Hindawi Publishing Corporation
Journal of Metallurgy
Volume 2012, Article ID 438659, 6 pages
doi:10.1155/2012/438659

Research Article

Control of Carbides and Graphite in Cast Irons Type Alloy's Microstructures for Hot Strip Mills

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Received 31 August 2011; Accepted 9 December 2011

Academic Editor: Hao Chen

The carbide and graphite formation and redistribution of alloy elements during solidification were investigated on high-speed steel (HS) and Ni-hard type cast irons with Nb and V. The crystallization of hypereutectic HSS proceeds in the order of primary MC, $\gamma + \mathrm{MC}$, $\gamma + \mathrm{M_6C}$, $\gamma + \mathrm{M_7C_3}$, and $\gamma +$ graphite eutectic, in hypoeutectic alloys proceeds in the order of primary γ, $\gamma + \mathrm{MC}$, $\gamma +$ graphite, $\gamma + \mathrm{M_6C}$, and $\gamma + \mathrm{M_7C_3}$ eutectic, and in Ni-hard proceeds in the order of primary γ, $\gamma + \mathrm{MC}$, $\gamma + \mathrm{M_3C}$, and $\gamma +$ graphite eutectic. The $\gamma +$ graphite eutectic solidifies with the decrease of V, Nb, and Cr and the increase of Si and C contents in residual liquid during solidification. The behavior in graphite forming tendency in the residual liquid is estimated by the parameter $\sum C_L^i m_i'$. The eutectic graphite crystallizes at the solid fraction when $\sum C_L^i m_i'$ takes a minimum value. The amount of graphite increases with the decrease in $\sum C_L^i m_i'$ of initial alloy content in both specimens. Inoculation with ferrosilicon effectively increases the graphite content in both specimens.

1. Introduction

In the roll material for hot rolling, the alloys which disperse a large amount of carbide in the matrix are widely used because they are superior in abrasion resistance. High-alloy white cast irons, in which a large amount of carbides disperse in the hardenable matrix, are widely used for abrasion resistant parts. Steel strip mills are also one of their important application fields, though the durability of high-alloy cast iron rolls is superior to conventional low-alloy ones. The scoring could sometimes shorten the life service and impair the surface quality of products [1, 2]. It is expected that the dispersed graphite flakes eliminate the scoring and sticking that could appear in alloy white cast iron. Therefore, the control of the amount and distribution of carbides and graphite is essential to get a high-quality cast iron roll. It is well known that the addition of Nb and V to white cast iron promotes the formation of MC type carbide [3]. The dispersion of MC carbide in the matrix would raise the wear resistance performance on the cast iron alloy where it is added. However, as they are the stronger carbide formers, the effects of Nb and V on the microstructure and the graphite formation must be investigated. In this study, carbide and graphite formation and redistribution of alloy elements during solidification were investigated on high-speed steel alloys (HS) and Ni-hard type cast irons.

2. Experimental Procedures

The chemical compositions of specimens tested are shown in Table 1. For HS type cast iron, different amounts of niobium (Nb), vanadium (V), tungsten (W), and cobalt (Co) were added, and V is used to disperse the larger amount of MC carbide in matrix. However, as γ + MC eutectic line for Fe-Cr-C-Nb system is located at lower concentration level of MC former than Fe-Cr-C-V system [3], the same amount of MC former addition results in a rise to more eutectic MC.

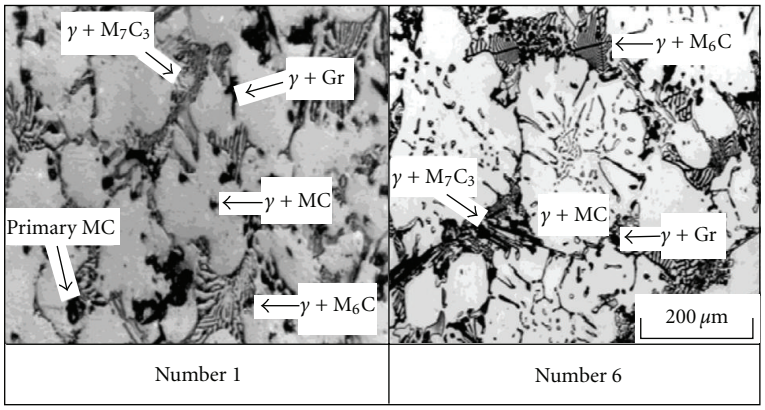

Figure 1: Microstructures of HS type specimens.

Table 1: Chemical composition for tested samples.

		Chemical composition (mass %)									Carbide
		C	Cr	V	Nb	Ni	Si	Mo	W	Co	
High-speed steel type (HS)	1	2.64	4.58	—	2.94	7.01	3.27	2.21	—	—	MC + M_6C + M_7C_3
	2	2.66	0.99	2.30	2.05	4.98	3.46	—	—	—	MC
	3	2.53	2.88	1.82	1.92	6.06	3.01	—	—	—	MC + M_7C_3
	4	2.63	2.97	2.08	1.86	5.92	3.35	5.05	—	—	MC + M_6C + M_7C_3
	5	2.73	3.02	3.22	0.97	6.09	3.25	5.15	4.93	—	MC + M_6C + M_7C_3
	6	2.79	3.05	2.95	0.99	6.10	3.23	5.16	—	5.11	MC + M_6C + M_7C_3
	7	2.81	2.97	2.89	0.94	6.45	3.45	5.14	—	—	MC + M_6C + M_7C_3
	8	2.74	3.09	2.10	0.87	5.99	4.46	5.09	—	—	MC + M_6C + M_7C_3
Ni-hard type	1	3.37	1.87	—	—	4.26	0.90	0.55	—	—	M_3C
	2	3.25	1.85	0.04	—	4.20	0.94	0.49	—	—	MC + M_3C
	3	3.16	1.81	1.86	0.53	4.24	0.93	0.46	—	—	MC + M_3C
	4	3.20	1.67	1.93	0.75	4.16	1.19	0.51	—	—	MC + M_3C
	5	3.25	1.59	0.96	0.90	4.12	1.24	0.52	—	—	MC + M_3C
	6	3.31	1.04	0.76	0.74	4.08	0.84	0.50	—	—	MC + M_3C
	7	3.35	1.24	1.94	0.35	4.32	0.88	0.54	—	—	MC + M_3C
	8	3.30	1.20	1.94	0.62	4.40	0.88	0.54	—	—	MC + M_3C
	9	3.33	0.71	0.97	1.80	4.41	0.90	0.53	—	—	MC + M_3C
	10	3.35	0.96	0.97	1.82	4.40	0.96	0.54	—	—	MC + M_3C

Furthermore, almost all Nb crystallizes in MC carbide; therefore, the effect of Nb addition on graphitization is very small. On the other hand, it is commonly recognized that NbC-γ interface sometimes shows lower bonding characteristics. Therefore, V and Nb contents in samples were controlled.

Ni-hard type cast iron series were based on alloy no. 1, and variable amounts of vanadium (V) and niobium (Nb) which are MC carbide formers were changed systematically. The amounts of Cr and Si were also controlled in some specimens. Thermal analysis was carried out for each specimen, and every specimen was melted over 1773 K in a siliconit furnace under argon atmosphere and then cooled at 10 K/min until 1173 K and quenched in oil. Distribution of carbides and graphite was analyzed in relation with the solidification sequence of the alloy. Moreover, EPMA analysis was carried out for the specimen quenched during solidification, and the relation between the behavior of alloy elements during solidification and crystallization of graphite was investigated.

Inoculation tests were also carried out for High-speed steel type cast iron and Ni-hard type cast iron. The specimens were remelted in a carbon resistance furnace, inoculated with Fe-75% Si, and then poured into the sand mold preheated at 1173 K. The amount of graphite in all specimens was examined metallographically.

3. Experimental Results and Discussions

3.1. The Graphite Formation in HS Type Cast Iron. The typical microstructures are shown in Figure 1. The specimens nos. 1 to 4 are hypereutectic, and specimens nos. 5 to 8

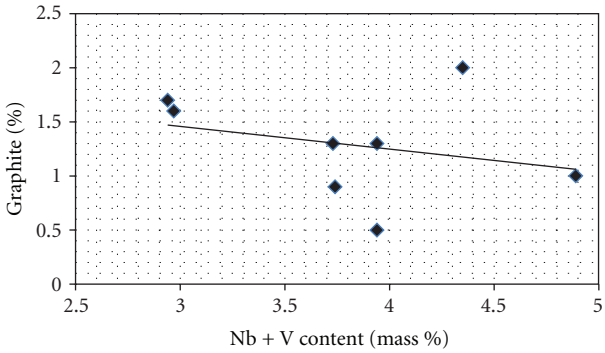

Figure 2: Amount of graphite-tested specimens.

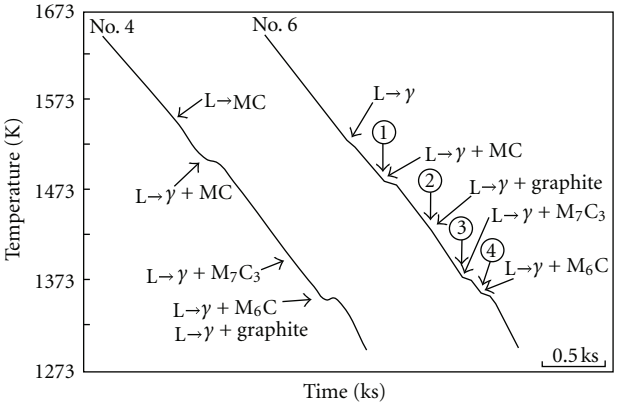

Figure 3: Thermal analysis curves of HSS samples.

are hypoeutectic alloys. In hypereutectic alloys, primary and eutectic MCs crystallize, and graphite flakes and particles distribute in the boundary of γ + MC eutectic cells. Meanwhile in hypoeutectic alloy, the graphite also distributes in cellar boundary. MC, M_6C, and M_7C_3 carbides crystallize, and the total amount of carbide changes from 13 to 24% depending on the chemical composition.

The amount of graphite in all specimens measured is from 0.5 to 2% showing a tendency to decrease as the amount of Nb and V increases as is shown in Figure 2, and the results are scattered due to the change on the amounts of Ni, Cr, and Mo, and the addition of W and Co in some specimens. The numbers of graphite flakes counted are from 50 to 400/mm^2.

Thermal analysis curves of hyper- (no. 4) and hypoeutectic (No. 6) alloys are shown in Figure 3. For hypereutectic alloy, the crystallization proceeds in the order of primary MC, γ + MC, γ + M_6C, γ + M_7C_3, and γ + graphite eutectic. Eutectic graphite crystallizes at the final stage of solidification because of the decreasing of carbide formers and the increasing of Ni and Si contents in residual liquid just like the case of low-Cr and high-Cr cast iron [4]. On the other hand, for hypoeutectic alloys, the solidification proceeds in the order of primary γ, γ + MC, γ + graphite, γ + M_6C, and γ + M_7C_3 eutectic. Graphite crystallizes after the γ + MC eutectic reaction.

The influence of each element on graphite formation is commonly evaluated based on the solubility of C in molten

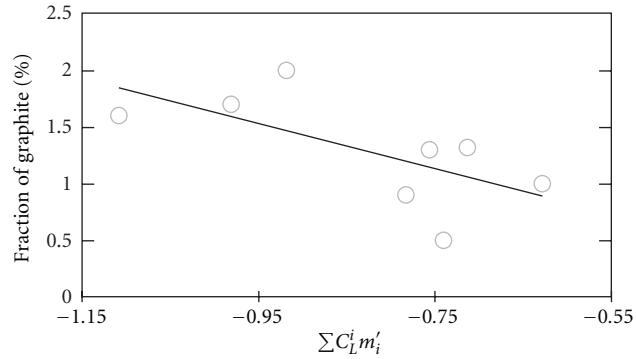

Figure 4: Relation between graphite fractions and $\Sigma C_L^i m_i'$.

iron [5]. Therefore, the change in graphite forming tendency of residual liquid is estimated by the parameter $\Sigma C_L^i m_i'$ [5] that is shown in (1). The elements that decrease the solubility of C promote the graphitization, while the elements which decrease the solubility of C prevents the graphitization promoting the formation of carbide compounds

$$\begin{aligned}\Sigma C_L^i m_i' = {} & 0.07[\mathrm{Cr}\%] + 0.14[\mathrm{V}\%] + 0.07[\mathrm{Nb}\%] \\ & - 0.06[\mathrm{Ni}\%] - 0.31[\mathrm{Si}\%] + 0.02[\mathrm{Mo}\%] \\ & - 0.01[\mathrm{W}\%] - 0.03[\mathrm{Co}\%],\end{aligned} \tag{1}$$

where C_L^i is chemical composition of each element, m_i' is the parameter showing the influence of each element on the solubility limit of C to molten iron.

The higher values of $|m'|$ of Si and V indicate that Si promotes graphite formation and V interferes with the crystallization of graphite. The relation between the amount of graphite and the $\Sigma C_L^i m_i'$ value estimated with the initial composition is shown in Figure 4. The amount of graphite becomes larger by decreasing $\Sigma C_L^i m_i'$; thus, the amount of graphite can be predicted from the $\Sigma C_L^i m_i'$ value calculated using initial alloy contents.

3.2. The Graphite Formation in Ni-Hard Type Cast Iron. Conventional Ni-hard specimen consists of austenite (γ), eutectic M_3C, and graphite. On the other hand, the specimens with Nb and V consist of austenite (γ), eutectic MC, eutectic M_3C, and graphite. Figure 5 shows the typical microstructure and distribution of graphite of specimens solidified at 10 K/min.

Fine graphite particles crystallize in the specimen with Nb and V content. Primary MC crystallizes in the specimen contained over 0.5% Nb (alloy no. 9). As shown in Figure 6, the amount of graphite is 2.2% in the specimen without Nb and V (base alloy), when the Nb and V contents increase the graphite content on the specimen decreases. Although the data scatter slightly, due to different additions of Si and Cr a decreasing trend is observed. The cooling curves for the specimens no. 1 and no. 7. are shown in Figure 7.

The specimen no. 1 crystallizes in the order of primary austenite (γ), γ + M_3C, and γ + graphite, while in the specimen no. 7 γ + MC, eutectic crystallizes after primary γ.

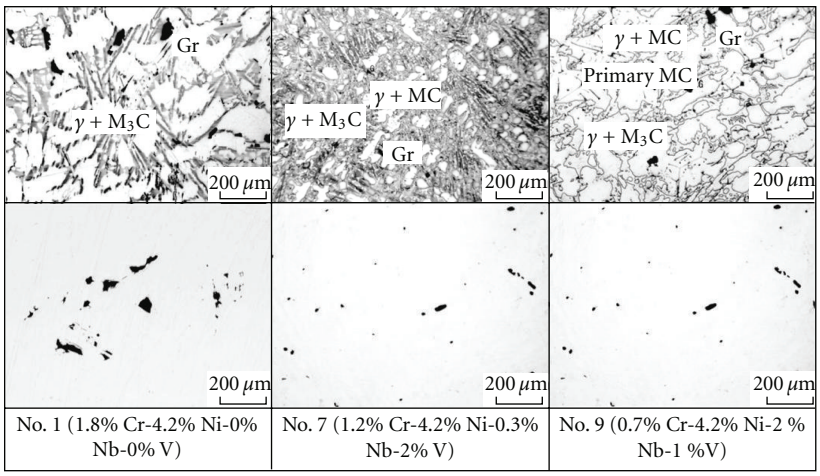

Figure 5: Microstructures of Ni-hard type cast irons.

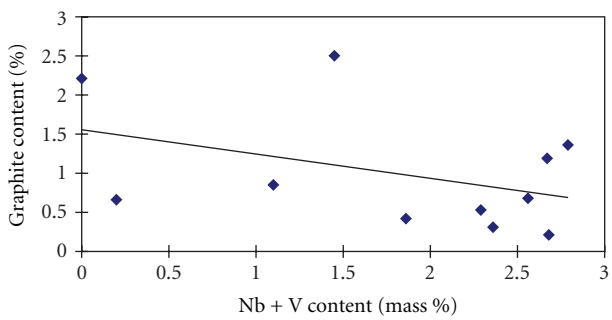

Figure 6: Effect of Nb and V content on the amount of graphite.

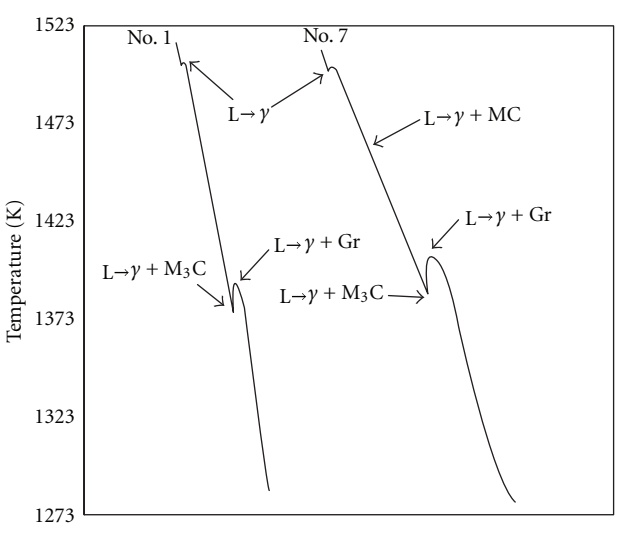

Figure 7: Thermal analysis curves of Ni-hard samples.

Since the partition coefficients of Nb and V to primary γ are less than unity, both elements are enriched in the residual liquid during the growth of primary γ, and the liquid composition reaches the γ + MC eutectic composition at 1448 K. Moreover, the growth of γ + MC eutectic diminishes

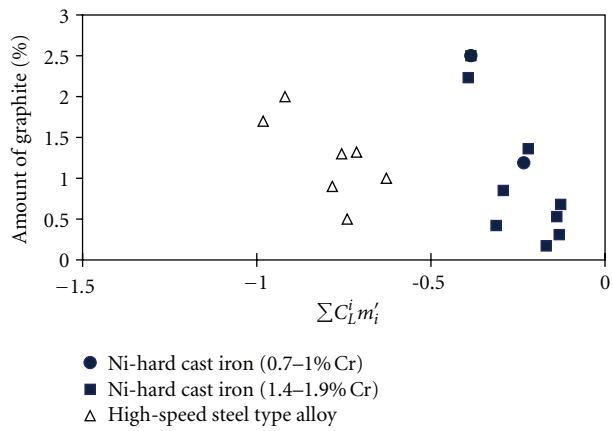

Figure 8: Relation between graphite's fraction and $\Sigma C_L^i m_i'$.

the Nb and V contents and increases the C content of residual liquid, and then γ + M_3C eutectic starts crystallizing.

Moreover, the growth of γ + M_3C eutectic decreases the carbide formers content and increases the Si and Ni contents on the residual liquid, and γ + graphite crystallizes in both lines at the final stage of solidification.

The relation between the amount of graphite and $\Sigma C_L^i m_i'$ values for all tested specimens was calculated as follows (2), and the results are show in Figure 8:

$$\begin{aligned}\Sigma C_L^i m_i' = {} & 0.07[\%\mathrm{Cr}] + 0.14[\%\mathrm{V}] + 0.07[\%\mathrm{Nb}] \\ & - 0.06[\%\mathrm{Ni}] - 0.31[\%\mathrm{Si}] + 0.02[\%\mathrm{Mo}],\end{aligned} \tag{2}$$

where ΣC_L^i and m_i' have the same meaning as (1).

The amount of graphite of Ni-hard type cast iron increases with the $\Sigma C_L^i m_i'$ value decreasing in a similar way as the case of high-speed steel type cast iron. A linear relationship is recognized for Ni-hard type cast irons and high-speed steel type cast irons except low-Cr Ni-hard type irons.

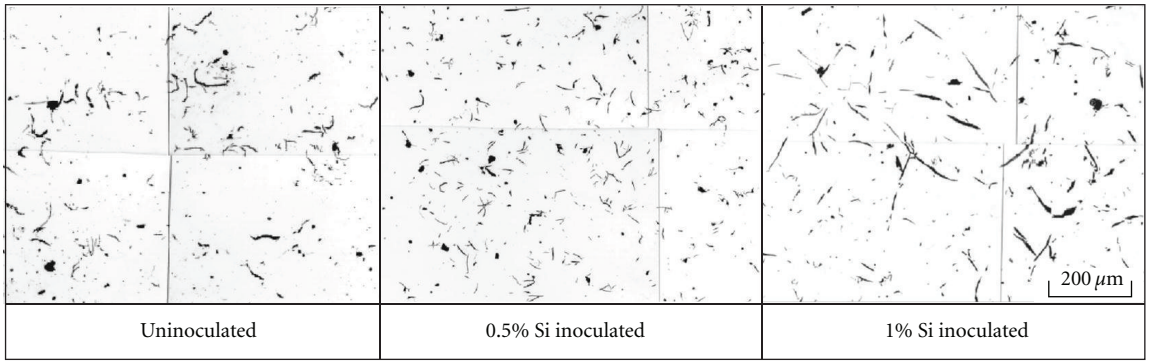

Figure 9: Inoculation effect on high-speed steel type cast iron.

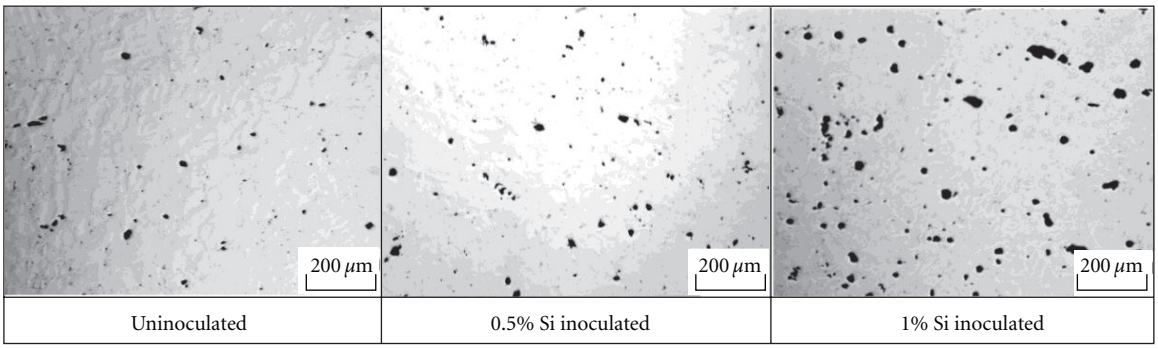

Figure 10: Effect of inoculation on Ni-hard type cast iron.

3.3. Inoculation Test

3.3.1. Inoculation Test in HS Type Cast Iron. The graphite distribution on alloy no. 7 specimens inoculated with Fe-75% Si alloy (0.5 and 1.0% Si added) is shown in Figure 9. The increasing of Si added as inoculant promotes the formation of graphite flakes, and the specimen with 1.0% Si added shows a random distribution of well-defined graphite flakes.

3.3.2. Inoculation Test in Ni-Hard Type Cast Iron. The specimen's composition no. 8 was used to study the effect of inoculation by using Fe-75% Si, and the results are shown in both Figures 10 and 11. On Figure 8, the photographs show that the amount and size of graphite increase when the amount of inoculant added increases. Moreover, the inoculation gives more uniform distribution of graphite flakes. Figure 11 shows that when 0.2% Si is added, the amount of graphite increases almost three times compared with not inoculated specimen and more than four times when 1.0% Si is added to the alloy.

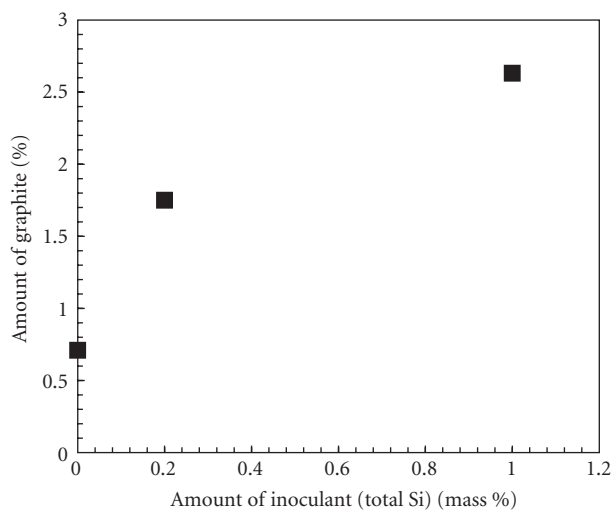

Figure 11: Relation between the amount of graphite and the amount of inoculant.

4. Conclusions

The effects of alloy elements and inoculation on graphite formation were investigated for high-speed steel type cast iron and Ni-hard type cast iron. The following conclusions were obtained.

(1) In case of high-speed steel type cast iron, the crystallization of hypereutectic alloy proceeds in the order of primary MC, γ + MC, $\gamma + M_6C$, $\gamma + M_7C_3$, and γ + graphite eutectic, while hypoeutectic alloys solidify in the order of primary γ, γ + MC, γ + graphite, $\gamma + M_6C$, and $\gamma + M_7C_3$ eutectic. The γ + graphite eutectic solidifies with the decrease of carbide forming elements V, Nb, and Cr and

the increase of Si and C contents in residual liquid during solidification.

(2) In case of Ni-hard type cast iron, by the addition of Nb and V, γ + MC eutectic reaction appears between the primary γ and γ + M_3C eutectic. γ + graphite eutectic crystallizes at the final stage of solidification. The solidification sequence is interpreted based on the behaviors of alloy elements and the change in the composition of residual liquid.

(3) The amount of graphite increases almost linearly with decreasing of solubility parameter $\Sigma C_L^i m_i'$ in both high-speed steel type and Ni-hard type cast iron.

(4) In both high-speed steel type cast iron and NI-hard type cast iron, the inoculation with Fe-75% Si alloy effectively increases the amount of graphite, and higher amount of inoculant results in more uniform distribution of larger flakes and particles graphite.

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