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.9,11–12) This lowers the alloy content of the austenite, raising the MS temperature and thus enables the austenite to transform to martensite on forced air-cooling. The resultant microstructure consists of eutectic carbide (M7C3) and secondary carbides within a martensite matrix together with some retained austenite. Single, or sometimes double, tempering treatments are then used to temper the martensite and to reduce the amount of the residual austenite.12)

The nature of secondary carbide formation has been the subject of several studies.1,11–12) It has been shown that the secondary carbides do not nucleate and grow on the eutectic carbides but form separately within the original dendritic regions.11–13) The secondary carbides in 15–20% Cr irons have been identified as M7C3 and as M23C6 in 25–30% Cr irons.4,13–15) Destabilisation treatments do not appear to have any significant effects on the form of the eutectic carbides in irons containing up to about 28% Cr. However at

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the 30% Cr level destabilisation treatments do affect the eutectic M7C3 carbide, causing it to partially transform to M23C6 carbide. Under TEM examination this M23C6 carbide can be recognised as shells surrounding the M7C3 cores. Unlike the highly faulted M7C3, the M23C6 is free from stacking faults but does contain dislocation networks and grain boundaries.13,16,18) This structural change in the eutectic carbides could be part of the reason for an observed lack of improvement in high stress abrasion resistance of 30% Cr iron after a conventional hardening heat treatment in which the micro-hardness of the dendritic regions was increased to 800 HV compared to 500 in the as-cast condition, but the wear abrasion resistance did not improve.2) Although some TEM characterisation of 30% Cr irons had been performed during previous work,3,13,18) no attention was given to the effects of heat treatment variables on the M7C3 to M23C6 transition in the eutectic carbides. Hence the objective of the present work is to study how variations in destabilisation temperatures and times can influence this transformation and other microstructural aspects of a 30% Cr cast iron.

2. Materials and Methods

2.1. Materials Preparation and Heat Treatment

A 30wt%Cr–2.3wt%C high chromium cast iron was prepared by melting a charge based on low Si pig iron and ferroalloys in an induction furnace. The molten iron was cast at a pouring temperature of 1500°C into a CO2 silicate sand mould as cylindrical bars with a diameter of 2.50 cm. The chemical composition of the as-cast alloy is shown in Table 1. The bars were then sectioned as specimens with a thickness of about 1.50 cm. These as-cast specimens were heat treated (destabilised) in a muffle furnace at the temperature range of 900–1100°C for times of 2–8 h, followed by cooling to room temperature in still air. A controlled atmosphere was not used.

2.2. Sample Preparation for Microstructural Investigation

Specimens for light microscopy (LM) and scanning electron microscopy (SEM) were ground on silicon carbide papers down to 1000 grits and then polished with 6, 3 and 1 μm diamond paste. The etchants used were (i) Mura-kami’s reagent, containing 10 g potassium ferricyanide and 10 g potassium hydroxide in 100 mL distilled water and (ii) 4 g potassium permanganate and 4 g sodium hydroxide in 100 mL distilled water. The microstructure was studied using an Olympus BX60M optical microscope and a JSM-5410LV scanning electron microscope equipped with secondary and back-scattered electron detectors. The scanning electron microscope was operated at 20 kV and a working distance of 14 mm from the objective lens pole piece. Thin foils for transmission electron microscopy (TEM) were prepared by sectioning heat treated specimens, perpendicular to the axis of the as-cast cylindrical rod, by a CBN saw to obtain thin slices with thickness of about 200 μm. Both sides of the slices were then ground manually on silicon carbide papers down to 1200 grits to reduce the thickness to about 80–100 μm. 3 mm discs were punched out and then thinning by a Struer, Tenupol-3 twin-jet electropolisher operated at 20–26 V, 22°C and approximately 0.1 A, using 10 vol% perchloric acid in acetic acid as an electrolyte. Thin foils were examined by a JEOL JEM-1200EXII transmission electron microscope operating at 100 kV. Figure 1 schematically illustrates the sample preparation procedure for LM, SEM and TEM.

2.3. Quantitative Metallography

The volume fraction of the secondary carbide within the matrix was determined by point counting choosing only

Table 1. Chemical composition of the high chromium cast iron.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Cr</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
<th>Ni</th>
<th>Cu</th>
<th>Mo</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>(wt%)</td>
<td>2.26</td>
<td>29.98</td>
<td>0.52</td>
<td>0.30</td>
<td>0.013</td>
<td>0.025</td>
<td>0.30</td>
<td>0.02</td>
<td>0.08</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Fig. 1. Sample preparation procedure for LM, SEM and TEM.
those particles which were greater than 0.2 μm. To obtain this information, an intercept plan was superimposed on the enlarged SEM micrographs. The spacing distance of the plan is equivalent to 0.3 μm. The mean value is based on ten different areas.

The distribution of the secondary carbide was compared by measuring counts per area (Cs/100 μm²) of secondary carbide particles. The area was calculated from the micron bar on SEM micrographs. Only the particles which are greater than 0.1 μm were counted. The mean value is based on ten different areas.

The mean value of the volume fraction of M23C6 in duplex structure of eutectic carbides was also determined from SEM micrographs using the same procedure.

2.4. Hardness Measurement

The specimens prepared for LM and SEM were also used for the hardness measurements. Vickers microhardness of the dendritic regions was measured on etched specimens using 100 gf load and 15 s indenting time. The mean values are based on twelve different indentations. A Galileo microhardness tester was utilised in this experiment. Vickers macrohardness testing was performed on non-etched specimens using 30 kgf load and 15 s indenting time. The mean value are based on sixteen different indentations. A Brooks hardness tester was used in this experiment.

3. Results and Discussion

3.1. General Observation on Microstructure

The microstructure in the as-cast condition consists of primary austenite (γ) dendrites with a eutectic structure (eutectic austenite partially transformed to martensite and eutectic M7C3 carbide) as shown in Fig. 2. After destabilisation heat treatment, as shown in Fig. 3, the microstructure of the iron consists of precipitated secondary carbides within a martensite matrix and possibly some retained austenite, together with eutectic M7C3 carbide partially transformed to M23C6.

The morphologies of secondary carbides illustrated in Fig. 4 are cube, discrete-rod or plate-like shapes. The secondary carbide particles in the region close to the eutectic carbides are apparently smaller than in the region far away from the eutectic carbides. This precipitation characteristic can be attributed to the segregation of carbon and chromium to the outer regions of the dendrites as they grew during solidification.15,19) Higher destabilisation temperatures resulted in coarser particles as seen in Fig. 5.

After destabilisation, a duplex structure was found in the eutectic carbides. It is thought that a thermodynamically more stable M23C6 replaced the metastable M7C3 carbide during destabilisation heat treatment.18) Therefore, the duplex carbides consist of M23C6 shells surrounding eutectic M7C3 cores as clearly seen under backscattered electron mode in Fig. 6. At a particular destabilisation time, the magnitude of transition from M7C3 to M23C6 in eutectic carbides was increased as the destabilisation temperature was increased. This can be seen in Fig. 7 where the outer regions of eutectic carbides, i.e. M23C6, were preferentially etched out by the etchant, leaving islands of eutectic M7C3 as cores. It should be noted that the etchant in this case,
which is 4 g potassium permanganate and 4 g sodium hydroxide in 100 mL distilled water, is superior than Murakami’s reagent in revealing such a duplex structure.

3.2. TEM Examination

Results from TEM examination revealed that the dendritic matrix after destabilisation is martensite \((\alpha')\). The results confirmed the duplex core-shell structure of the eutectic carbides formed after destabilisation, as shown in Fig. 8. The two carbides are clearly distinguished since faulting contrast is observed only in the M7C3. Pearce\(^9\)\(^{,}\)\(^{18}\) reported that this contrast in the hexagonal M7C3 is believed to result from the presence of stacking faults or twins.

Secondary carbides precipitated within martensite matrix are shown in Fig. 9. The corresponding selected area diffraction pattern confirms that they are M7C3, as reported previously.\(^18\) It has also been reported\(^9\)\(^{,}\)\(^{15}\) that secondary carbide does not precipitate on the eutectic carbides but formed preferentially within the dendritic matrix and this is again confirmed by the TEM investigation in this study. A doubt could then been asked why such a heterogeneous site as eutectic carbide/dendritic primary austenite interphase boundaries did not act as a preferential site for secondary M23C6 carbide. The likely explanation is two folds. Firstly, the formation of the M23C6 carbide as a shell of M7C3 carbide along the eutectic structure is perhaps a peritectoid type consuming both M7C3 and the adjacent austenite matrix. Secondly, the formation of the M23C6 may not only a result from the M7C3-M23C6 transformation alone, but also from the secondary precipitation from the adjacent austenitic matrix. After nucleation, probably on M7C3, those grains of M7C3 carbide shell should be able to grow also into the dendritic primary austenite during the destabilisation heat treatment by diffusional growth and elements \(i.e.\) Cr and C could be conveyed between the M23C6 shell and the dendritic austenite via. interphase boundary diffusion or even volume diffusion. Schematic illustration of the formation of M23C6 is given in Fig. 10. The moving interphase boundary as such is therefore not a preferential site for nucleation of a new grain of secondary M23C6 carbide. However, more
evidence is needed before any conclusion can be drawn.

3.3. Quantitative Metallography

Effects of destabilisation conditions on the volume fraction of secondary carbides were shown in Fig. 11(a). The volume fraction of secondary carbide formed after destabilisation conditions used in this experiment is in the range of about 10–20 vol%. The deviation of the volume fraction of secondary carbides at different destabilisation conditions was within the error limit. Therefore, destabilisation temperatures and times in the range used in this experiment have seemingly no significant effect on the volume fraction of the secondary carbide.

The distribution of secondary carbide was compared by measuring number per area of secondary carbides. Higher destabilisation temperatures reduced the number per area of secondary carbides. For example, the counts per 100 µm² at 900°C is about a factor of three compared to that at 1025°C. This can be attributed to the thermodynamic effect on enhancing nucleation rate at lower destabilisation temperature. The results are also in agreement with the microstructural examination shown in Fig. 5, where, at higher destabilisation temperature, coarser secondary carbide particles and their agglomerate were observed preferentially on heterogeneous sites. Even it is not clear, longer destabilisation times at the destabilisation temperature up to 950°C tend to increase the number per area of secondary carbides, as can be seen in Fig. 11(b). However, at higher destabilisation temperatures, the reverse effect is observed and this could result from coarsening or Ostwald ripening of the secondary carbide particles.

From Fig. 11(c), the volume fraction of M23C6 within the duplex structure of eutectic carbides in this experiment is in the range of 20–99 vol%. It was increased as the destabilisation temperature and time were increased and, at a longer destabilisation time, tended to reach a limited value which could possibly be close to the equilibrium value at a particular temperature.

3.4. Overall Macrohardness and Microhardness of the Dendritic Region

Figures 12(a) and 12(b) illustrate the microhardness within the dendritic regions and the overall macrohardness as a function of time and temperature of destabilisation, respectively. The hardness values of the as-cast iron are also shown. Destabilisation heat treatment of this iron increased the microhardness of the dendritic regions from about 426 up to about 800 HV (100 gf/15 s) and the overall macrohardness from about 510 up to about 770 HV (30 kgf/15 s).
This is comparable to what has been reported previously.\textsuperscript{2)} The macrohardness was increased as the destabilisation temperature increased up to 1\textdegree{}C, while the microhardness of the dendritic regions reached the maximum value at 1\textdegree{}C for 4–6 h. This behaviour is complicated because many factors get involved including volume fraction of secondary carbide, their distribution, the different properties of martensite formed, and the amount of the retained austenite at a particular temperature. Precipitation of the secondary carbide is a hardening effect for the dendritic regions.

Fig. 8. (a) A bright field TEM micrograph shows a duplex core-shell structure of eutectic carbides. The core area with a faulting contrast is M\textsubscript{7}C\textsubscript{3} surrounding by grains of M\textsubscript{23}C\textsubscript{6}. \(\alpha'\) denotes the martensite matrix. (b) and (c) are corresponding selected area diffraction patterns from M\textsubscript{7}C\textsubscript{3} and M\textsubscript{23}C\textsubscript{6} respectively (1\textdegree{}C, 4 h).

Fig. 9. (a) A bright field TEM micrograph shows secondary carbide particles within the martensite matrix after destabilisation. \(\alpha'\) denotes the martensite matrix. (b) A corresponding selected area diffraction pattern from a particle of secondary M\textsubscript{23}C\textsubscript{6} carbide (900\textdegree{}C, 6 h).

Fig. 10. A schematic illustration suggesting a possible mechanism of M\textsubscript{23}C\textsubscript{6} shell formation on eutectic M\textsubscript{7}C\textsubscript{3} (a) before and (b) after destabilisation heat treatment.
However, this factor have to counteract with others leading to softening effects for the dendritic regions e.g. the softer martensite when it is less in carbon due to the higher volume fraction of secondary carbides precipitated, and possibly the more retained austenite in air quenched structures at high destabilisation temperatures. 3) The compensation between these factors could result in an optimum destabilisation condition giving the maximum microhardness of the dendritic regions at 1 025°C. The explanation for the overall macrohardness is even more difficult since we needs to take into account the structure and properties of the eutectic carbides.

4. Conclusions

(1) Destabilisation heat treatment of a 30wt%Cr–2.3wt%C high chromium cast iron in the temperature range of 900–1 100°C for 2–8 h led to precipitation of secondary M23C6 carbide with the volume fraction and the number per area in the range of 10–20 vol% and 30–200 Cs/100 μm², respectively.

(2) Higher destabilisation temperatures resulted in coarser secondary carbide precipitated preferentially at heterogeneous sites with comparable volume fraction, but lesser number per area.

(3) M7C3 eutectic carbide transformed to M23C6 carbide during destabilisation heat treatment forming a core-shell structure. The volume fraction of M23C6 shell is in the...
range of 20–99 vol%, increasing with destabilisation temperature and time. Formation of this $M_23C_6$ shell is believed to be either a peritectoid type or a result of not only the $M_7C_3$-to-$M_23C_6$ transformation, but also the secondary precipitation from dendritic primary austenite.

(4) Destabilisation heat treatment raised the microhardness of the dendritic regions from the as-cast condition of about 426 up to about 800 HV (100 gf/15 s). The maximum microhardness of the dendritic regions was obtained at 1025°C with the value of 800 HV (100 gf/15 s).

(5) Destabilisation heat treatment conditions used in this experiment increased the overall macrohardness of the 30wt%Cr–2.3wt%C iron from the as-cast condition of about 510 up to about 770 HV (30 kgf/15 s).

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