Solute Concentration and Carbides Formation for Steel Milling Rolls

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(Received on January 19, 2009; accepted on March 9, 2009)

The selection and the formation of carbide govern quality and the service life of hot steel milling rolls. Thus the microsegregation and the formation of the carbides and the graphite during the solidification have been investigated for high speed steel type cast iron and Ni-hard type cast iron. The crystallization of high speed steel type cast iron proceeds in the order of primary austenite (γ), γ+MC and γ+M2C eutectic. On the other hand, in Ni-hard type cast iron, eutectic graphite flakes can crystallize after the formation of primary γ, and γ+M6C eutectic by controlling the content of Ni and Si in spite of containing strong carbide formers such as Cr. As γ+carbide eutectic grows, the residual liquid among eutectic cells becomes rich or poor in carbide formers according to the partition coefficient between residual liquid and eutectic cell. It is realized that the change of composition of carbide formers during the solidification is estimated with Scheil-Gulliver equation and computed phase diagrams in both of cast irons. The graphite forming tendency is also evaluated by applying the parameter, which expresses the solubility limit of carbon to the molten iron for Ni-hard type cast iron.

KEY WORDS: carbide; graphite; segregation; eutectic cell; solidification; roll.

1. Introduction

White cast irons, which disperse a large amount of primary and eutectic carbides in the matrix, are widely applied to abrasion resistant parts of various machines and industrial plants, because of their superior abrasion and thermal resistance.1–3) High chromium cast iron, high-speed-steel (HS) type cast iron and Ni-hard type cast iron are generally selected for the steel milling rolls.4) However, the recent development in milling technique demands the remarkable improvement and the precise control of roll quality. The wear resistance of conventional white cast iron, composed of γ+M2C eutectic, is significantly improved by adding higher amount of Cr, V, Nb and Mo, since these alloy elements crystallize harder carbides of M3C, MC or M2C in austenite (γ) matrix. HS type cast iron, which contained W, Mo and V such as high speed steel tools, consists of MC, M2C or M6C eutectic carbides. As shown in Fig. 1, MC type carbides are relatively harder than other carbides. Additional of Nb and V to white cast iron results in the formation of fine MC carbide and enhance the abrasion resistance.3–8) On the other hand, Ni-hard type cast iron consists of matrix, M3C carbide and graphite. The formation of graphite generally suppressed in white cast iron, since the graphite-austenite eutectic structure is preferentially worn out. However, distribution of a small amount of graphite flakes or particles, which is characteristics of cast iron, can improve flaking and scoring resistance as a lubricant in the steel making operation. It is necessary to understand the composition change of strong carbide formers such as Cr, V and Nb to control the both of harder carbides and graphite crystallization. Furthermore, the matrix transforms to martensite structure during rapid cooling to a room temperature. Therefore, the analysis of redistribution of alloying elements during solidification and the optimization of effective alloying design is desirable for the development of...
the proper solidification microstructure. Computed phase diagram, which was based on CALPHAD method and in which Gibbs energy, activity and interaction coefficient of phases were calculated, has been well developed recently for the alloy design field. This diagram can be remarkably useful for the estimation of crystallization of primary γ, carbides and graphite especially for the multi-alloy system.

In the present study, the analysis of redistribution of alloying elements during solidification has been performed in order to understand the carbide and graphite formation mechanisms and the solidification sequence has been evaluated with the aid of experimental and computed phase diagrams for HS type cast iron and Ni-hard type cast iron.

2. Experimental Procedure

Blocks of 99.99% pure Fe, Cr and Ni and ferroalloys of Fe–5.3mass%C (hereby abbreviate to %), Fe–75%Si, Fe–64%Nb, Fe–83%V, Fe–62%Mo were charged into an alumina crucible at 1 kg in weight. Specimen was melted in a carbon resistant furnace at 1 673 K in a argon atmosphere. The alloy composition of HS type cast iron specimen was Fe–2.48%C–5.17%Cr–5.27%Mo–5.31%V–4.73%W. Because that the HS type cast iron, which applied to the hot steel strip finishing mills, generally contains around 2% C, 5% Cr, 5% Mo, 5% W, 5% V, these composition were set as target. On the other hand, Fe–3.37%C–1.87%Cr–0.55%Mn–0.26%Ni–0.9%Si alloy was cast for Ni-hard type cast iron. The as-cast specimens were smoothly polished by SiC sheets and a diamond paste, and the amount and shape of primary carbides and graphite were examined by using an optical microscope. The specimens were etched by two reagents of Pickral reagent and Murakami’s solution to examine metallographically.

Thermal analysis was carried out to measure the liquidus temperatures of phases in a SiC electric resistance furnace. The specimen was placed inside of an alumina-silica crucible, then heated at 10 K/min until 1 723 K in argon atmosphere. After holding the melt bath for 10 min to dissolve the alloying elements completely, the specimen was cooled at 10 K/min to 1 173 K, and subsequently quenched into water. The solidification sequence of each phase was also evaluated based on the temperature profile and the quenched microstructure. Chemical composition of each alloy element was measured by EPMA (Shimadzu Co. Ltd., EPMA-1600) as the relative intensity, and then corrected it by ZAF method to get accurate composition. Twenty micrometers of electric beam-size was also introduced to measure the average composition of eutectic microstructure to regard the eutectic phase as a single phase. Microsegregation and solute distribution were evaluated and the partition coefficient was calculated as the ratio of composition of liquid and solid phase. The solubility parameter was also calculated to predict the graphite forming tendency.

Liquids projection of each system was calculated by phase diagram software (Thermo-Calc (Thermo-Calc Software, Inc.)) with the standard database of SSOL, and then the compositional changing during solidification sequence was compared with experimental phase diagram.

3. Results and Discussion

3.1. Compositional Development in High Speed Type Cast Iron

Microstructure consists of primary γ dendrite, MC type carbide, which is un-etched by both of two reagents, and M₇C and M₇C₃ type carbides, which are colored in brown by Murakami’s solution. MC carbide contains 57% V, 53% Cr, 7% Mo, 3% Fe, thus large amount of V. The compositions of M₇C carbide are 35%Mo–30%W–15%Cr–12%V–8%Fe. Generally, distribution of V rich MC type carbide and Mo, W rich M₇C type carbide remarkably improve the wear resistance of roll and prolong the service life. Furthermore, small amount of M₇C₃ type carbide, which contains 58%Fe–21%Cr–11%Mo–6%W–4%V, is distributed. This tendency of crystallization of enriched Cr in M₇C₃ type carbide is similar to the result of the high speed tool steel reported by Fischmeister.

From the result of thermal analysis, primary γ initially solidifies 1 548 K for HS specimen. Then, γ+MC eutectic occurs at 1 492 K, γ+M₇C eutectic at 1 437 K, finally γ+M₇C₃ eutectic is solidified at 1 388 K until the complete solidification at 1 365 K. As-solidified specimen shows the area ratio of 25% of primary γ, 52% of γ+MC eutectic, 15% of γ+M₇C eutectic, and 6% of γ+M₇C₃ eutectic structure. MC carbide crystallizes rod-like or plate-like shape with the area fraction of 22% in γ+MC eutectic cell. Thus, MC carbide could be dispersed more uniformly in comparison with M₇C, which comprise 41% of γ+M₇C eutectic or M₇C₃, which comprise 62% of γ+M₇C₃ eutectic cells.

The morphology and volume fraction of eutectic cells change depending on the composition of specimen. Figure 2 shows the summary of the compositional change of each element on the basis of the several quenched specimen, which is partially solidified at each stage. Where, the area fraction is regarded as the volume fraction. Solid symbols show the development of solute element of the residual liquid phase at solid/liquid (S/L) interface. On the other hand, open symbols explain the estimation of compositional change by partition coefficient, the volume fraction, the initial composition and Scheil–Gulliver model, in which no diffusion occurs in solid phase, as shown in Eq. (1).

![Fig. 2. Changes of concentration of alloy elements in residual liquid due to the microsegregation for high speed steel type cast iron.](image-url)
\( C_L = C_0(1 - f_s)k^{(k-1)} \) ......................................(1)

Where, \( C_L \) is the composition of residual liquid, \( C_0 \) is the initial composition, \( f_s \) is the volume fraction of primary \( \gamma \) or eutectic cells, \( k \) is partition coefficient. Partition coefficient of each element is estimated by solute composition of the solid phase and that of the residual liquid at S/L interface of quenched specimen. Since eutectic cell consist of fine \( \gamma \) and carbide phases, it is quite difficult to distinguish the partition coefficient of \( \gamma \) and carbide. Thus, the mixed phase of \( \gamma \) and carbide was regarded as a single phase unit, and average partition coefficient was defined even to the eutectic microstructure in present study as shown in Table 1. The composition of each alloy element should be also evaluated in relation with compositions of other alloy element, since the compositional development depends on the balance of those of all elements at a certain temperature. However, the composition was estimated individually in present study because of the simplification of calculation. According to the Fig. 2, Cr, Mo, W and V are slightly rejected into residual liquid during the crystallization until 25% of volume fraction, since they have small partition coefficients. However, V compositions reduce soon due to the large partition coefficients during the \( \gamma + MC \) eutectic crystallization. This depletion of V can be predicted, because that MC type carbide remarkably contains V, which indicates the large amount of V is consumed to crystallize the MC carbide. On the contrary, due to the lower partition coefficient of Cr, Mo and W to \( \gamma + MC \) eutectic cell, the compositions of these elements still increase until the crystallization of \( M_2C \) carbide at 70% of volume fraction. However, once \( \gamma + M_2C \) eutectic starts to form, the compositions of Mo and W reduce significantly because of the larger partition coefficients to \( \gamma + M_2C \) eutectic cells. Finally, \( M_3C_3 \) crystallizes from Cr-rich residual liquid at 94% of volume fraction. The compositional distribution, which is estimated by Scheil–Gulliver model using initial compositions and the assumption of eutectic phase as the single phase, changed in relation with values of the partition coefficients at each solidification stage, and result in the similar tendency to the experimental results in spite of some deviation between them.

![Graph](image)

The solute distribution of alloying elements during solidification influences the crystallization and the volume fraction and follows eutectic microstructure in multi alloy system. Thus it is necessarily to compare and evaluate the computed estimation and experimental result. Therefore, compositional development was studied by the aide of the computed phase diagram, in which Gibbs energy, activity and interaction coefficient of phases were calculated.9) Comparison of phase diagrams resulted from experimental results for high speed steel type cast iron. Table 1. Partition coefficient to dendrite and eutectic structures for high speed steel type cast iron.

| Phase        | \( k_{Cr} \) | \( k_{Mo} \) | \( k_{V} \) | \( k_{V} \) |
|--------------|--------------|--------------|--------------|--------------|
| \( \gamma + MC \) | 0.80         | 0.34         | 0.32         | 0.42         |
| \( \gamma + M_2C \) | 0.56         | 0.65         | 2.65         | 0.84         |
| \( \gamma + M_3C_3 \) | 0.52         | 1.57         | 1.59         | 2.63         |

* Average of two phases

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3.2. Compositional Development in Ni-hard Type Cast Iron

Microstructure consists of primary \( \gamma \) dendrite, MC type carbide, which is slightly etched by Murakami’s solution, \( M_3C \) type carbides, which are colored in gray by Pickral reagent in Ni-hard type cast iron. From the result of thermal analysis at 10 K/min of cooling velocity, primary \( \gamma \) initially solidifies 1 505 K for Ni-hard specimen. Then, \( \gamma + M_3C \) eutectics occurs at 1 385 K, and \( \gamma + \) graphite eutectic immediately starts. In case of Ni-
hard type cast iron, the area ratios of 35% of primary $\gamma$, 63% of $\gamma+M_3C$ eutectic and 2% of graphite are obtained. Ni-hard type cast irons with a small amount of graphite are still applied to the finishing mills because of their better performance such as flaking and scoring resistance, and 2% in area fraction of graphite is generally enough to improve the flaking resistance. Figure 4 shows the compositional change of each element on the basis of the several quenched specimen, which is partially solidified at each stage similarly to HS specimens. Solid symbols show the experimental results and open symbols explain the estimation by the initial composition and Scheil–Gulliver equation. Obtained partition coefficient of each element for Ni-hard type specimen is listed in Table 2. According to the Fig. 4, Cr and Mo are slightly rejected into the liquid during the crystallization until 35% of volume fraction. On the contrary, Ni and Si compositions reduce because of small partition coefficients. During the solidification of $\gamma+M_3C$, the compositions of Mo, Si and Ni increase and that of Cr decreases until the crystallization of graphite at 98% of volume fraction. From Fig. 5, Si composition slightly reduces from 0.9% of initial composition to 0.79%, then $\gamma+M_3C$ eutectic stars, that solidification path is quite similar to the compositional development as shown in Fig. 4. Furthermore, the enrichment of Si followed Scheil–Gulliver equation. Then graphite is crystallized, when Si composition reached to 3%, where graphite can crystallize in liquids surface of stable phase diagram. Therefore, solidification path could be predicted such as arrows and circles. On the contrary, Cr composition slightly increases from 1.87% of initial composition to 2.57%, then $\gamma+M_3C$ eutectic stars. Depletion of Cr roughly to 0.5% reaches to the graphite area in liquids surface of stable phase diagram. Therefore, solidification path of Cr could be also predicted such as arrows and circles as shown in Fig. 5(b). However, it is necessary to improve the accuracy of composition to attain more accurate estimation on solidification microstructure.

### 3.3. Prediction of Graphite in Ni-hard Type Cast Iron

The effect of each element on the graphite formation tendency is quite important, since distribution of graphite is most remarkable characteristics of Ni-hard type cast iron. The graphite formation is quantitatively evaluated based on the influence of element (i) on the solubility of C in molten iron ($m_i$). The synthetic influence of alloying elements on graphite formation was appropriately estimated by the fol-
following solubility parameter (Eq. (2)), a simple summation of $C_iL$, in the case of high alloy cast iron such as Ni-hard type cast irons.\(^{12}\)

$$
\sum C_i m'_i = 0.063 [\%Cr] + 0.015 [\%Mo] - 0.31 [\%Si] - 0.06 [\%Ni]
$$

Where, $C_iL$ is the composition of each element in molten iron. The change in solubility parameter of residual liquid is evaluated as shown in Fig. 6. The solid symbol corresponds the parameter, which calculated by experimental composition, and open symbol corresponds the calculated value by the Scheil–Gulliver equation. Firstly the solubility parameter increases by the formation of primary $\gamma$, since the Cr, which is carbide former, rejected to liquid phase. However, the enrichment of Si and Ni, which are graphite former, result in the depletion of the parameter following the Scheil–Gulliver model with the crystallization of $\gamma+M_2C$ eutectic, and the parameter finally takes the value of $-0.52$ at 96% of the solid fraction, where $\gamma$+graphite eutectic starts.

4. Conclusion

Redistribution of alloying elements during solidification were investigated for High Speed Steel type cast iron and Ni-hard type cast iron in order to understand the carbide and graphite formation mechanisms and evaluated the solidification sequence. The following conclusions were obtained.

1) Solidification of High Speed Steel type cast iron proceeds in the order of primary $\gamma$, $\gamma+M_2C$, $\gamma+M_3C$ and $\gamma+M_xC_y$ eutectic. The solidification path and development of V composition could be predicted on the experimental and computed liquidus projection.

2) Two percent in volume of fine $\gamma+\text{graphite}$ appears in Ni-hard type cast iron after primary $\gamma$, and $\gamma+M_2C$ eutectic solidification. Depletion of Cr and enrichment of Si as well as existence of Ni in residual liquid promote the formation of graphite. The solidification sequence, formation of carbides and changing of Si and Cr is interpreted based on the microsegregation, rejection of alloying element into residual liquid and Scheil–Gulliver model.

3) The influences of alloy elements on the amount of graphite are also evaluated based on the Solubility parameter for Ni-hard type cast iron.

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