Article

Precipitation of M23C6 Secondary Carbide Particles in Fe-Cr-Mn-C Alloy during Heat Treatment Process

Nguyen Thi Hoang Oanh and Nguyen Hoang Viet *

School of Materials Science and Engineering, Hanoi University of Science and Technology, Hanoi 100000, Vietnam; oanh.nguyenthahoang@hust.edu.vn

* Correspondence: viet.nguyenthoang@hust.edu.vn; Tel.: +84-43-868-0409

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Abstract: The initial as-cast microstructure of high-chromium white cast iron (2.08% C, 12.1% Cr), including austenitic dendrites in a matrix of a eutectic mixture of austenite and M7C3 carbides. Heat treatment of as-cast iron leads to a transformation of the matrix from austenite to martensite phase. The secondary M23C6 carbide precipitated from matrix improving the hardness of sample from 48 HRC to 62 HRC. JMatPro simulations of volume fraction phase for Fe-Cr-Mn alloy shows M7C3 and austenite phases are stable at austenitization temperature (1000 °C). Eutectic carbide of M7C3 is a stable phase in the alloy which is undissolved in the matrix during the heat treatment process. The HR-TEM images of heat-treated sample revealed that both eutectic M23C6 carbide and ultrafine secondary M23C6 carbide particles distributed on the martensite matrix.

Keywords: high chromium white cast iron; M7C3 and M23C6 carbides; JmatPro; HR-TEM; microstructure

1. Introduction

High Cr white cast iron (HCCI) alloys containing chromium between 12 and 30% have a good abrasion resistance which is widely used in wear applications, such as mineral processing, cement production and steel manufacturing industries [1–6]. The abrasion resistance of HCCI alloys is about 20–25 times better than low carbon steels, due to the distribution of carbide phases on the matrix [2,7]. The production of HCCI alloys in the as-cast state consisted of primary austenite dendrites and a eutectic mixture of M7C3/austenite. A coarse carbide phase network formed directly from liquid solution leads to poor fracture properties and relatively high wear rate [8,9]. Moreover, this network is very stable and unaffected by the heat treatment (HT) process. Therefore, the mechanical properties of as-cast irons can be enhanced by using a suitable HT method, such as destabilization and then sub-critical. In the destabilization HT process, secondary carbide phases are precipitated at low austenitization temperature, causing a reduction in carbon and chromium content results in a diffusionless transformation phase from austenite to martensite. Martensite phase is considered as an advantageous effect on the wear resistance, while the pearlite and ferrite phases reduce abrasion resistance [10,11]. The main disadvantage of martensite is that it is very brittle. A sub-critical HT is useful to reduce the retained austenite and reinforce martensite matrix by precipitation of considerable secondary carbides [12]. The sub-critical temperature is relatively low temperature can avoid distortion and fissuring the cast sample [5]. As a result, the toughness is improved because of the strain stress release in martensite during sub-critical, and the hardness can be increased by secondary carbide precipitation hardening. That is a good combination of toughness and strength can be obtained for HCCI [9]. The formation and structure characterization of secondary carbide M23C6 in HCCI has attracted the attention of scientists. Qiang Liu reported that in HCCI alloys, containing 15–20% Cr the secondary carbides are M7C3 type, with higher Cr content of 25–30%, they are M23C6 type [13].
Shengqiang Ma and et al. observed only M₇C₃ carbide after casting when studying with 20Cr-4C composition [14]. K.Wieczerak and et al. investigated that an in-situ transformation in eutectic carbides from hexagonal M₇C₃ to cubic M₂₃C₆ after heating in the rapidly solidified hypoeutectic Fe-Cr-C alloy with a composition of 25Cr-0.8C [15]. J.Wang and et al. heated as-cast sample at 1000 °C for 0.5 h and then air-cooled to room temperature and found that there are two types of M₂₃C₆ with the size of 200nm, including cubic morphology with a special relative to the matrix and another has grainy morphology with no specific orientation in 16.38Cr-2.77C alloy [12]. A. Wiengmoon reported that a mixture of M₂C₃ type and M₂₃C₆ type carbides exist after heat treatment in the case of 2.7C-16Cr and 2.7C-26.6Cr composition [2]. The sizes of secondary carbides vary from 0.2–0.6 µm and distribution being influenced by prior annealing and destabilization conditions. C.P. Tabrett and I.R. Sare destabilized a 14.8Cr-3.08C HCCI alloy at 1100 °C, then cooled to various sub-ambient temperatures [16]. The matrix of the destabilized alloy contained a significant amount of secondary carbides, which were unrepresented in the as-cast structure. Xiaoshuai Jia et al. applied a multicycle quenching-partitioning-tempering process and found only M₇C₃ carbide formed during the casting process of HCCI alloy with composition 12Cr-2.4C [5]. With reducing the Cr content to 12% Cr, it is not easy to get secondary carbide phase after the heat treatment process.

In this work, the combination of theory calculation by JMatPro is applied for Fe-12Cr-2.08C alloy to give suitable heat treatment parameters to improve the properties of the alloy. The formation of ultrafine secondary carbide M₂₃C₆ particles and matrix phase transformation into martensite is characterized by different microscopy methods.

2. Materials and Methods

HCCI alloy was cast from 1460 °C by using bentonite sand mold. The chemical composition of the alloy is produced under the specification for class II and type A followed the A 532M standard [17], as given in Table 1. Continuous cooling transformation (CCT) diagram for the alloy using JMatPro simulation was presented in Figure 1. The ingots subjected to destabilizing treatment, namely, austenitization in two step heating to 700 °C for 2 h and then continuing heating to 1000 °C for 2 h and finally forced-air cooling in 8 min. The tempering process was done at 250 °C for 2.5 h and air cooled [18].

Table 1. Chemical composition of HCCI alloy analyzed via arc spark emission spectrometer.

| Element | Fe   | C     | Si    | Mn   | P     | S     | Cr    | Mo    | Ni    | Cu    | Al    |
|---------|------|-------|-------|------|-------|-------|-------|-------|-------|-------|-------|
| wt.%    | Bal. | 2.08  | 0.284 | 1.30 | 0.093 | 0.058 | 12.1  | 0.046 | 0.270 | 0.102 | 0.05  |

![Figure 1. JMatPro simulation of continuous-cooling transformation diagram for the alloy.](image-url)
The samples were ground on silicon carbide papers to 800 grits and then polished by 1 μm diamond paste. The etchant used was 10% HCl and 90% methanol for about 40 s swept on the polished surface of the sample for optical microscopy (Leica DM4000M, Solms, Germany). To extract the carbides from HCCI alloy, samples need to etch deeply and longer time of 48 h for field emission scanning electron microscopy (FE-SEM-JEOL JSM-7600F, JEOL Ltd., Tokyo, Japan). Transmission electron microscopy (TEM-JEOL JEM-2100, JEOL Ltd., Tokyo, Japan) was used for characterization of secondary carbide M23C6. The phase transformation of the as-cast sample was determined by the NETZSCH STA 449 C (Netzsch, Selb, Germany) using differential thermal analysis (DTA) mode with a heating rate of 10 K/min under constant Ar gas flow to compare with the JMatPro result.

The thermodynamic modeling for the equilibrium and phase relationships, austenite composition at quenching temperature for HCCI alloy were simulated using JMatPro software [19,20], (Java-based Materials Property simulation software, version 7.0.0) (Sente Software Ltd., Surrey Technology Center, 40 Occam Road, Guildford, Surrey GU2 7YG, UK).

3. Results and Discussion

Figure 2 shows thermodynamic simulation for Fe-12Cr-2.08C alloy. The calculation was performed in order to predict phase compositions in the equilibrium state using JMatPro software [19]. The crystallization of alloy starts at 1352 °C with the precipitation of austenite from the liquid in the temperature range of 1249 °C-777 °C, the rest of the liquid crystallizes in line with the eutectic reaction of “L → Austenite + M7C3”. The maximum eutectic carbide M7C3 is about 23.9 vol.%. The phase transformation of austenite (BCC) to ferrite (FCC) below 776 °C leads to decrease density value. It is well known that the solubility of carbon in the FCC crystal structure is much greater than in BCC, as well as that the diffusivity of both substitutional and interstitial atoms also changes substantially [21]. Consequently, this kind of transformation significantly affects the kinetics of the diffusion-controlled processes in the alloy, e.g., homogenization, in-situ carbides transformation, etc. Upon completion of the reaction, the alloy contains 83.5% for austenite and 16.5% for the M7C3 carbide. When the temperature is below 180 °C, the residual austenite phase together with a small amount of M23C6 carbide appeared. Furthermore, the presented content of M23C6 and austenite are stable at austenitization temperature (1000 °C). That means carbides of M7C3 did not dissolve in the matrix. The density of alloy also gradually increases when the phase transformation of liquid to austenite occurred, as seen in Figure 3.

Figure 2. JMatPro simulation of volume fraction phases vs temperature for the Fe-12Cr-2.08C alloy, in the case where the formation of the M7C3 and M23C6 carbides.
The phase transformation of the as-cast sample with a heating rate of 10 K/min is observed in the DTA curve (Figure 4). There are two thermal events at 680 and 825 °C. The first exotherm peak at 680 °C is related to austenite-ferrite transformation as Y. F. Zhou and et al. mentioned [22]. The second endothermal peak appears corresponding to the solid-state transformation of M$_7$C$_3$ secondary carbide as reported in [23,24]. The JMathPro result (Figure 2) is quite close to the DTA curve. The optical micrographs of cast iron, shown in Figure 5. The solidification process starts with the formation of dendritic austenite and followed by M$_7$C$_3$ formation when the temperature drops to eutectic temperature. This is also entirely consistent with the Fe-Cr-C phase diagram [21]. In HT sample, most of the austenite phase is transferred to the martensite phase. With a high content of carbon and alloy elements, remained austenite phase can avoid perlite formation and reduce the temperature beginning to transfer the martensite phase. The network eutectic carbides are still observed, but the microstructure within the dendrites cannot be distinguished from the as-cast and HT samples. The morphology of the structure of carbides phase can be seen more clearly through SEM images in Figure 6. A strong corrosion solution of 10% volume of HCl with 90% methanol was used for deep etching for 48 h.
The HR-TEM and its selected area diffraction pattern (SADP) confirmed that the matrix phase is martensite (Figure 7b), rod carbides belong to M\(_7\)C\(_3\), and the secondary particles are M\(_{23}\)C\(_6\) carbides. The secondary carbide of M\(_{23}\)C\(_6\) in the form of particles is rarely mentioned in HCCI alloy (12% Cr) after HT. TEM micrographs of Fe-Cr-C alloy showing M\(_7\)C\(_3\) eutectic carbide and SADP (in the corner) from the region in this micrograph. The secondary carbide can be precipitated from residual austenite when cooling temperature beginning at 1273 K to room temperature as G.L.F. Powell observed. Austenite phase get transformed into the martensite phase together with the formation of M\(_{23}\)C\(_6\) carbide particles without orientation with the matrix [25].
Figure 6. SEM images of (a,b) as-cast sample; (c,d) HT sample and (e) bright field TEM image for an as-cast sample and (f) bright field TEM image for HT sample.

Selected points for EDS measurements are marked in Figure 8a and its EDX spectra are shown in Figure 8b. Table 2 shows the compositions of primary $M_7C_3$, $M_{23}C_6$ carbides and matrix phase. In spectrum 1, the ratio of chromium and iron atoms to C atoms is 7:3, which agrees with the stoichiometry of $M_7C_3$ carbide. The Cr/Fe ratio is near 1, which is in accordance with the (Fe,Cr)$_7C_3$ carbide [9]. Compared with primary $M_7C_3$ carbide, martensite contains more Fe atoms, but fewer Cr and C atoms as seem in spectrum 3. Results of EDX spectrum analysis of background phase (spectrum 3) show that Fe content is 79.37% atoms. Analysis of EDX spectrum for secondary particles (spectrum 4) shows that the atomic proportions of elements C, Cr and Fe correspond to the phase (Fe,Cr)$_{23}C_6$. 
Figure 7. TEM characterization of microstructure in the HT sample (a) Bright field image; (b) HR-TEM image of matrix and inserted SADP pattern (at point 1) refer to martensite phase; (c) HR-TEM image and SADP (at point 2) refer to carbide M$_7$C$_3$; and (d) HR-TEM image and SADP (at point 3) refer to M$_{23}$C$_6$.

Table 2. Chemical composition of observed phases determined by EDX (at %).

| Spectrum | Atomic (%) | Phase     |
|----------|------------|-----------|
|          | Mn  | Si  | O  | C  | Cr  | Fe  | Cr/Fe | Crt/C | Fe/C  | (Cr+Fe)/C |       |
| 1        | 1.66 | -   | -  | 17.71 | 41.39 | 39.22 | 1.05  | 2.33  | 2.21  | 4.55     | M$_7$C$_3$  |
| 3        | 1.21 | 1.25 | -  | 15.72 | 4.79  | 77.02 | 0.06  | 0.30  | 4.90  | 1         | M$_{23}$C$_6$ |
| 4        | 1.13 | -   | 3.09 | 20.33 | 37.98 | 37.46 | 1.01  | 1.87  | 1.84  | 3.71     | M$_{23}$C$_6$ |

The HT process increased the hardness value of 62 HRC compared to that of the as-cast sample of 48 HRC. This can be explained that matrix transformation from austenite to martensite and the precipitation of secondary carbide particles M$_{23}$C$_6$ from matrix improve the hardening of HCCI alloy. The fine secondary carbide particles act as obstacles for grain boundary migration during the deformation in working conditions. The distribution of elements in dendrites and eutectic carbides for HT sample can be seen clearly in scanning transmission electron microscopy (STEM) images in Figure 9a–e. The carbides in the investigated alloy are enriched in chromium because this element has a greater affinity for carbon than iron. The eutectic carbides are depleted in iron, which is in a good
agreement with data in Table 2. Figure 9 also shows that regions surrounding carbides are depleted, mainly in Cr, but enriched in Fe. Furthermore, carbon element distributes rather homogeneous in both martensite matrix and carbides phase. The secondary carbide M23C6 particles are precipitated in the matrix, which is uniform, in order to improve the hardness and toughness of HT sample.

Figure 7. TEM characterization of microstructure in the HT sample (a) Bright field image; (b) HR-TEM image of matrix and inserted SADP pattern (at point 1) refer to martensite phase; (c) HR-TEM image and SADP (at point 2) refer to carbide M7C3; and (d) HR-TEM image and SADP (at point 3) refer to M23C6.

Figure 8. (a) Bright field image of HT sample; (b) EDX spectra corresponding to positions (spectrum 1) a dark primary carbide; (spectrum 3) a secondary carbide and (spectrum 4) a needle shape of a matrix.

Figure 9. (a) STEM image of HT sample; The elemental distribution of (b) Cr; (c) Fe; (d) C and (e) Mn.

The sequence of carbide formation during crystallization in investigated Fe-Cr-Mn-C alloy could be determined as following: L → γ + M7C3 eutectic reaction (as-cast) → martensite + M7C3 or/and M23C6 eutectic reaction (HT). At the beginning of solidification austenite dendric appeared in liquid at 1352 °C, cooling at a lower temperature the residual liquid transformed to γ + M7C3 by the eutectic
reaction. In HT process, while the austenite phase transferred to martensite (a diffusion-less mechanism) resulting in the change of composition in the matrix, $M_{23}C_6$ carbide particles also precipitated.

4. Conclusions

The calculation by JMatPro software shows that the formation of austenite, the eutectic carbide $M_7C_3$ and secondary carbides of an as-cast sample. The microstructure of HCCI alloy after HT process shows the continuous eutectic carbides spreading widely throughout the matrix. DTA of as-cast sample shows that there are two exothermal peaks at 680 and 825 °C corresponding to $M_7C_3$ phase and ferrite-austenite transformation, respectively. The change of the microstructure of HCCI alloy from the cast state to the HT state can be clearly seen from the electron microscopy image through the bright field. After the HT in addition to the bar-shaped coarse carbide of $M_7C_3$, there is also a phase of nanoparticles with the needle-shaped martensite phase matrix. The secondary carbides were characterized by HR-TEM technique. The appearance of a fine carbide phase may increase the abrasion resistance of the martensite matrix, as well as improve the properties of the materials. Analysis of electron diffraction images for background phase results is martensite and nano-sized particles of $M_{23}C_6$ carbide, while coarse carbides are of the same type as $M_7C_3$. The matrix hardenability can be improved by the appearance of martensite and secondary carbides $M_{23}C_6$. The hardness of the as-cast sample increase from 48 to 62 HRC after heat treatment.

From theory calculation combines with experiment shows that thermodynamic simulation by JMatPro software can forecast the structure and phase composition of alloys, especially, it can provide recommendation for casting technology or thermal treatment in foundry plants.

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Conflicts of Interest: The authors declare no conflict of interest.

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