Control of Wear-Resistant Properties in Ti-added Hypereutectic High Chromium Cast Iron

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Abstract

High chromium cast iron (HCCI) is considered as one of the most useful wear resistance materials and their usage are widely spread in industry. The wear resistance and mechanical properties of HCCI mainly depend on type, size, number, morphology of hard carbides and the matrix structure (γ or α). The Hypereutectic HCCI with large volume fractions of hard carbides is preferred to apply in wear applications. However, the coarser and larger primary M₇C₃ carbides will be precipitated during the solidification of the hypereutectic alloy and these will have a negative influence on the wear resistance.

In this thesis, the Ti-added hypereutectic HCCI with a main composition of Fe-17mass%Cr-4mass%C is quantitatively studied based on the type, size distribution, composition and morphology of hard carbides and martensite units. A 11.2μm border size is suggested to classify the primary M₇C₃ carbides and eutectic M₇C₃ carbides. Thereafter, the change of the solidification structure and especially the refinement of carbides (M₇C₃ and TiC) size by changing the cooling rates and Ti addition is determined and discussed. Furthermore, the mechanical properties of hypereutectic HCCI related to the solidification structure are discussed.

Mechanical properties of HCCI can normally be improved by a heat treatment process. The size distribution and the volume fraction of carbides (M₇C₃ and TiC) as well as the matrix structure (martensite) were examined by means of scanning electron microscopy (SEM) and electron backscattered diffraction (EBSD). Especially for the matrix structure, EBSD is a useful tool to classify the fcc (γ) and bcc (α) phases. In conclusion, low holding temperatures close to the eutectic temperature and long holding times are the best heat treatment strategies in order to improve wear resistance and hardness of Ti-alloyed hypereutectic HCCI.

Keywords: High Chromium Cast Iron, cooling rate, Ti addition, M₇C₃, TiC, carbides size distributions, volume fraction, heat treatment, microstructure, mechanical properties, wear resistance
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Qiang Liu, Stockholm, September 2012.
Preface

This is a systematic study from melting and solidification to heat treatment of a wear resistant high chromium cast iron. The results on Ti-added hypereutectic high chromium cast iron can be widely be applied to improvements of wear resistant parts in mineral industry plants, power plants, steel making plants, and others. Moreover, for the development of new superior wear resistant materials. I wish you can get some 'hint' when you read this thesis, which is intend to contribute with new knowledge in the production of wear parts.

The present thesis is based on the following supplements:

Supplement 1:

“Effect of Cooling Rate and Ti Addition on the Microstructure and Mechanical Properties in As-Cast Condition of Hypereutectic High Chromium Cast Irons”

Qiăng Liu, Hongwei Zhang, Qiang Wang, Xiangkui Zhou, Pär G. Jönsson, Keiji Nakajima
Accepted for publication in ISIJ Int., 52(2012), No. 12.

Supplement 2:

“Effect of Heat Treatment on Microstructure and Mechanical Properties of Ti-alloyed Hypereutectic High Chromium Cast Iron”

Qiăng Liu, Peter Hedström, Hongwei Zhang, Qiang Wang, Pär G. Jönsson, Keiji Nakajima
Accepted for publication in ISIJ Int., 52(2012), No. 12.

Qiăng Liu performed the literature survey, a major part of the experimental work, and a major part of the writing.
Contents

Chapter 1 General Overview ................................................................. 1
  1.1 Introduction .................................................................................. 1
  1.2 The purpose and outline of thesis .................................................. 2

Chapter 2 Experiment Methods and Theoretical Works .............................. 5
  2.1 Experiment Methods ..................................................................... 5
    2.1.1 Melting and solidification process .......................................... 5
    2.1.2 Heat treatment process .......................................................... 7
    2.1.3 Microstructure observations and image analysis ...................... 8
    2.1.4 Mechanical properties measurement ...................................... 10
  2.2 Theoretical works ........................................................................ 11

Chapter 3 Microstructure and Properties in As Cast Condition ..................... 13
  3.1 Microstructure of Ti-added hypereutectic HCCI .................................. 13
  3.2 Phase diagram .............................................................................. 14
  3.3 Effect of Cooling Rate on Solidification Structure ............................ 15
  3.4 Effect of Ti addition on Solidification Structure ............................... 17
    3.4.1 Effect of Ti addition on the carbides distributions .................... 17
    3.4.2 Effect of Ti addition and cooling rate on the volume fraction ...... 21
  3.5 Classification of M_{7}C_{3} carbides .................................................. 22
  3.6 Effect of Cooling Rate and Ti Addition on the Mechanical Properties in As-Cast Condition of the hypereutectic HCCIs .................................................. 26

Chapter 4 Improvement of Properties by Heat Treatment ........................... 29
  4.1 Phase diagram .............................................................................. 29
  4.2 Evolution of M_{7}C_{3} ................................................................. 30
  4.3 Evolution of TiC ........................................................................... 33
  4.4 Evolution of Matrix ....................................................................... 34
  4.5 Mechanical properties ................................................................... 37

Chapter 5 Conclusions ........................................................................... 39

Suggestions for Future Work .................................................................. 41

References ......................................................................................... 43
Chapter 1

General Overview

1.1 Introduction

The Fe-Cr-C system alloys have widely been applied to wear resistant parts in steel making plants, power plants, mineral industry plants, and others [1,2]. In all industrial fields, however, the improvement of the abrasion wear-resistance is strongly required because of its short life.

In the first half of the 1980s, High Chromium Cast Iron (HCCI) with a composition range of 2.0-4.3%C [2] and 12-30%Cr [3] were started to be applied to roll materials for hot rolling. The wear performance level of hypereutectic HCCIs is mainly controlled by a high volume fraction (30 to 60%) of M₇C₃ type carbides (1200~1600 HV) [4], M₂₃C₆ type carbides (1600-2520HV) [5], MC type carbides (2400-4000HV) [5], etc. These carbides will precipitate during the solidification and heat treatment and will influence the final material properties.

Compared to the Hypoeutectic HCCI, as the result of carbonization inside the Hypereutectic HCCIs highly increased, the hardness of Hypereutectic HCCIs is obviously improved via a higher carbon and chromium content. These higher addition will also cause an increase of the volume fraction of carbides. However, the coarser and larger primary carbides will be precipitated during the solidification of the hypereutectic HCCI. These coarser primary carbides have a negative effect on the improvement of the wear resistance of all alloy. Therefore, many investigations have been executed with the aim of refining the solidification structure and improving the properties of hypereutectic HCCIs. Here, additions of alloy elements have been used to form the NaCl type carbides, such as Ti, Nb, V, Nb, Zr etc.[6-13]

Those elements, which are strong carbide forming elements, will react with carbon and form NaCl type carbides, such as TiC, NbC, VC etc.. These can act as heterogeneous nuclei for the precipitation of M₇C₃ type carbides during the cooling and solidification of the melt.[6-8] This, in turn, results in significant refinements of the final carbides size. Moreover, we should point out that the size, volume fraction and distribution of these carbides will also affect the final properties of the hypereutectic HCCIs significantly.

For many applications, a higher wear resistance is required to improve the service life of the wear components. In comparison to as-cast cast iron, heat-treated cast irons with higher wear
resistance are prior to service. The reason is that the matrix changes from an austenitic structure (fcc, \( \gamma \)) into a martensitic structure (bct, \( \alpha' \)) and new carbide precipitates (\( \text{M}_7\text{C}_3 \)) or \( \text{M}_{23}\text{C}_6 \)) form within the matrix. Therefore, many studies focusing on improving the properties of cast iron, by alternative heat treatment processes, have been reported. Most of the previous studies are focused on identifying the new carbides by using transmission electron microscopy (TEM). They have furthermore studied how the new carbides influence the final properties. However, we also should point out that the mechanical properties to a large extent are determined by the shape, size distribution and volume fraction of martensite and carbides formed in the HCCI.

1.2 The purpose and outline of thesis

At present, few reports discuss how the carbide size distribution influences their final solidification structure and properties. However, they only show the effects of the average diameter and volume fraction of the total amount of carbides on the material properties. In addition, for heat treated HCCI, only a few studies quantitatively discuss how the size distribution of carbides and martensite units affect the final properties of hypereutectic HCCI. Therefore, a quantitative study on the carbides, martensite units and their influence on mechanical properties is desired.

In this thesis, in order to develop superior abrasion resistant castings, a research is done on solidification and heat treatment related to the control of carbides precipitation and final material properties in Ti-added hypereutectic high chromium cast iron. We quantitatively study the size distribution, composition and morphology of carbides and martensite units in the Ti-added hypereutectic HCCI with main composition of Fe-17mass%Cr-4mass%C.

An outline of thesis is given and organized as follows:

Supplement 1:

(Melting and solidification)

- In order to refine the primary \( \text{M}_7\text{C}_3 \) type carbides in Hypereutectic HCCI, different cooling rates and Ti addition were used. The size distribution, composition, volume fraction and morphology of carbides (\( \text{M}_7\text{C}_3 \), TiC) are quantitatively measured and their influence on the mechanical is discussed.
Prediction of precipitation, solidification structure phase diagram and fraction of HCCI (Fe-17mass%Cr-4mass%C multicomponent alloys) is done by using a multiphase micro-segregation model, which is coupled with the CALPHAD method using the Thermo-Calc software. Overall, the prediction results agree well with the experimental results.

Supplement 2:

(Heat treatment)

The relationship between carbide precipitation, martensite units and mechanical properties are discussed based on the volume fraction and the size distribution of carbide precipitates (M₇C₃ and TiC) as well as the martensite units. A possible mechanism is finally proposed to explain the improvement of mechanical properties through the heat treatment process. In addition, the best heat treatment strategy is suggested.
Chapter 2

Experiment Methods and Theoretical Works

In the present thesis, carbides precipitation behavior, phase transformation and their influence on the mechanical properties in the Ti-added Hypereutectic HCCI were studied both experimentally and theoretically. However, experimental studies were taken as the major research tools in this thesis.

2.1 Experiment Methods

2.1.1 Melting and solidification process

Based on the requirements during actual production, melts were prepared in a laboratory furnace. High-carbon ferro-chromium (Fe-8mass%C-60mass%Cr), ferro-molybdenum (Fe-0.05mass%C-58.4mass%Mo), pure iron, pig iron (Fe-3.8mass%C-0.34mass%Mn-1.8mass%Si), ferro-titanium(Fe-30mass%Ti), ferro-manganese(Fe-75.9mass%Mn), and pure nickel were melted in a 8 kg capacity graphite crucible. This was done using a medium frequency induction furnace (45Kw, 7k Hz) and using an air atmosphere.

<table>
<thead>
<tr>
<th>Mold</th>
<th>Composition C</th>
<th>Cr</th>
<th>Ti</th>
<th>Mn</th>
<th>Mo</th>
<th>Ni</th>
<th>Si</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>P</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>4.01</td>
<td>16.2</td>
<td>-</td>
<td>2.04</td>
<td>1.01</td>
<td>1.24</td>
<td>0.775</td>
<td>0.020</td>
<td>0.018</td>
<td>0.0086</td>
<td>0.026</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>3.79</td>
<td>17.0</td>
<td>1.53</td>
<td>2.08</td>
<td>1.05</td>
<td>1.09</td>
<td>0.416</td>
<td>0.016</td>
<td>0.017</td>
<td>0.014</td>
<td>0.025</td>
<td>Bal.</td>
</tr>
<tr>
<td>Graphite</td>
<td>4.9</td>
<td>16.4</td>
<td>-</td>
<td>1.59</td>
<td>0.75</td>
<td>1.09</td>
<td>0.845</td>
<td>0.019</td>
<td>0.022</td>
<td>0.0046</td>
<td>0.025</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>4.03</td>
<td>15.6</td>
<td>0.74</td>
<td>1.72</td>
<td>0.93</td>
<td>1.08</td>
<td>0.992</td>
<td>0.014</td>
<td>0.020</td>
<td>0.0047</td>
<td>0.023</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>4.01</td>
<td>17.4</td>
<td>1.48</td>
<td>1.91</td>
<td>0.89</td>
<td>1.11</td>
<td>0.951</td>
<td>0.015</td>
<td>0.017</td>
<td>0.011</td>
<td>0.024</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>3.91</td>
<td>17.5</td>
<td>3.36</td>
<td>1.95</td>
<td>1.01</td>
<td>1.08</td>
<td>0.966</td>
<td>0.025</td>
<td>0.025</td>
<td>0.031</td>
<td>0.022</td>
<td>Bal.</td>
</tr>
<tr>
<td>Metal</td>
<td>3.92</td>
<td>14.7</td>
<td>-</td>
<td>1.950</td>
<td>0.95</td>
<td>1.05</td>
<td>0.529</td>
<td>0.015</td>
<td>0.020</td>
<td>0.0037</td>
<td>0.024</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>3.90</td>
<td>16.8</td>
<td>1.06</td>
<td>1.95</td>
<td>0.99</td>
<td>1.15</td>
<td>0.708</td>
<td>0.014</td>
<td>0.014</td>
<td>0.0094</td>
<td>0.024</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 2.1 Chemical compositions of high chromium cast iron (HCCI) used in the experiments. (mass.%)
The alloy compositions are shown in Table 2.1. Pure iron, pig iron and high carbon ferro-chromium were first melted. Then, ferro-manganese and ferro-molybdenum were added. At last, pure nickel and ferro-titanium were added into this mother alloy.

Fig. 2.1 Schematic diagram of melting process of hypereutectic HCCIs with 1.5mass% Ti addition and casting in the graphite mold.

The holding time over the TiC precipitation temperature was controlled as 3min±1min, in order to prevent the agglomeration of TiC carbide precipitation. Finally, the molten hypereutectic HCCIs were poured into the mold at 1450±10°C. The following three mold types were used: sand mold (silica sand), graphite mold, metal mold (ASTM: 1045). The schematic diagram of melting process is shown in Fig. 2.1.

The dimension of the ingot is 120mm L×84mm W×55mm H. A schematic view of the ingot and the thermocouple (Type-B) position is shown in Fig. 2.2.

Fig. 2.2 Schematic view of ingot and cutting position of sample for microstructure observation.
In addition, the cooling curves obtained from the three different molds are shown in Fig. 2.3. From this information the following different cooling rates were obtained: 25°C/min, 80°C/min and 110°C/min within 10% errors for the sand mold, graphite mold and metal mold, respectively.

2.1.2 Heat treatment process

The specimens used for heat treatments were selected from the as-cast ingots, which were casted in a graphite mold with a 1.5mass% titanium addition. Samples of the dimensions 10mmL×10mmW×10mmH were cut and then heat-treated at a furnace temperature of 900°C, 1000°C and 1050°C for 2hr and 6hr respectively. The samples were air cooled from the elevated temperature to room temperature. The surface temperature of the sample during heat treatment was measured using a R-type thermocouple and the temperature cycle is shown in Fig. 2.4. It was found that the difference between the furnace temperature and the actual temperature of the sample surface was less than 10°C.
2.1.3 Microstructure observations and image analysis

2.1.3.1 Carbide analysis by LOM and SEM

The ingot samples were cut at a position close to the thermocouple measurement position, as shown in Fig. 2.2. Thereafter, the samples were polished and etched by using a solution of 5g FeCl$_3$+10ml HCl+100ml ethanol. Then, the size distribution of carbides (M$_7$C$_3$ and TiC) was measured on photographs obtained by using a light optical microscope (LOM) (Leica DMR) at a ×10 magnification, where one pixel represented 0.3356 μm. And back scattered electron (BSE) setting in the scanning electron microscopy (SEM) (Hitachi: S-3700N) at ×600 magnifications, where one pixel represented 0.1656 μm. The composition of carbides including Fe, Cr, Ti, Mo, Mn and other elements were determined with the Energy Dispersive X-ray spectrometer (EDX) method.

The number of carbides per unit area, $N_A$, was calculated using Equation (2-1).

\[
N_A (i) = \frac{n_{(i)}}{S_{\text{obs}}}
\]  

(2-1)

where $n_{(i)}$ is the counted number of carbides for each selected step (i) of the size distribution. Moreover, $S_{\text{obs}}$ is the total area which was observed on the photographs, which were taken by LOM ($S_{\text{obs}}=0.3152$ mm$^2$) and SEM ($S_{\text{obs}}=0.0314$ mm$^2$), respectively. The size of carbides, d, and the volume fraction of carbides were calculated as the equivalent diameter of a circle by
using an image analyzer, which is commercial software, Winroof ©. The size distributions for carbides and martensite unit are plotted using a logarithmic scale. The value of size $d_{(j)}$, for the j-th step, $\Delta(j)$, of a log-normal distribution can be determined as follows:

$$d_{(j)} \text{ or } D_{(j)} = 10^{\Delta_{(j)}}$$

(2-2)

where $\Delta_{(j)}$ is the width of the j-th step for log-normal distributions ($\Delta_{(j)}= \Delta_{(j+1)}+0.15$). This range is from -0.15 to 2.4 for $\text{M}_7\text{C}_3$ carbides (d), from -1.05 to 2.1 for TiC carbides (d) and from -2.25 to 2.4 for martensite unit (D). In this case, the mean value for the j-th step of the size distribution, $d_{(j)}$ or $D_{(j)}$ varies from 0.85 to 214.51 $\mu$m, from 0.11 to 107.51 $\mu$m, and from 0.0068 to 214.5038$\mu$m respectively.

2.1.3.2 Carbide and matrix analysis by EBSD

Electron backscattered diffraction (EBSD) analysis was carried out to identify the phases in the specimens. [25, 27] Austenite (fcc, $\gamma$), martensite (bct, $\alpha'$) and carbides ($\text{M}_2\text{C}_6$, $\text{M}_7\text{C}_3$ and TiC) were included in the analysis. The flatness and surface quality of specimens is crucial for EBSD analysis [26] in order to properly index phases such as e.g. martensite. [27] In this study, the specimens used for EBSD analysis were polished; first by manual polishing using SiC abrasive papers (P240-P320) together with water, secondly with 9 $\mu$m and 3 $\mu$m diamond suspensions. Finally, specimens were polished with a 0.05$\mu$m colloidal SiO$_2$ by automatic polishing. The detailed preparation procedure for the hypereutectic HCCI is shown in Table 2.2.

<table>
<thead>
<tr>
<th>Step</th>
<th>Disk name and type No. (Company: BUEHLER)</th>
<th>Abrasive Size and suspension</th>
<th>Load(N)</th>
<th>Speed(rpm) and Direction</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>ApexHercules® S rigid No.41-27400-412-001</td>
<td>9$\mu$m diamond suspension</td>
<td>30</td>
<td>150 (Comply)</td>
<td>5</td>
</tr>
<tr>
<td>Step 2</td>
<td>MicroFloc No.40-8322</td>
<td>3$\mu$m diamond suspension</td>
<td>30</td>
<td>150 (Comply)</td>
<td>5</td>
</tr>
<tr>
<td>Step 3</td>
<td>ChemoMet® No.40-7922</td>
<td>0.05$\mu$m colloidal silica</td>
<td>30</td>
<td>150 (Contrary)</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2.2 EBSD sample preparation for the hypereutectic HCCI
The EBSD measurements were performed using a LEO 1530 FEG (Field Emission Gun)-SEM installed with the HKL system and the HKL Channel 5 software. The specimens were tilted 70° towards the detector and the microscope was operated at an acceleration voltage of 15kV, in high current mode, and using an aperture of 120μm. Two different step sizes of 0.1μm and 0.03μm were used. The area scanned with a 0.1μm step size was 200μm×150μm and the area scanned with the step size 0.03μm was 10μm×10μm. The reason for using two step sizes was the rather broad size distribution. The size and volume fraction of carbide and martensite units were determined using image analysis made on EBSD maps.

The EBSD measurements were further complemented by energy dispersive X-ray spectroscopy (EDS) mapping using the INCA software. The EDS analysis was conducted using a 20kV acceleration voltage and a 30μm aperture in high current mode. The EDS analysis enabled a more sound identification of the phases since both crystal symmetry (EBSD) as well as chemical composition (EDS) could be considered for the observed microstructural features.

The number of carbide precipitates and martensite units per unit area (Nₐ) was calculated by Equation (2-1). In this case, the parameter S_obs is the total area of the micrographs, which was 0.0314 mm² for SEM. For EBSD S_obs=0.0001 mm² (0.03μm step) and S_obs=0.03 mm² (0.1μm step) was used.

The size of martensite units (D) was calculated as the equivalent diameter of a circle, which has the same area as the measured martensite unit.

### 2.1.4 Mechanical properties measurement

The mechanical properties: bulk hardness and wear loss of the hypereutectic HCCIs was investigated in the as-cast condition and each heat treatment. The bulk hardness was measured by using a Rockwell type hardness tester, HR-150A with the Rockwell C scale (HRC). Overall, eight measurements were done for each sample. The wear resistance was evaluated by using a single platform rotary abraser (model: ML-100 type, Zhangjiakou Taihua Machine Factory). The wear tests were performed at a platform speed of 60rpm under a load of 100N. The size of the wear test samples was 4.1mm (φ)×10mm(H). The tests were performed on a 80 mesh Al₂O₃ abrasive paper at room temperature. The total sliding distance and the testing time of the samples on the abrasive paper were 9m and 25s, respectively. The mass loss of the specimens due to abrasion was calculated by measuring the weight of the specimens before and after tests with a 0.001mg accuracy. Three measurements were carried out per sample.
2.2 Theoretical works

In this thesis, the phase diagram and volume fraction of carbides in HCCIs were predicted numerically by coupling the micro-segregation model with thermodynamic equilibrium calculations at solid/liquid interfaces.

The Scheil model, which is based on an assumption of no diffusion in solids, indicates that the new phases always precipitate from the residual liquid in a solidification sequence. Furthermore, the already formed solids remain frozen.

The Partial Equilibrium (PE) model distinguishes the diffusivities of substitutionals as zero and interstitials as infinite in solids. In the present HCCI system, only C behaves as an interstitial. Then the compositions and the amounts of the phases are adjusted based on equalization of the chemical potentials of the interstitials, following the equations below:

\[ \mu_C^L = \mu_C^S \]  
(2-3)

The mass conservation of the interstitial component C before and after partial equilibrium:

\[ \frac{(w_C^L)' - w_C^L}{1 - (w_C^L)'} \cdot f^L + \frac{(w_C^S)' - w_C^S}{1 - (w_C^S)'} \cdot f^S = 0 \]  
(2-4)

The unchanged u-fraction of substitutional components such as Fe element before and after partial equilibrium in each phase:

\[ (w_{Fe}^L)' = \frac{1 - (w_{Fe}^L)'}{1 - w_{Fe}^L} \cdot w_{Fe}^L \]  
(2-5)

\[ (w_{Fe}^S)' = \frac{1 - (w_{Fe}^S)'}{1 - w_{Fe}^S} \cdot w_{Fe}^S \]  
(2-6)

The mass conservation of the substitutional components before and after partial equilibrium:

\[ (f^L)' = \frac{1 - w_C^L}{1 - (w_C^L)'} \cdot f^L \]  
(2-7)

\[ (f^S)' = \frac{1 - w_C^S}{1 - (w_C^S)'} \cdot f^S \]  
(2-8)

The chemical potential of C in a phase is determined through phase equilibrium calculations, based on data of the phase composition, temperature and pressure. In the above equations, \( w_C^L \), \( (w_C^L)' \) are the mass compositions of carbon in the liquid before and after partial equilibrium, \( w_C^S \), \( (w_C^S)' \) are the corresponding averaged mass composition of C in solid \( S_1 \).
\[ w_c^k = \sum_k (w_{C}^{S_k} \cdot f^{S_k}) / \sum_k f^{S_k} \]  

(2-9)

where \( w_{C}^{S_k} \) is the newly formed composition in \( S_1 \) at the \( k \)th step. The parameters \( f^L, f^{S_k} \) (\( = \sum f^{S_k} \)) are the mass fractions of the liquid and the solid phases \( S_1 \) at \( k \)th step, respectively.

The partial equilibrium among several phases (i.e. liquid and solid phase \( j = 1, m \)) is regarded as equivalent to several partial equilibriums between two phases (e.g. liquid and one of the solids, \( S_1 \)). Therefore, the mass conservation of the interstitial component among all phases follows **equation (2-10)** instead of equation (2-4),

\[
\frac{(w_c^L)' - w_c^L}{1 - (w_c^L)} \cdot f^L + \sum_j \frac{(w_c^{S_j})' - w_c^{S_j}}{1 - (w_c^{S_j})'} \cdot f^{S_j} = 0
\]

(2-10)

The calculations are based on the ideas of Chen and Sundman. [28, 29] They are performed in Thermo-Calc/TQ interface [30] by a coupling of thermodynamic equilibrium calculations with the alloy database TCFE6. [31] A temperature step of -1 °C was used in the calculations. The calculations by the PE and Scheil models were stopped when the liquid fraction in mass was less than \( 10^{-4} \).
Chapter 3

Microstructure and Properties in As Cast Condition

This chapter concerns the solidification structure evolution and its influence on the final properties of Ti-added hypereutectic HCCI with a main composition of Fe-17mass%Cr-4mass%C. Different cooling rates and Ti additions were applied to refine $\text{M}_7\text{C}_3$ type carbides. A quantitative discussion for carbides ($\text{M}_7\text{C}_3$, TiC) was done based on the size distribution, composition, volume fraction and morphology of these carbides. Finally, the effect of cooling rates and Ti addition on the mechanical properties in as cast condition of hypereutectic HCCI is discussed.

3.1 Microstructure of Ti-added hypereutectic HCCI

The solidification microstructure consists of primary $\text{M}_7\text{C}_3$ carbides with a large hexagonal columnar structure, eutectic $\text{M}_7\text{C}_3$ carbides with an irregular shape, TiC carbides with a cubic structure and a matrix containing mainly of an austenite phase ($\gamma$), as shown in Fig. 3.1(a)-3.1(c). After heat treatment, matrix changes from austenite into martensite, as shown in Fig. 3.1(c)-3.1(d), and the secondary carbides also precipitate, as shown in Fig. 3.1(d).

Fig. 3.1. Microstructure of Ti-added hypereutectic HCCI, (a) LOM and (b) SEM for carbides, (c) and (d) EBSD for matrix
3.2 Phase diagram

The phase diagram of Ti-added hypereutectic HCCI, which is based on the sample composition given in Table 2.1, is created by thermodynamic equilibrium calculations by using the Thermo-Calc® software. [30, 31] The phase diagrams of the hypereutectic HCCIs with different Ti content are shown in Fig. 3.2.

![Fig. 3.2. Phase diagram of the hypereutectic HCCIs with (a): 0mass%, (b): 0.75mass%, (c):1.5mass% and (d): 3.0mass% Ti addition by using Thermo-Calc calculation. A zone: LIQUID; B zone: LIQUID+ TiC (FCC_A1#2); C zone: LIQUID+M7C3; D zone: LIQUID+ γ (FCC_A1)+TiC (FCC_A1#2)+M7C3; E zone: γ (FCC_A1)+M7C3.](image)

It was found that the solidification was initiated with a formation of primary M7C3 carbides, which began to precipitate at 1337°C. Thereafter, the eutectic reaction L → γ+M7C3 took place during the cooling from 1256 °C to 1215 °C. This is valid for the case without Ti additions, as illustrated in Fig. 3.1(a). On the other hand, in the case with a Ti addition, the precipitation sequence is changed as shown in Fig. 3.1(b), 3.1(c) and 3.1(d). In the case of a 1.5mass% Ti addition, FCC_A1#2 (corresponds to the NaCl type carbides such as TiC carbide) first precipitates at 1549°C. Then, the primary M7C3 carbides precipitate at 1317°C.
Finally, the eutectic reaction $L \rightarrow \gamma + M_7C_3$ occur from 1258°C. Moreover, the precipitation temperature of the TiC carbide increases from 1459°C to 1734°C with an increased Ti content from 0.75mass% to 3.0mass%.

### 3.3 Effect of Cooling Rate on Solidification Structure

As mention in chapter 2, we obtained three kinds of cooling rates, which were examined in the three kinds of mold. The idea for refining the microstructure by increasing cooling rates is based on: that the nucleation probability of primary $M_7C_3$ carbides increases due to the increase of the precipitation undercooling degree.

It is apparent from the photographs in Fig. 3.3(a) that in the case without Ti addition, the size of primary $M_7C_3$ carbides decreases as the cooling rate increase. It is also apparent from the comparison between Fig. 3.3(a) and 3.3(b) that the size of $M_7C_3$ carbides in the case of a 1.5mass% Ti addition is significantly smaller than that in the case without a Ti addition. This is due to a precipitation of TiC carbides.

![Fig. 3.3. Optical Microscope Observations for $M_7C_3$ carbide under different cooling rate, (a) Ti=0mass%, (b) Ti=1.5mass%](image)

As shown in Fig. 3.4(a) representing a case without Ti additions, the maximum size of primary $M_7C_3$ carbides (>11.2 μm) decreases from 151.9 to 53.9 μm with an increased cooling rate (from a sand mold to a metal mold). In addition, the number of eutectic $M_7C_3$ carbides, which in general has a size less than 11.2 μm, increases from $0.81 \times 10^3$ mm$^{-2}$ to $4.80 \times 10^3$ mm$^{-2}$ with an increased cooling rate. Moreover, as shown in Fig 3.4(b) representing a case with a 1.5mass% Ti addition, the maximum size of primary $M_7C_3$ carbides (>11.2 μm) is not changed too a large degree. However, the number of eutectic $M_7C_3$ carbides (<11.2 μm)
Fig. 3.4. Effect of cooling rate on $M_7C_3$ carbide size distribution of the hypereutectic HCCIs with (a): without Ti addition; (b): 1.5mass% Ti addition by using optical microscope photos.

increases from $1.29 \times 10^3$ mm$^{-2}$ to $2.49 \times 10^3$ mm$^{-2}$ with an increased cooling rate, when a 1.5mass% Ti addition is used.

Comparing Fig. 3.4(a) with Fig. 3.4(b), it can be seen that the size of primary $M_7C_3$ carbides in the case of a 1.5mass%Ti addition is significantly smaller than that in the case without a Ti addition. Furthermore, that the maximum sizes are 53.9 μm and 151.9 μm respectively. Making the story short, the size of primary $M_7C_3$ carbides of the hypereutectic HCCIs can be refined both by Ti additions and by increasing the cooling rate.
3.4 Effect of Ti addition on Solidification Structure

As mentioned in chapter 1, strong carbide forming elements, such as Ti, Nb, V, Nb, Zr etc., will react with carbon to form NaCl (MC) type carbides. Those MC type carbides can act as heterogeneous nuclei for the precipitation of M₇C₃ type carbides during the cooling and solidification of the melt. Therefore, based on this idea, we chose Ti to study its influence on the solidification structure of HCCI.

![Fig. 3.5. SEM and EDX analysis for TiC carbide with 1.5mass% Ti addition in the graphite mold.](image)

(Point A and C : Ti(C,N); Point B and D: (Ti,Mo)C)

As shown in Fig. 3.5, it is confirmed that the TiC carbides can act as a nuclei of M₇C₃ carbides. More specifically, it was found that TiC carbides can not only act as nuclei of M₇C₃ carbides, but they also contain a Ti(C, N) core. This is illustrated by the black point A, C in Fig. 3.5. Furthermore, EDX results show that the main composition particle in B and D is Ti, Mo and C, it should be (Ti, Mo)C. However, the chemical composition of the black points A and C shows that Ti, C and N are dominant, and that the TiC carbides should be Ti(C, N).

3.4.1 Effect of Ti addition on the carbides distributions

Fig. 3.6 shows the micrographs solidification structure for different Ti additions. The microstructure of M₇C₃ carbides is refined significantly with increasing Ti contents.
Fig. 3.6. Light optical microscope Observations for $M_7C_3$ carbide precipitate found in the graphite mold 
(a). Ti=0%, (b). Ti=0.75%, (c). Ti=1.5%, (d). Ti=3.0%.

Fig. 3.7. Effect of Ti addition on $M_7C_3$ carbides size distribution of the hypereutectic HCCIs in the graphite mold obtained by using optical microscope photos.

As shown in Fig. 3.7, the size distributions of $M_7C_3$ carbides also resemble a log-normal distribution. It can be seen that the maximum size of the primary $M_7C_3$ carbides decreases
Fig. 3.8. SEM observation for TiC carbide, (a): Ti=0.75mass%, (b): Ti=1.5mass%, (c): Ti=3.0mass%.

from 151.9 to 27.0 μm with an increased Ti addition in the graphite mold. However, the size and number of eutectic M$_7$C$_3$ precipitates do not change too a large degree (from 2.00×10$^3$ mm$^{-2}$ to 2.84×10$^3$ mm$^{-2}$) with an increased Ti content. The reason for this will be explained in section 3.2.3. The back scattered electron (BSE) observations for TiC carbides are shown in Fig. 3.8. TiC carbides are mostly located inside or at the boundary of M$_7$C$_3$ carbides, as shown in Fig. 12. Moreover, TiC carbides starts to grow and agglomerate when the Ti content is 1.5mass%, as shown in Fig. 3.8 (b). It is also apparent from the photographs in Fig. 3.8(c) that larger and coarser clusters of TiC carbides exist.

The size distribution of TiC carbides in the graphite mold for different Ti additions is shown in Fig. 3.9. These carbides generally have a size less than 10 μm. Moreover, it can be seen that both the size and number of TiC carbides increase with an increased Ti addition.

Also, Fig. 3.10 shows the size distribution of TiC carbides with 1.5mass% Ti addition in a sand mold, a graphite mold and a metal mold. The average size of TiC carbides with a 1.5mass% Ti addition does not change practically with an increased cooling rate. Also, the number of TiC carbides does not change due to the increased cooling rate. Consequently, it is clear that the precipitation of TiC carbides was not seemingly affected by the cooling rate.
Thus, it is confirmed that the cooling rate will not affect the precipitation behavior of TiC carbides.

**Fig. 3.9.** Effect of Ti addition on TiC carbide size distribution of the hypereutectic HCCIs in the graphite obtained by using SEM photos

**Fig. 3.10.** Effect of cooling rate on TiC carbide size distribution of the hypereutectic HCCIs with 1.5 mass% Ti addition obtained by using SEM photos
3.4.2 Effect of Ti addition and cooling rate on the volume fraction

Calculation results and experiment results of the volume fractions of M₇C₃ carbides and TiC carbides are shown in Fig. 3.11. It can be seen that the volume fraction of M₇C₃ carbides decreases with an increased cooling rate. The condition in the low cooling rate seems to be more close to the condition in the equilibrium state. However, the 5-10vol.% of M₇C₃ carbides did not fully precipitate in the high cooling rate condition. Moreover, the volume fraction of M₇C₃ carbides decreases with a Ti addition due to the reaction between Ti and C. Furthermore, the volume fraction of Ti carbides increases with increased Ti additions in the graphite mold. However, the volume fraction of TiC carbides does not change although the cooling rate changed.

If the experimental results are compared to the calculation results, it can be seen that the tendency is the same. Moreover, that the experimental results are closer to the PE calculation results. The agreement between experiment and calculation results is within 5%, which is
encouraging. This is due to the PE calculation considers the carbon back diffusion and consequently the results will be closer to the real experimental situation.

3.5 Classification of $M_7C_3$ carbides

In this study, it is suggested that the $M_7C_3$ type carbides in the HCCIs can be classified into primary $M_7C_3$ carbides and eutectic $M_7C_3$ carbides depending on the time of precipitation. The primary carbides precipitate in the melt before solidification (that is during cooling of the melt until the solidification temperature is reached). The eutectic $M_7C_3$ carbides precipitate during the eutectic reaction. The precipitation possibility of $M_7C_3$ carbides before and during solidification is estimated for the sample composition given in Table 2.1. This was done based on thermodynamic equilibrium calculations by using Thermo-Calc©. The volume fraction of precipitated primary $M_7C_3$ carbides, eutectic $M_7C_3$ carbides and TiC carbides are plotted against the temperature in Fig. 3.12.

![Fig. 3.12. Volume fraction of $M_7C_3$ carbide and TiC carbide of the hypereutectic HCCIs with different Ti addition obtained by using PE model calculation for Fe-3.98mass%C-16.8 mass%Cr-1.86 mass%Mn-0.943 mass%Mo-1.09 mass%Ni-0.970 mass%Si. *transformation points of $M_7C_3$ carbide](image-url)
It can be seen that the precipitation temperature of primary $M_7C_3$ carbides decreases with an increased Ti content. However, the precipitation temperature of TiC carbides increases slightly with an increased Ti content.

![Graph showing Thermo-Calc calculation and experimental results of total, primary and eutectic $M_7C_3$ carbides in hypereutectic HCCIs with different Ti additions.](image)

**Fig. 3.13.** Thermo-Calc calculation and experimental results of total, primary and eutectic $M_7C_3$ carbides in the hypereutectic HCCIs with different Ti additions. $M_7C_3$ carbide’s border size: (a) $d=7.9$ μm, (b) $d=11.2$ μm

**Fig. 3.13** shows Thermo-Calc calculation and experiment results of total, primary and eutectic $M_7C_3$ carbides in the hypereutectic HCCIs for different Ti additions. Here, (a) $d=7.9$ μm and
(b) \( d = 11.2 \, \mu m \) were adopted as the \( M_7C_3 \) carbide’s border size, \( d \). Comparing Fig. 3.13(a) with 3.13(b), it can be seen that experimental results with a 11.2 \( \mu m \) border size are closer to the calculation results from the viewpoint of the primary \( M_7C_3 \) carbides volume fraction (see \( \circ \) mark). Regarding eutectic \( M_7C_3 \) carbides (see \( \Delta \) mark), the experiment data are 5% lower than the calculation curve. This might be due to the difficulty of deciding the threshold from the gray images of the optical microscope photos. Moreover, the experimental results are close to the Partial Equilibrium (PE) prediction. The difference between the experimental results and the calculation results is lower than 5%. This can be explained by that the carbon back diffusion is taken into consideration in the PE calculation. Therefore, the results will be closer to experiment results. It is also found that the C content has a large influence on the total volume fraction of \( M_7C_3 \) carbides. More specifically, the total volume fraction increases with an increased C content, as shown in Fig. 3.13.

In summary, Fig. 3.13 shows that the total volume fraction of \( M_7C_3 \) carbides decreases as the Ti content increases; the volume fraction of primary \( M_7C_3 \) carbides decreases with an increased Ti content. However, the volume fraction of eutectic \( M_7C_3 \) carbides increases with an increased Ti content.

The contents of Fe, Cr, Ti, Mo, Mn in primary \( M_7C_3 \) carbides and eutectic \( M_7C_3 \) carbides are plotted against the carbide sizes in Fig. 3.14 for the sand, graphite and metal molds for a 1.5mass% Ti addition. As a general characteristic, it is shown that the content of Cr and Ti increases with an increased \( M_7C_3 \) carbide size, \( d \).
Fig. 3.14. Relationship between composition and size of primary M$_7$C$_3$ carbides and eutectic M$_7$C$_3$ carbides of the hypereutectic HCCIs with 1.5 mass% Ti addition under different cooling rate: (a) Metal mold, (b) Graphite mold and Sand mold.

However, the content of Fe and Mo decreases with an increased M$_7$C$_3$ carbide size; Moreover, the content of Mn does not change with an increased M$_7$C$_3$ carbide size for the sand, graphite and metal molds. It is concluded that the primary M$_7$C$_3$ carbides are dominant at higher Cr contents, and that the eutectic M$_7$C$_3$ carbides have lower Cr contents.

In summary, based on the analysis of size distribution and chemical composition, the M$_7$C$_3$ carbides were roughly classified into primary M$_7$C$_3$ carbides, which in general have size larger than 11.2 μm. Moreover, into eutectic M$_7$C$_3$ carbides which in general have a size smaller than 11.2 μm.
3.6 Effect of Cooling Rate and Ti Addition on the Mechanical Properties in As-Cast Condition of the hypereutectic HCCIs

In this chapter, the effect of cooling rate and Ti addition on the mechanical properties of the hypereutectic HCCIs is discussed, but only for as-cast conditions.

The bulk hardness of the hypereutectic HCCIs is determined by the hardness of carbides, such as TiC and $M_7C_3$ [21] and the matrix. The matrix of the hypereutectic HCCIs will obviously not change by a Ti addition. This is due to that it will mainly exist as a single austenite phase ($\gamma$-phase) together with small amounts of martensite ($\alpha$-phase) under as-cast conditions. Therefore, the bulk hardness of the hypereutectic HCCIs is mainly affected by the volume fraction of carbides.

Fig. 3.15 shows the bulk hardness of the hypereutectic HCCIs with different Ti additions for different cooling rates. The tendency is that the bulk hardness increases slightly with increased titanium contents. As shown in Fig. 3.11, when Ti is added, the volume fraction of TiC carbides increase and the volume fraction of $M_7C_3$ carbides decrease. TiC carbides might make a bigger contribution to the bulk hardness than $M_7C_3$ carbides, because the hardness of TiC carbides is in the range of 2000-3200HV. [4] However, the bulk hardness of the hypereutectic HCCIs in the graphite mold shows a big scatter because the TiC carbides are not uniformly distributed.

![Fig 3.15. Mechanical properties of the hypereutectic HCCIs with different Ti additions and different cooling rates.](image-url)
The wear loss of the hypereutectic HCCIs is determined by the amount of matrix and M₇C₃ carbides, although the hardness of TiC carbides is larger than that of the M₇C₃ carbides and the matrix. However, the presence of a small amount of TiC carbides will not contribute to the wear loss.

It can be seen that there is a tendency of an increased wear loss with an increased Ti content in the graphite mold experiments. This is due to the decrease of the volume fraction of M₇C₃ carbides. It seems that the austenite phase (γ-phase) which surrounds the agglomerated TiC might be easily peeled off during the wear process. This is leads to an increased Ti content. In summary, the hardness and wear loss of the hypereutectic HCCIs do not change significantly with increased Ti contents and cooling rates under as-cast conditions.

As a summary for this chapter, the mainly focus point on the carbides (M₇C₃ and TiC) evolution is quantitative discussed for as-cast condition by changing the cooling rates and titanium contents. Base on this work, the heat treatment process was performed in order to improve the mechanical properties of the hypereutectic HCCIs.
Chapter 4

Improvement of Properties by Heat Treatment

As mention in the previous chapter, the specimens, which were casted in a graphite mold with a 1.5mass% titanium addition, were used for heat treatments. The reason for the casting process and selected chemical composition (Table 2.1) is that: 1) primary M\(_7\)C\(_3\) carbides becomes finer because of the higher cooling rate provided by the graphite mold and the Ti addition, which enables TiC precipitations that can act as favorable nucleation sites for the primary M\(_7\)C\(_3\) carbides, 2) and it is possible to form secondary M\(_7\)C\(_3\) carbides during heat treatment, since the total volume fraction of primary M\(_7\)C\(_3\) carbides and eutectic M\(_7\)C\(_3\) carbides do not reach the equilibrium fractions in the as-cast condition.

In this chapter, we will set our focus point on how carbides (M\(_7\)C\(_3\) and TiC) and martensite evolution and their influence on the mechanical properties after heat treatment.

4.1 Phase diagram

Estimation of the Fe-17mass%Cr-4mass%C multicomponent system phase diagram is done by using the Thermo-Calc software, as shown in Fig. 4.1.

![Phase diagram](image_url)
It shows that the matrix phase changes from a fcc phase (an austenitic structure) into a bcc phase (a martensitic structure) at around 800°C. The MC type carbides (TiC carbides), M₇C₃ type carbides (primary, eutectic and secondary carbides) and bcc phase remained after the final cooling. It is in agreement with the experimental observations by SEM and EBSD.

**4.2 Evolution of M₇C₃**

The carbides mainly include primary M₇C₃ carbides and eutectic M₇C₃ carbides both before and after heat treatment, as shown in Fig. 4.2 and Fig. 4.3.

![Fig. 4.2. SEM observations of M₇C₃ and TiC after different heat treatments.](image)

![Fig. 4.3. EBSD phase colored maps using 0.1μm step size.](image)

(Color in phase maps: Blue: M₇C₃; TiC: Yellow; Green: Austenite; Red: Martensite; Greyscale: band contrast)
It is also noticed based on SEM and EBSD observations that fine secondary carbides precipitate in the matrix after heat treatment, as shown in Fig. 3.1(d) and Fig. 4.2. Especially, in Fig. 3.1(d), fine precipitates were clearly recognized as secondary M$_7$C$_3$ type carbides by using an EBSD analysis with a 0.03 μm step size.

The size distribution of M$_7$C$_3$ carbides from SEM and EBSD are shown in Fig. 4.4(a), and (b).

**Fig. 4.4.** M$_7$C$_3$ carbide size distribution in the hypereutectic HCCI by using (a): SEM images, (b): EBSD maps

From Fig. 4.4(a) and (b), we can clearly recognize the precipitation of secondary carbides (<1μm) after heat treatment. In order to understand the precipitation behavior of M$_7$C$_3$ carbides, besides the size distribution, the total carbide volume fraction has to be taken into
consideration. The total volume fraction of $M_7C_3$ carbides (primary, eutectic and secondary) obtained from SEM images and EBSD maps using image analysis is shown in **Fig. 4.5**.

![Fig. 4.5. Volume fraction of $M_7C_3$ and TiC carbides](image)

From the size distribution in **Fig. 4.4** and the total carbide volume fraction in **Fig. 4.5**, the precipitation behavior of $M_7C_3$ carbides is summarized as follows:

(1) For lower holding temperatures and shorter holding times during the heat treatment, such as $900^\circ C \times 2hr$, the number of fine secondary $M_7C_3$ carbides (less than 1 $\mu$m) and eutectic $M_7C_3$ carbides (less than 11.2 $\mu$m) increases. On the contrary, at higher holding temperatures and longer holding times of heat treatment, such as $1050^\circ C \times 6hr$, the size of coarse primary $M_7C_3$ carbides larger than 11.2 $\mu$m increases.

(2) This behavior is due to the following reasons. The precipitation of secondary $M_7C_3$ occurs actively at $900^\circ C$ close to the eutectic temperature and finishes completely within 2hr. The coarsening of all sizes of $M_7C_3$ carbides occur actively at higher holding temperatures and longer holding times during heat treatment.

(3) Thus, from the viewpoint of the precipitation of $M_7C_3$ (volume fraction) and the growth control/refinement of $M_7C_3$ (size distribution), a lower holding temperature such as $900^\circ C$ is preferred. This is regardless of the holding time during heat treatment.
(4) According to the reports of Wiengmoon, et al. [16, 22, 32] and Pearce, [33] in cast irons with higher Cr contents, such as 30mass% Cr, the secondary carbides were of $M_7C_3$ type or $M_{23}C_6$ type. These precipitate during conventional heat treatment, as shown in Table 4.1, however, we did not detect any $M_{23}C_6$ carbides in the hypereutectic HCCI in the present work. Therefore, only the $M_7C_3$ type carbides were examined based on the EBSD results.

Table 4.1 Secondary carbide type under different C and Cr content

<table>
<thead>
<tr>
<th>Type</th>
<th>C (mass%)</th>
<th>Cr (mass%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_7C_3$ type</td>
<td>2.8</td>
<td>18</td>
<td>S.K. Hann, et al</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>30</td>
<td>J.T.H. Pearce, et al</td>
</tr>
<tr>
<td>$M_{23}C_6$ type</td>
<td>2.4</td>
<td>30</td>
<td>A. Wiengmoon, et al</td>
</tr>
<tr>
<td></td>
<td>1.09</td>
<td>10.48</td>
<td>Y. Wang, et al</td>
</tr>
</tbody>
</table>

4.3 Evolution of TiC

The TiC carbides with a high precipitation temperature are uniformly distributed within the $M_7C_3$ carbides and the matrix, as shown in Fig. 4.2 and Fig. 4.3. The size distributions of TiC in as-cast condition and after various heat treatments are shown in Fig. 4.6(a) and (b).

![Graph showing size distribution of TiC carbides](graph.png)
Based on the volume fraction in Fig. 4.5 and the size distribution in Fig. 4.6, the precipitation behavior of TiC can be summarized as follows:

(1) At longer holding times of heat treatment, such as 6hr, the number of all sizes of TiC carbides increases.

(2) This behavior is caused due to the following reasons. The precipitation of TiC occurs mainly in the melt and finishes completely at higher temperatures above 1100°C. Moreover, the coarsening of all sizes of TiC particles occurs actively under longer holding times during heat treatment.

(3) Thus, from the viewpoint of the precipitation of TiC (volume fraction, size and number), longer holding time such as 6hr is preferred, regardless of the holding temperature level, as the heat treatment condition.

4.4 Evolution of Matrix

The matrix of hypereutectic HCCI includes both austenite and martensite before and after heat treatment, as shown in Fig. 4.3 and Fig. 4.7. However, the austenite is dominating in the as-cast condition and the martensite dominates after heat treatment.

EBSD phase maps with 0.1μm and 0.03μm step sizes are shown in Fig. 4.3 and Fig. 4.7,
respectively. It is clear that the matrix essentially consists of austenite with a small amount of martensite in the as-cast condition. The inverse pol figure (IPF) map in Fig. 4.7 shows the orientation of the martensite units, and it is clear that the martensite unit size differs between the different heat treatment conditions.

The size distribution of martensite units in as-cast condition and after the different heat treatments is shown in Fig. 4.8. It shows the results combining data from 0.03μm and 0.1μm step size. These are also plotted with a logarithmic scale. From Fig. 4.8, it is seen that large
Martensite:

As cast
900°C × 2hr
1000°C × 2hr
1050°C × 2hr
900°C × 6hr
1000°C × 6hr
1050°C × 6hr

Martensite:

As cast
900°C × 2hr
1000°C × 2hr
1050°C × 2hr
900°C × 6hr
1000°C × 6hr
1050°C × 6hr

Fig. 4.8. Size distribution of martensite unit.

martensite units above 4μm is present under the conditions of high temperatures or long holding time: 900°C×6hr, 1000°C×6hr and 1050°C×6hr.

Compared to the higher temperatures, the size of the martensite unit decreased at lower heat treatment temperatures. The volume fraction of martensite is shown in Fig. 4.9.

The EBSD maps, which were used for calculating the volume fraction of martensite includes the non-indexed regions. The volume fraction of martensite calculated by using the 0.1 μm and the 0.03 μm step size EBSD maps give quite different results, as shown in Fig. 4.9. Thus, from the viewpoint of size distribution and volume fraction of martensite, the formation
behavior of martensite is summarized as follows:

1. At longer holding times during heat treatment, such as 6hr, the volume fraction of martensite increases.
2. At long holding times, such as 6hr, a lower holding temperature results in a more refined martensite.
3. Thus, from the viewpoint of the transformation promotion of martensite (volume fraction) and the refinement of martensite unit (size distribution), longer holding time such as 6hr and lower holding temperatures such as 900°C is recommended.

4.5 Mechanical properties

Previous studies on the effect of a matrix structure on the wear resistance suggest that a martensitic matrix offers a better wear resistance than an austenitic matrix. [33, 34] It is also reported [1,2] that two competing effects will influence the final properties. These effects are (a) a high carbon martensite phase, which forms at higher temperatures tends to increase the hardness, and (b) the increasing retained austenite content at higher temperatures, tends to reduce the hardness.

**Fig. 4.10** gives the correlation between hardness and wear resistance in as-cast condition and after heat treatment. It is seen that both the hardness and the wear resistance is improved markedly after heat treatment. In addition, the wear resistance increases with an increased holding time from 2hr to 6hr. However, both the hardness and wear resistance decrease with an increased holding temperature from 900°C to 1050°C.

![Fig. 4.10. Mechanical properties of the hypereutectic HCCI.](image-url)
In the as-cast condition, the matrix almost consists solely of austenite. Clearly the hardness of austenite is lower than that of martensite.

By considering the results of volume fraction and size distribution of M\textsubscript{7}C\textsubscript{3}, TiC and martensite units in sections 4.2, 4.3, 4.4, on the observed properties in Fig. 4.10, the mechanism of improved mechanical properties was deduced as follows:

Longer holding time leads to the growth promotion of TiC (volume fractions), and the transformation promotion of martensite (volume fraction) as well as the refinement of martensite units (size distribution). However, it also leads to a coarsening of M\textsubscript{7}C\textsubscript{3}. Consequently, longer holding times will increase the wear resistance, due to the altered matrix toughness and the decreased hardness, which is due to the coarsening of M\textsubscript{7}C\textsubscript{3}.

A lower holding temperature leads to precipitation promotion of M\textsubscript{7}C\textsubscript{3} (volume fraction) and the growth control/ refinement of martensite unit (size distribution). Consequently, lower holding temperatures will generate increased wear resistance and hardness due to the fine dispersion of M\textsubscript{7}C\textsubscript{3}.

Finally, a lower holding temperature close to eutectic temperature and a longer holding time is the most suitable heat treatment conditions for Ti- added hypereutectic HCCI.

As a summary, the relationship between carbide precipitation, martensite units and mechanical properties are discussed base on the volume fraction and the size distribution of carbide precipitates (M\textsubscript{7}C\textsubscript{3} and TiC) as well as martensite units. Possible mechanism is proposed to explain the improvement of mechanical properties through the heat treatment process. And the best heat treatment strategy is found.
Chapter 5

Conclusions

This thesis focus on refining the microstructure and improving the properties of Ti-added hypereutectic high chromium cast iron. The size distribution, composition and morphology of carbides and martensite units in the Ti-added hypereutectic HCCI with main composition of Fe-17mass%Cr-4mass%C are quantitatively studied. The most important conclusions reached in this study can be summarized as follows:

General conclusions of supplement 1:

1) $M_7C_3$ carbides were classified into “primary $M_7C_3$ carbides” and “eutectic $M_7C_3$ carbides” with a 11.2$\mu$m border size;
2) The maximum size of the primary $M_7C_3$ carbides decreased to 53.9 $\mu$m and the number of eutectic $M_7C_3$ carbides increased to $4.80 \times 10^3$ mm$^{-2}$ when the cooling rate was $110 ^\circ C/min$;
3) Meanwhile, the maximum size of the primary $M_7C_3$ carbides decreased from 151.9 to 27.0 $\mu$m and the total volume fraction of $M_7C_3$ carbides decreased with an increased Ti content. Moreover, The size and number of TiC carbides both increase with an increased Ti addition;
4) TiC carbides with high formation temperatures can not only act as nuclei of $M_7C_3$ carbides, but they also contain a core, Ti(C, N). It was also found that TiC carbides precipitation was not obviously affected by the cooling rate;
5) The properties (hardness and wear loss) of the hypereutectic HCCIs do not change significantly with increased Ti contents and cooling rates under as-cast conditions.

General conclusions of supplement 2:

1) From the viewpoint of the precipitation promotion of $M_7C_3$ (volume fraction) and the growth control/ refinement of $M_7C_3$, the growth promotion of TiC (volume fractions) and the transformation promotion of martensite (volume fraction) and the refinement of martensite unit (size distribution), the best heat treatment process is $900 ^\circ C \times 6hr$;
2) Moreover, both wear resistance and hardness were improved in case of lower holding temperatures and longer holding time $M_7C_3$ carbides.
**Suggestions for Future Work**

In this thesis, we select Ti as a carbide promoter to refine the microstructure of Hypereutectic HCCI. Actually, other strong carbides forming elements, such as Zr, Hf, V, Nb and B can also be used to refine the microstructure of Hypereutectic HCCI. Moreover, the complex addition of those elements in Hypereutectic HCCI may also improve the microstructure.

In order to control and understand the carbide precipitation behavior of Hypereutectic HCCI in as cast condition deeply, the accurate transformation temperature from a liquid phase to a solid phase should be clear. In this case, differential scanning calorimetry (DSC) thermal-analysis method can be applied to predict the accurate transformation temperature.

Although the volume fraction of the secondary carbides is low (~5%), the precipitation behavior of Hypereutectic HCCI during the heat treatment should be discussed deeply. It will help us to understand the mechanism of improvement of mechanical properties after heat treatment.

Statistical analysis of carbides is also very important to understand the characteristic of carbides. We can analysis the maximum size of carbides by using extreme value of statistics and estimate the 3D carbides size distribution base on 2D carbides size distribution by using Schwartz-Saltykov (ss) method. Furthermore, the electric extraction experiment for Hypereutectic HCCI can be used to separate carbides from the matrix. Thus, it will be possible to get more clearly three-dimensional experimental results on the carbides size distribution. These results may thereafter be used to verify the calculation.
References