Interface temperature measurement of $\text{M}_2\text{C}$ and $\text{M}_6\text{C}$ eutectic carbides in the Fe–Mo–C system

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Abstract

The high speed cast iron, which is used for hot rolling parts, needs high fracture toughness and wear resistance. To improve these properties, the control of eutectic carbides, $\text{M}_2\text{C}$, $\text{M}_6\text{C}_2$, $\text{M}_6\text{C}$ and MC is important by adding elements such as Cr, W, V and Mo.

The aim of this study is to estimate which carbide will solidify under certain solidification conditions and compositions. This prediction criterion can be gained by measuring the interface temperature of each carbide in various samples with different solute elements, composition and growth rate.

In this report, the solidified temperature of $\gamma + \text{M}_2\text{C}$ and $\gamma + \text{M}_6\text{C}$ eutectic carbide in the Fe–Mo–C ternary system in the composition range near to the eutectic monovariant line, was measured during the unidirectional solidification process. The relationship between solidified interface temperature and growth rate was obtained. In eutectic solidification along the $\gamma + \text{M}_6\text{C}$ monovariant line, a coefficient of undercooling, the $k$ value, was obtained.

The authors have already measured the $k$ values of other eutectic carbides, such as $\gamma + \text{M}_6\text{C}$, austenite + $\text{M}_6\text{C}_2$, and $\gamma + \text{VC}$ in Fe–Cr–C and Fe–V–C system. The paper also discusses the relationships between these properties of eutectic carbides. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: High speed cast iron; Phase selection; Eutectic carbide

1. Introduction

1.1. Selection of eutectic carbide

As seen in the peritectic system, when two stable/metal-stable phases are grown in competition, it is possible to predict the phase which will solidify by the phase selection criterion. The interface temperature dependence on the growth rate in each stable and metastable phase is determined using cell/dendrite growth theory. The criterion that the highest interface temperature phase is grown among all competitive phases, can be adapted [1].

Also, this phase selection criterion can be applied, in the eutectic system, for example, to understand the transfer of eutectic carbide solidified in cast iron.

In the binary Fe–C system, metastable cementite grows under high cooling rate. The eutectic interface temperature can be estimated by the eutectic temperature and undercooling, as derived by Jackson and Hunt [2]:

$$\Delta T = k\sqrt{V}$$

(1)

The critical growth rate is estimated by using the coefficient $k$ of $\gamma + \text{M}_2\text{C}$ eutectic and $\gamma + \text{graphite}$ in the Fe–C binary system [3].

In the ternary system, for the high chromium cast iron, Fe–Cr–C system, there is a problem of the solidification of $\text{M}_6\text{C}$ in the high growth rate range. For example, according to the path followed in the phase diagram, i.e. under relatively slow growth rate, the sample, initial composition at hypoeutectic, first becomes the solidified austenite phase. Then $\gamma + \text{M}_6\text{C}_2$ eutectic carbide is grown. After the liquidus composition passes through the peritectic–eutectic reaction, $\gamma + \text{M}_6\text{C}$ eutectic is grown. In the high growth rate range, the solidification sequence changes. In this case, followed by the austenite, the growth of $\gamma + \text{M}_6\text{C}$ eutectic without $\text{M}_6\text{C}_2$ eutectic is expected. To clarify this phenomenon, the solidification path during $\gamma$ growth and the undercooling function of both monovariant eutectics need to be made clear. In ternary monovariant eutectic growth, the interface temperature equation was derived by McCartney et al. [4],

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these purposes, measuring the interface temperature of each eutectic carbide is necessary in various Fe–C–M systems with different solute elements, compositions and growth rates.

In previous work, the $k$ values of $\gamma + M_6C$ and $\gamma + M_2C_3$ eutectic in the Fe–Cr–C system were measured by using the unidirectional solidification process. Then, a $\gamma + M_2C_3/\gamma + M_6C$ phase selection map was calculated using these $k$ values [5]. The $k$ value of $\gamma + VC$ eutectic carbide in the Fe–V–C system for the composition near to the $\gamma + VC$ eutectic monovariant line was also measured [6]. The paper also discussed the microstructure selection near to the $\gamma + VC + M_2C$ ternary eutectic composition.

In this report, the solidification temperature of $\gamma + M_6C$ and $\gamma + M_2C$ eutectic carbide in the Fe–Mo–C ternary system was measured during the unidirectional solidification process.

2. Experiment

Fig. 1 shows the liquidus projection of the Fe–Mo–C system. $\gamma$ forms eutectic with $M_6C$ carbide along the $\gamma + M_6C$ monovariant line at high Mo and low C content. After the liquidus composition passes through the peritectic–eutectic reaction at 18.98 mass%Mo, 2.97 mass%C, the eutectic monovariant line change to $\gamma + M_2C$. Finally, $\gamma + M_2C + M_6C$ ternary eutectic forms at 13.37 mass%Mo, 4.17 mass%C. For the experiments, two compositions of samples with Fe–19.8Mo–1.98C and Fe–15.8Mo–3.07C...
(mass%) marked as E and F, respectively, in Fig. 1 were used. The apparatus for measuring the interface temperature of the eutectic carbides during a unidirectional solidification with thermocouple elements was almost of the same construction as reported earlier [5,6].

The temperature gradient of this furnace in the solidification range was 14 K mm⁻¹ by using a water-cooled Ga–In liquid metal bath. The moving rate of sample changed from 1 μm s⁻¹ to 0.5 mm s⁻¹.

A crucible was connected to the moving element at the top, and thermocouple elements were put into the crucible at this connecting part. An Ar atmosphere is maintained inside the crucible. The experimental procedure was as follows. The sample was set in the furnace, which keeps the prescribed temperature. After melting of the upper part of the sample in the temperature gradient, a thermocouple element was inserted into it. The thermocouple element was made up to two thermocouples (Pt–6%Rh/Pt–30%Rh). For temperature measurement at different heights, the thermocouples were set 5 mm apart from each other.

Then a sample was pulled down by motor to effect unidirectional solidification whilst logging the thermocouple data. Quenching was performed after a prescribed time beyond the interface. The sample was cut and polished in longitudinal and cross-sections to determine the kind and order of the solidified phases, then to measure the freezing interface position of these phases and thermocouple position. The distance between a quenched interface and a thermocouple position divided by the growth rate yields the time from an interface crossing the thermocouple position to quenching. Then the interface temperature could be obtained from the temperature history. At that time, the growth rate is calculated from the difference of growth distance between samples of a different pulling time under the same conditions.

From these results, the relation between growth rate and solidification temperature, and the relation between growth rate and eutectic spacing for each eutectic carbide was measured. Finally, from these curves, the coefficient of undercooling, i.e. the values of k and the constant parameter $\lambda \sqrt{V}$, were obtained.

3. Experimental results and discussion

3.1. Unidirectional solidification microstructure

Unidirectional solidification microstructure at 10 μm s⁻¹ growth rate are shown in Fig. 2. The microstructure of composition E(Fe–19.8 Mo–1.98C) was as follows. $\gamma$ dendrite grew as primary phase. Then, $\gamma + M_6\text{C}$ lamellar eutectic was observed at the inter-dendrite region at
1 \mu m s^{-1} growth rate. \gamma + M_2C eutectic was also observed between \gamma + M_6C eutectics at higher growth rate, which is consistent with the solidification path expected from the phase diagram. The micro-structure of composition F(Fe–15.8 Mo–3.07C) was that the cellular \gamma + M_2C eutectic was observed between \gamma dendrite. The M_2C carbide formed fine rods in eutectic because of the large composition difference between \gamma and M_2C as seen in Fig. 6, and the location of monovariant line.

The measured spacing of \gamma + M_6C and \gamma + M_2C eutectic is shown in Fig. 3, in which both eutectic satisfied the rule \lambda V^{1/2} = \text{const.} These constant values were 2.24 \times 10^{-4} mm^{3/2} s^{-1/2} for \gamma + M_6C and 1.05 \times 10^{-4} mm^{3/2} s^{-1/2} for \gamma + M_2C.

### 3.2. Interface temperature measurements

Fig. 4 shows the relation between interface temperature of \gamma + M_6C eutectic and the square root of the growth rate from the results for sample E. The slope of this plot gives the undercooling coefficient \kappa as 88 K mm^{-1/2} s^{1/2} for \gamma + M_6C eutectic. Fig. 5 shows the same relationships for \gamma + M_2C eutectic from the results for sample F. The \kappa value for \gamma + M_2C eutectic was obtained as 206 K mm^{-1/2} s^{1/2}.

In previous work [5], the inter-dendrite eutectic changed from \gamma + M_6C to \gamma + M_2C with increasing growth rate accompanied by \gamma + M_6C/\gamma + M_2C peritectic–eutectic reaction in the Fe–Cr–C system. This phenomenon can be understood by the interface temperature of \gamma + M_2C eutectic being higher than the interface temperature of \gamma + M_6C over some critical growth rate, because the \gamma + M_6C eutectic has a larger \kappa value than the \gamma + M_2C eutectic. In the Fe–Mo–C system, the peritectic–eutectic reaction point exists between two monovariant eutectics, \gamma + M_6C and \gamma + M_2C. However, lower temperature eutectic, \gamma + M_2C has a larger \kappa value than higher temperature eutectic, \gamma + M_6C. This suggests that the alloy which has a composition near to the \gamma + M_2C monovariant line will not change the secondary eutectic, followed by primary \gamma, to \gamma + M_2C.

### Table 1

Experimental results: \lambda V^{1/2} [mm^{3/2} s^{-1/2}]

|          | Fe–C       | Fe–Cr–C    | Fe–V–C     | Fe–Mo–C    |
|----------|------------|------------|------------|------------|
| \gamma + Graphite | 202\textsuperscript{a} |            |            |            |
| \gamma + M_6C       | 76\textsuperscript{b} | 60         |            |            |
| \gamma + M_2C       |             | 240        |            |            |
| \gamma + VC         |             |            | 306        |            |
| \gamma + M_6C       |             |            | 88         |            |
| \gamma + M_2C       |             |            | 206        |            |

\textsuperscript{a} Ref. [7].

\textsuperscript{b} Ref. [3].

### Table 2

Experimental results: \kappa [K mm^{-1/2} s^{1/2}]

|          | Fe–C       | Fe–Cr–C    | Fe–V–C     | Fe–Mo–C    |
|----------|------------|------------|------------|------------|
| \gamma + Graphite | 202\textsuperscript{a} |            |            |            |
| \gamma + M_6C       | 76\textsuperscript{b} | 60         |            |            |
| \gamma + M_2C       |             | 240        |            |            |

\textsuperscript{a} Ref. [3].

Fig. 6. Composition map of \gamma and eutectic carbides in the Fe–M–C (M = Cr, V, Mo) system.
composition distance, \( C' \), also has a larger \( k \) value, and a smaller \( \Delta V^{1/2} \) value.

4. Conclusions

1. In the Fe–Mo–C ternary system, the solidified temperature of \( \gamma + M_6C \) and \( \gamma + M_2C \) eutectic carbides was measured during the directional solidification process. The relationship between the solidified temperature and the growth rate was obtained. In eutectic solidification along the \( \gamma + M_6C \) and \( \gamma + M_2C \) monovariant line, a coefficient of undercooling, according to equation \( \Delta T = k\sqrt{V} \), i.e. the \( k \) value, is \( 88.2 \text{ K mm}^{-1/2} \text{ s}^{1/2} \) for the \( \gamma + M_6C \) and \( 206 \text{ K mm}^{-1/2} \text{ s}^{1/2} \) for \( \gamma + M_2C \).

2. The eutectic spacing dependence on the growth rate satisfies the rule \( \lambda \sqrt{V} = \text{const} \), in \( \gamma + M_6C \) and \( \gamma + M_2C \) eutectic. The constant value \( 2.24 \times 10^{-4} \text{ mm}^{3/2} \text{ s}^{-1/2} \) for \( \gamma + M_6C \) eutectic, and \( 1.05 \times 10^{-4} \text{ mm}^{3/2} \text{ s}^{-1/2} \) for \( \gamma + M_2C \) eutectic.

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