



## **Influence of Nb, V and Ta on the Microstructure of Ni-hard type Cast Iron for Hot Steel Strip Mills**

Sergio Villanueva B.<sup>1</sup>, Ishikawa S.<sup>2</sup>, Yamamoto Kaoru<sup>3</sup>, Miyahara Hirofumi<sup>1</sup> and Ogi Keisaku<sup>4</sup>

<sup>1</sup>Dept. of Materials Science and Engineering, Kyushu University, Fukuoka, 819-0395, JAPAN  
(present work: Autonomous San Luis Potosi University, San Luis Potosi, Mexico)

<sup>2</sup>(present work: Nippon Steel & Sumikin Rolls Corp, Kitakyushu, 804-0002)

<sup>3</sup>(present work: National Institute of Technology, Kurume College, Fukuoka, 830-8555, JAPAN)

<sup>4</sup>(Emeritus Professor Dept. of Materials Science and Engineering, Kyushu University, JAPAN)

### **ABSTRACT**

Typical Ni-hard type cast iron for hot strip milling rolls contains 3.37% C, 0.90% Si, 4.26% Ni, 1.87% Cr, and 0.55% Mo to crystallize a large amount of ledeburite and a small amount of graphite to achieve a good performance in hot milling of steel strip. Nb, Ta and V up to 2.0 mass % were added to the cast iron to distribute harder MC type carbides in the martensitic matrix. Although higher addition of MC formers results in a higher amount of MC carbides, the chemical composition should be adjusted to crystallize graphite and to suppress the formation of hyper-eutectic carbides which cause macro-segregation in a centrifugal casting. The crystallization of cast iron specimens with Nb-V and Ta-V proceeds in the order of primary  $\gamma$ ,  $\gamma$ +MC,  $\gamma$ +M<sub>3</sub>C and  $\gamma$ + graphite eutectic. The influence of alloying elements on the graphite

formation is estimated by their effects on solubility limit of C to the molten iron. The element which decreases the solubility limit, promotes the graphite formation tendency. A simple mixing rule is applied to the evaluation of the total effect of alloy elements.

## **1. INTRODUCTION**

Ni-hard type cast iron with a small amount of graphite has been utilized as roll material for hot steel strip mill. On the other hand, recent developments of high speed steel type cast iron indicate that MC type carbides extremely improve the abrasion resistance and the service life of rolls. The high speed steel type cast iron rolls are applied to the first 4 stands in the hot steel strip mill <sup>1),2)</sup> in the case of Ni-hard type the last two stands. To extend the service life of Ni-hard type cast iron rolls, MC carbide formers are added to distribute harder MC carbides in the microstructure consisted of ledeburite, graphite and martensitic matrix. V and Nb are utilized as MC formers in high speed steel type roll <sup>3)</sup>, However V-rich primary carbide particles segregate to the central part of roll in a centrifugal casting if the V addition exceeds the eutectic composition. Nb is sometime added to high V cast iron to adjust the density of V-rich carbide comparable to the molten iron to prevent the macro-segregation of carbides. The wear resistance of a roll becomes higher as the inter-carbide spacing becomes smaller. A small amount of Ti addition modifies the morphology of V-rich eutectic carbide. Since the solubility of Ti to molten cast iron is very small, tiny TiC particles first crystallize in the molten iron and then nucleate V-rich carbides, thus refining the V-rich MC carbide particles. However, TiC with much lower density may promote the macro-segregation <sup>4)</sup>. Though Ta also shows a lower solubility limit and the density of TaC is much higher than NbC, no studies have been made on effects of Ta on the crystallization of MC carbide and on the solidification structure of cast iron. Therefore, the solidification sequence and the structure were investigated on Ni-hard type cast iron containing V, Nb and Ta. The influences of these MC formers, as well as Cr and Si, were studied on the graphite formation. The effect of alloy element was evaluated based on the solubility limit of C in the molten cast iron.

## **2. EXPERIMENTAL PROCEDURES**

To examine the effects of V, Nb, and Ta on the formation of MC carbides and graphite in Ni-hard type cast iron, thermal and metallographic analyses were made on two series of cast iron specimens with (0- 2.0)%V, (0-2.0)% Nb and with (0-2.0)%V, (0-2.0)%Ta. Each specimen was remelted and then cooled at 10K/min in a siliconit (SiC resistant) furnace under an argon atmosphere. As  $\gamma$ +MC eutectic line for Fe-Cr-C-Nb system is located at lower concentration level of MC former than Fe-Cr-C-V system<sup>5)</sup>, the same amount of Nb and Ta addition might give rise to more eutectic MC. Since V, Nb and Ta depressed the graphite formation, Cr and Si contents of the alloy were also systematically changed to promote the graphite formation, as shown in Table 1. Distribution of carbides and graphite was analyzed in relation with the alloy compositions.

**Table 1 Chemical analysis of tested samples**

Alloy Number	Element ( mass % )								Carbide
	C	Si	Ni	Cr	Mo	V	Nb	Ta	
1*	3.37	0.90	4.26	1.87	0.55	--	--	--	M <sub>3</sub> C
2	3.17	0.94	4.20	1.87	0.49	--	0.02	--	MC + M <sub>3</sub> C
3	3.07	0.93	4.24	1.87	0.46	1.86	0.53	--	MC + M <sub>3</sub> C
4	3.05	1.19	4.16	1.87	0.51	1.93	0.75	-	MC + M <sub>3</sub> C
5	3.08	1.24	4.12	1.87	0.52	0.96	0.90	--	MC + M <sub>3</sub> C
6	3.10	0.92	4.56	1.00	0.56	0.71	0.74	--	MC + M <sub>3</sub> C
7	3.12	0.84	4.08	1.40	0.50	0.76	0.34	--	MC + M <sub>3</sub> C
8	3.07	0.88	4.32	1.40	0.54	1.94	0.35	--	MC + M <sub>3</sub> C
9	3.06	0.88	4.40	1.40	0.54	1.94	0.62	--	MC + M <sub>3</sub> C
10	3.04	0.90	4.41	0.70	0.53	0.87	1.80	--	MC + M <sub>3</sub> C
11	3.04	0.96	4.40	1.20	0.54	0.97	1.82	--	MC + M <sub>3</sub> C
2A	3.09	1.12	4.07	1.48	0.52	1.81	--	--	MC + M <sub>3</sub> C
3A	2.86	1.10	3.81	1.41	0.49	--	--	1.61	MC + M <sub>3</sub> C
4A	2.96	1.02	3.93	1.43	0.51	1.05	--	0.95	MC + M <sub>3</sub> C
5A	3.02	1.15	3.95	1.45	0.51	1.93	--	0.50	MC + M <sub>3</sub> C

\* Base alloy

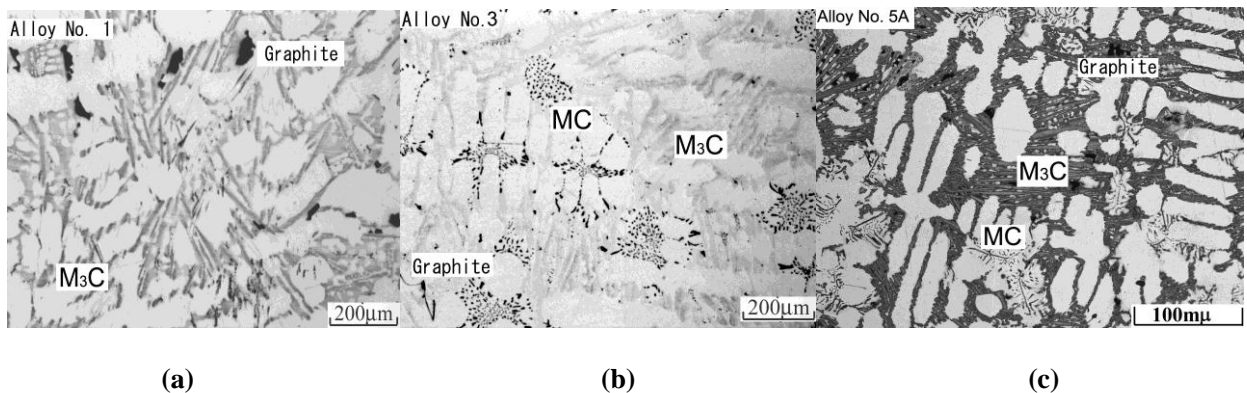
The graphite formation tendency of each melt was evaluated based on the solubility of C in

molten iron. The Solubility Parameter  $\Sigma C_L^i m'_i$  (where  $C_L^i$  is the content of alloying element  $i$ , and  $m'_i$  is the change in solubility limit of C in molten iron of the element  $i$ ) was evaluated on each specimen.

The influence of inoculation on the graphite formation was also evaluated. The tests were carried out for the specimen with 0.4 %Nb and 1.95 %V (Alloy No. 8). The specimens were remelted in a carbon resistance furnace, inoculated with Fe-75%Si alloy particles until 1% addition, and then poured into the sand mold preheated at 1173K. The amount of graphite was metallographically examined on the 8mm thick cast specimens.

### 3. RESULTS AND DISCUSSION

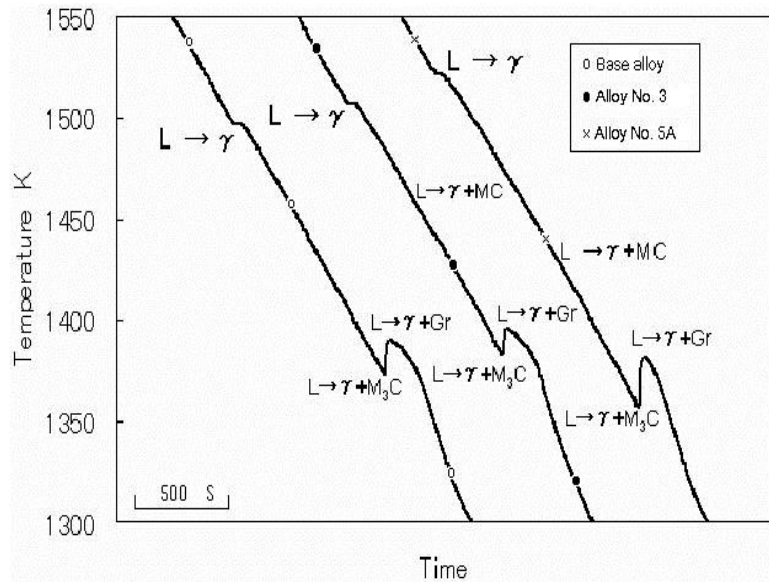
The microstructures of specimens are shown in Figure 1. The conventional Ni-hard type cast iron used for rolls Alloy No. 1, consists of dendritic  $\gamma$ ,  $\gamma+Fe_3C$  eutectic (ledeburite) and graphite. Eutectic  $Fe_3C$  is etched grey, and primary and eutectic  $\gamma$  appear as white structure in the microphotograph (a). In the Alloy No.3 (b) and Alloy No.5A (c), MC carbide (etched black) is present together with dendritic  $\gamma$  and ledeburite. Fine graphite particles also crystallize in Alloy specimen 5A with V, Nb and Ta content. In Alloys No.3, 4, 5, 6, 9, 10 and 11 which contain Nb higher than 0.53%, primary MC crystallizes on austenite matrix, in the case of specimen No. 2 and 7 small amounts of MC type carbide appear in the matrix. In Alloys who contain Ta, the Alloys 3A and 4A also show primary MC crystal.



**Figure 1. Microstructures for Ni-Hard specimens**

Cooling curves during crystallization for alloys 1, 3 and 5A are shown in Figure 2. The Alloy 1

crystallizes in the order of primary  $\gamma$ ,  $\gamma+M_3C$ , and  $\gamma+Graphite$ , while  $\gamma+MC$  eutectic starts crystallizing at the temperature between primary  $\gamma$  and  $\gamma+M_3C$  eutectic temperatures in the Alloys 3 and 5A. This was confirmed by the metallographic observation on the specimen quenched just below the second knick on the cooling curve.



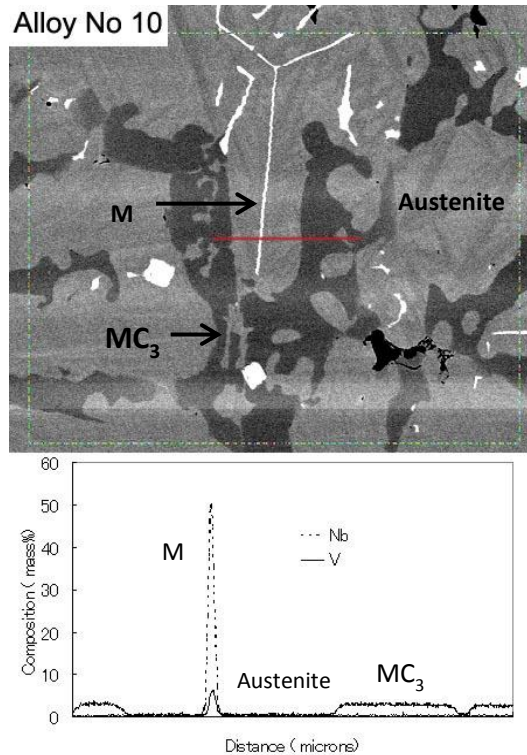
**Figure. 2 Thermal analysis of alloys 1,3 and 5A.**

Since the partition coefficients (Calculated by Thermocalc) of V, Nb, and Ta to primary  $\gamma$  are less than unity, both elements are enriched in the residual liquid during the growth of primary  $\gamma$ , and the liquid composition reaches the  $\gamma+MC$  eutectic at around 1448K on Alloy 3. Meanwhile in the alloy 5A reached the eutectic at around 1470K. The  $\gamma+MC$  eutectic grows cellularly in both specimens.

EPMA analysis reveals that Ta, as well as Nb and V, are enriched in MC carbide as shown in Figure 3. In this figure, linear analysis was performed on Alloy No. 10, the results show that Niobium predominantly distributes to MC phase (white), it contains until 55 mass % Nb and there is no detectable Nb content in austenite (light grey) nor in  $M_3C$  (dark grey). On the other hand, Vanadium is enriched in both MC and  $M_3C$  carbide.

The behavior of Ta is rather similar to Nb and different from Ti. Ta does not refine MC carbide, however, it can raise the density of V-rich carbide by dissolving in the carbide. The growth of  $\gamma+MC$  eutectic diminishes the Nb, Ta and V contents and increases the C content of residual liquid, then  $\gamma+M_3C$  eutectic starts crystallizing. Since the growth of  $\gamma+M_3C$  eutectic decreases the

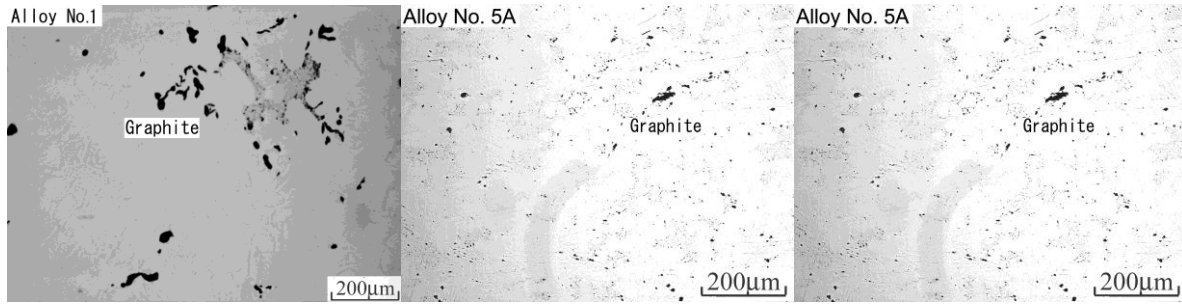
carbide formers and increases the Si and Ni content of residual liquid,  $\gamma+Gr$  could crystallize at the final stage of solidification when the graphite formation tendency of residual liquid exceeds a critical value for the graphite formation.



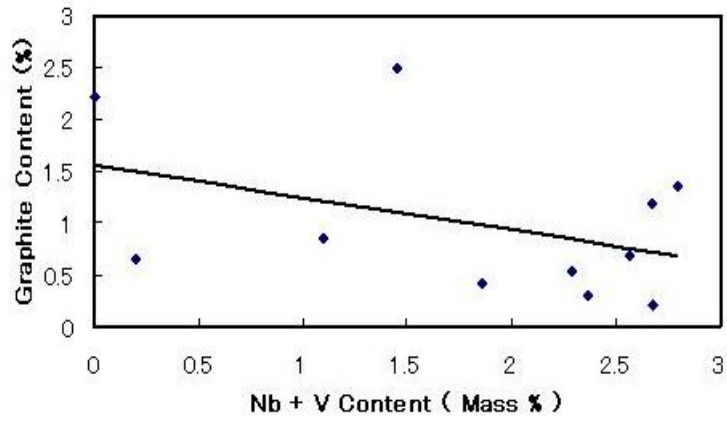
**Figure 3. EPMA linear analysis**

Figure 4 shows that vermicular-type graphite is present in Alloy No.1, with more granular and finer graphite in the Alloys 3 and 5A. The metallographic analysis on all the specimens revealed that the amount of graphite decreases with the increase in V, Nb and Ta content as shown in Figures 5 and 6.

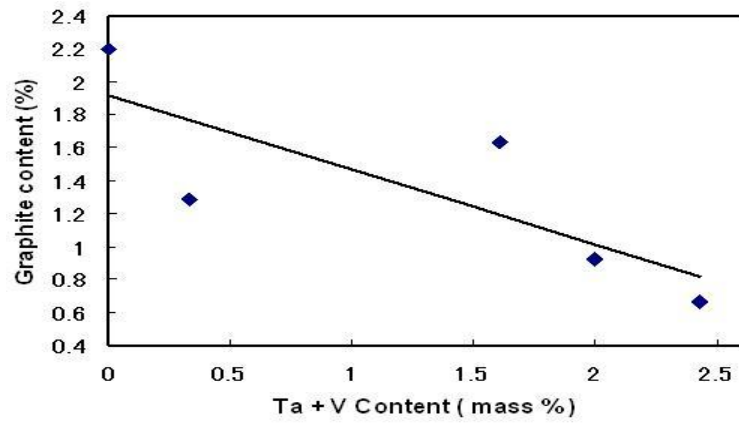
The amount of graphite is 2.2% in the specimen without Nb and V, and it decreases with the increase in Nb and V contents. The data scatter slightly, because of different additions of Si and Cr, moreover, in Figure 6 the data scatter slightly also due to the different additions of Si, showing a similar behavior to Nb-V alloys. The graphite size and shape are not uniform even in Alloy No 1.



**Figure 4. Graphite shape for tested specimens.**



**Figure 5. Graphite content for Nb-V alloys**



**Figure 6. Graphite content for Ta-V alloys**

The influence of each element on graphite formation is estimated based on C solubility in molten iron. The Solubility Parameter ( $\Sigma C_L^i m_i'$ ) of Ni-hard type specimens with Nb, Ta and V is calculated by Equation (1):

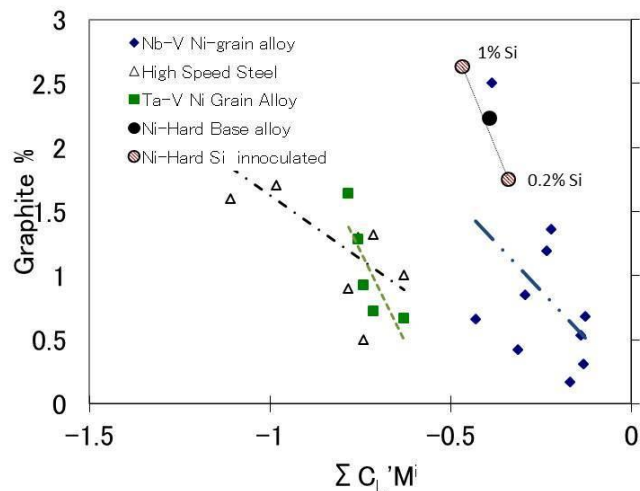
$$\Sigma C_L^i m_i' = 0.07(\%Cr) + 0.14(\%V) + 0.07(\%Nb) + 0.005(\%Ta) - 0.06(\%Ni) - 0.31(\%Si) + 0.02(\%Mo) \quad \text{Equation (1)}$$

Where:

$C_L^i$ : Chemical composition of each element i

$m_i'$ : the parameter showing the influence of each element i on the solubility limit of C to molten iron <sup>6)</sup>.

The calculation results are shown in Figure. 7. The data<sup>5)</sup> of high speed steel type alloys with (2.5-2.8)%C, (1.0-4.5)%Cr, 7%Ni, (3.0-4.5)%Si, (2.0-5.0)%Mo, 0.5%W, 0.5%Co, (0.0-3.0)%V and (1.0-3.0)%Nb) are shown in Figure 7. In case of V-Nb added specimens, the amount of graphite ( $V_{Gg}$ ) increases with the decreasing of  $\Sigma C_L^i m_i'$  in the similar way as the case of high speed steel type alloys. A linear  $V_{Gg}$ - $\Sigma C_L^i m_i'$  relationship is recognized for Ni-hard type cast irons and high speed steel type alloys, except low Cr Ni-hard type irons with V and Nb. However, Ni-hard type cast iron specimens with V and Nb show a slight linear relationship between the amount of graphite and the Solubility Parameter. Ni-Hard alloyed with Nb and V and Si Inoculated specimens were also evaluated, as well as Nb-V specimens the  $V_{Cg}$  increase when  $\Sigma C_L^i m_i'$  parameter value decrease. On these specimen the solubility parameter values are in the range of  $\Sigma C_L^i m_i'$  values for Nb and V alloyed Ni-grain alloy.





### Figure 7. Relation between the amount of graphite and Solubility Parameter

The effect of inoculation on the graphite distribution was examined on Alloy No. 8 with 1.95 % V and 0.4 % Nb, as is shown in Fig. 8. . From 0.2% to 1% Si were inoculated by using Fe-75% Si. The amount of graphite was measured, near the surface and at the central part of the casting, Figure 8 shows the sand face microphotographs who depict the blue dots on Figure 9. from 0.2% to 1.0% Si was added by using Fe-75% Si alloy. The graphite amount examination results are shown in Figure 9. When 0.2% Si is added, the amount of graphite increases almost three times compared to not inoculated sample. when 1% Si is inoculated, the amount of graphite increase until 2.6%. Also an external (3.37% C, 1.70% Si, 4.26% Ni, 1.4% Cr, 0.55% Mo, 0.5% Nb, 2.0% V) Ni-hard as cast alloy was inoculated getting the highest graphite values in Figure 9. The inoculation gives more uniform distribution of graphite flakes.

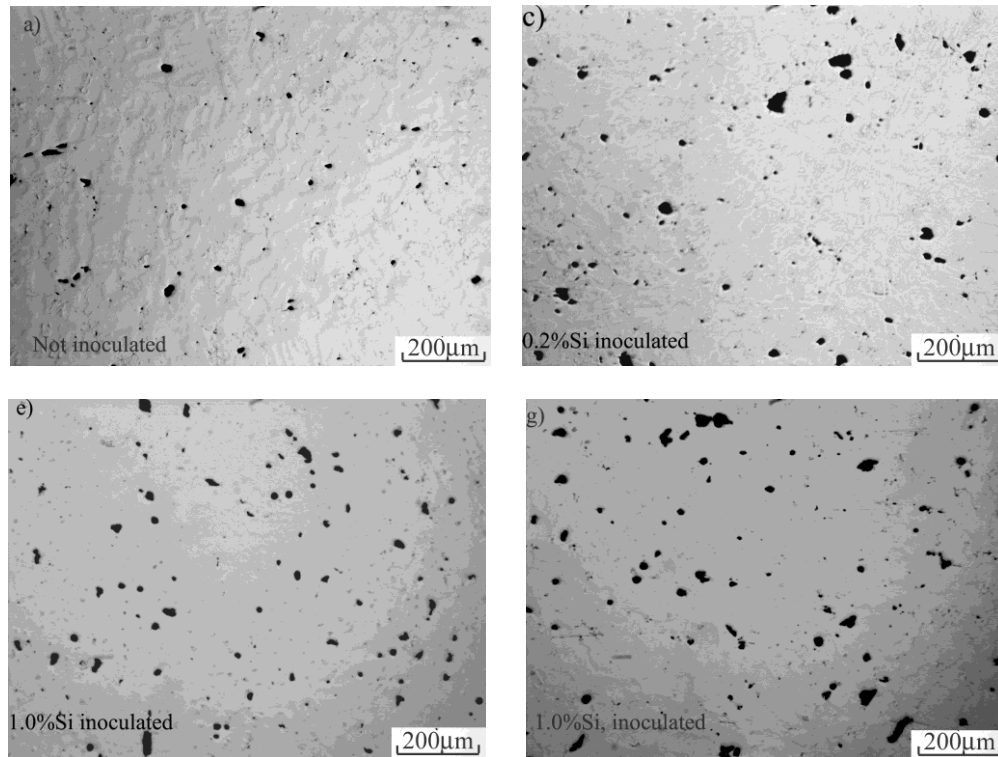
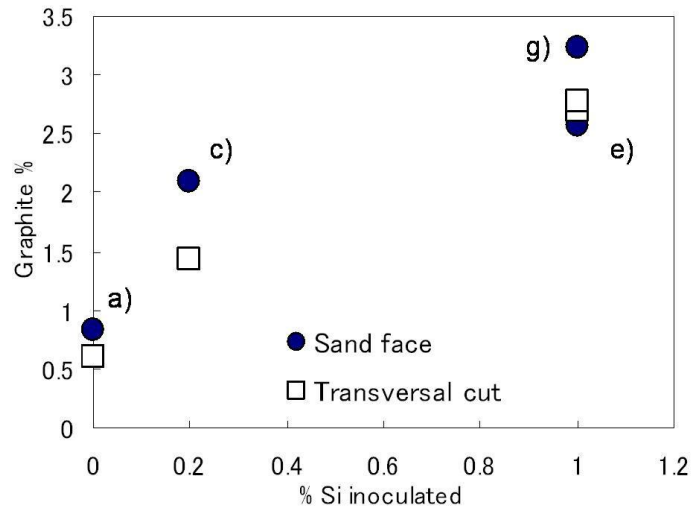


Figure 8. Graphite shape and content for inoculated specimens.



**Figure 9. Influence of inoculated Si content on the graphite content for Alloy No.8.**

#### 4. CONCLUSIONS

The effects of the addition of 1.0-2.0% V, 0.5-2.0% Nb and 0.5-2.0% Ta were investigated on the microstructure of Ni-hard type cast iron. The following conclusions were obtained:

1) By the addition of V, Nb and Ta,  $\gamma$ +MC eutectic reaction appears between the primary  $\gamma$  and  $\gamma$ +M<sub>3</sub>C eutectic. The solidification sequence is interpreted based on the behaviors of alloy elements and the change in the composition of residual liquid. The amount of MC carbides increases with increase in V, Nb and Ta contents. However, primary MC crystallizes in the specimen when having added over 0.53% Nb and Ta.

2) The  $\gamma$ +graphite eutectic crystallizes at the final stage of solidification. The influences of alloy elements on the amount of graphite are evaluated based on the Solubility Parameter. The amount of graphite increases almost linearly with decreasing of Solubility Parameter ( $\Sigma C_L^i m_i'$ ) in V-Nb alloyed Ni-hard type cast irons and high speed steel alloys. However, V-Ta alloyed Ni-hard type cast iron specimens show a slight linear relationship between the amount of graphite and the Solubility Parameter, which should be caused by too low  $m'$  value of Ta. Also  $\Sigma C_L^i m_i'$  on inoculated samples were evaluated, they showed a similar behavior than V-Nb alloyed Ni-hard type cast iron, although the Si content on the inoculated specimen is higher than the rest V-Nb alloyed

specimens, the  $\Sigma C_L^i m_i^2$  values are as negatives as those specimens.

3) The inoculation with Fe-75%Si alloy particles effectively increases the amount of graphite, and higher percentage amount of inoculant results in more uniform distribution of the larger amount graphite.

## REFERENCES

- [1] A.I. Tselikov, V.V. Smirnov., *Rolling Mills*, P 58, Pergamon Press
- [2] M. Pellizari, A. Molinary, G. Strafflelini., *Tribological behavior of hot rolling rolls*, p 1281 – 1289, *Wear* 259 (2005)
- [3] K Ogi, K Yamamoto, T. Fujita, *Alloy Design for Distributing Graphite Flakes in High Alloy White Cast Iron for Rolls*, p. 83- 90, Proceedings of the Sixth Asian Foundry Congress, January 1999, Calcuta India.
- [4] A. Sawamoto, K. Ogi, K. Matsuda: pp.403-416 AFS Transactions Vol.72 (1986)”
- [5] K. Yamamoto, T. Kubota, N. Murai and K. Ogi., *Solidification Process and Crystallization of Graphite in High Carbon High Speed Steel type Alloy*. pp 786-792, *Journal of Japan Foundry Society*, No. 11, Vol. 17, 1999.
- [6] F. Neumann, H. Schenck, W. Patterson, , *Zeitschrift für das gesamte giessereiwesen*, p 47,Heft 2, Januar 1960 ,Jahrgan