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# 다합금계 백주철에 있어서 탄소가 탄화물의 형태에 미치는 영향

류 성 곤

## Effects of Carbon Content on Microstructure and Amount of Austenite in As-Cast and Heat-Treated Multi-Component White Cast Iron

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### 요 약

주방상태 및 열처리를 행한 다합금계백주철(Fe-5%Cr-5%V-5%Mo-5%W-X%C(X=0.5, 1.0, 1.5, 2.0, 2.5, 3.0)에 있어서 탄소함량이 탄화물의 형태 및 잔류오스테나이트의 함량에 미치는 영향에 관하여 연구하였다. 주방상태의 경우, 2.0% 이하의 탄소함량에서는 편상MC 및 층상 M<sub>2</sub>C탄화물만 관찰되었으나 2.5%C 이상의 경우, 편상 및 괴상MC, 층상M<sub>2</sub>C 그리고 셀형 M<sub>7</sub>C<sub>3</sub>탄화물이 관찰되었다. 또한, 기지조직내 오스테나이트의 함량도 탄소첨가와 더불어 점차 증가하여 2.5%C에서 84.8%의 최대함량을 나타낸 후, 3.0%C에서는 다시 감소하였다. 또한 열처리한 시편의 경우, 1차탄화물의 형상은 주방상태의 그것과 비슷하였으나 열처리중 기지조직내 용해되었던 C, Cr, V, Mo, W등이 아주 미세한 2차탄화물의 형태로 석출되어 기지조직내 오스테나이트의 함량은 주방상태의 그것에 비해 감소하였다.

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### 1. Introduction

Multi-component white cast iron is a recently developed wear resistant material for hot strip and mineral pulverizing mills[1, 2]. It contains reasonable amounts of carbide forming elements such as Cr, V, Mo and W for the precipitation of MC, M<sub>2</sub>C and M<sub>7</sub>C<sub>3</sub> carbides during solidification. Sometimes, a large amount of austenite can be formed or retained in as-cast and heat-treated specimens whereby inferior properties are resulted in. The carbon content in multi-component white cast iron is known to have a close relationship with the type and morphology of carbides precipitated, and the matrix structure, especially with the amount of austenite in the matrix (V<sub>γ</sub>). Therefore, (Fe-5%Cr-5%V-5%Mo-5%W-X%C(X=0.5, 1.0, 1.5, 2.0, 2.5, 3.0) was studied to clarify the relationship among carbon content, type and morphology of carbides precipitated, and V<sub>γ</sub> in as-cast and heat-treated conditions.

### 2. Experimental Procedure

#### 2.1 Preparation of Specimen

Specimens were produced in a 15 kg-capacity silica lined high frequency induction furnace. Basic charge materials were clean pig irons and steel scraps. The ferroalloys like Fe-60%Cr, Fe-80%V, Fe-60%Mo and Fe-75%W, as necessary according to the charge calculation, were added to a slag free molten iron in the furnace so as to minimize oxidation loss and slag formation. The melt was subsequently heated to 1923 K, and transferred into a pre-heated teapot pouring ladle. After removal of any dross or slag, the melt was poured at 1873 K into a pep-set mold to produce cylindrical bars of 10 and 20 mm φ, and 165 mm in length.

#### 2.2 Heat Treatment

Castings were cooled in the molds until black, when they were shaken out. Specimen for heat treatment was cut into 10 mm thickness from the cylindrical bar of 20 mm φ. Before forced air cooling or tempering, the specimen was homogenized at 1223 K for 10.8 ks in N<sub>2</sub> atmosphere to minimize the segregation of the alloying elements in the matrix, and followed by furnace cooling to room temperature. Then, the homogenized specimen was austenitized at 1273, 1323 and 1373 K, respec-

ctively for 5.4 ks in N<sub>2</sub> atmosphere. These specimens were either hardened by forced air cooling to room temperature or tempered. In tempering process, the forced air cooled specimen was held at 573, 673 and 773 K, respectively for 10.8 ks, and then cooled to room temperature in still air.

### 2.3 X-Ray Diffraction Method

Using a X-ray diffractometer,  $V\gamma$  was measured in the range from 24° to 44° by employing Mo target, and simultaneously rotating and swinging the sample stage in order to reduce the effect of texture structure. The relative intensity of peaks were monitored from (200) and (220) planes of ferrite and martensite, and (220) and (311) planes of austenite. The area under each peak was calculated by using image analyzer, from which  $V\gamma$  was obtained. For the identification of the type of carbides, the specimens were deeply etched in (HF+H<sub>2</sub>SO<sub>4</sub>) solution for 1.8 ks. Then, the peaks of each carbide were monitored in the range from 15° to 40°, and compared with those of MC, M<sub>2</sub>C and M<sub>7</sub>C<sub>3</sub> carbides in ASTM cards.

### 2.4 Metallographic Examination

All specimens polished and etched were examined metallographically by optical microscope and SEM. The Murakami's (10 g of potassium ferricyanide, 10 g of potassium hydroxide and 100 ml of distilled water) and Vilella's (1 g of picric acid, 5 ml of hydrochloric acid and 100 ml of methyl alcohol) etchants were used for etching the specimens.

## 3. Results and Discussions

### 3.1 Chemical Analysis

A summary of the chemical analysis of 6 heats used in this study was 5.20 to 5.70 wt% Cr, 5.03 to 5.60 wt% V, 4.78 to 5.23 wt% Mo and 5.35 to 5.77 wt% W which included variations in actual chemical analysis as well as the tolerance in the chemical analysis. The actual values of carbon content were : 0.62 (target:0.5), 1.15 (target:1.0), 1.60 (target:1.5), 1.99 (target:2.0), 2.68 (target:2.5) and 3.11 (target:3.0) wt% C.

### 3.2 Effects of Carbon Content on the Carbide Structure

#### 3.2.1 For the case of as-cast specimen

The effect of carbon content on the carbide microstructure is shown in Fig. 1, a and b.

As shown in these figures, the volume fraction, type and morphology of carbides varied with the increase in carbon content. The volume fraction of carbides (MC, M<sub>2</sub>C and M<sub>7</sub>C<sub>3</sub>) in each heat is listed in Table 1.

As shown in this table, the amount of carbides in as-cast irons increased with increasing the amount of carbon. A drastic increase was observed when the value of C<sub>bal</sub> changed from negative to positive.

In multi-component white cast iron, a stoichiometric carbon balance (C<sub>stoich</sub>) with the carbide forming elements such as Cr, V, Mo, and W can be calculated from the following equation[3]:

$$C_{\text{stoich}} = 0.060\% \text{ Cr} + 0.235\% \text{ V} + 0.063 \text{ Mo} + 0.033\% \text{ W}$$

Here, Cr, V, Mo, and W are assumed to exist in forms of M<sub>7</sub>C<sub>3</sub>, MC and M<sub>2</sub>C, respectively. As shown in Table 1, the carbon balance (C<sub>bal</sub>=%C in iron-C<sub>stoich</sub>) of each heat was in the range of -1.455 to 1.045. In equilibrium condition, a positive value of C<sub>bal</sub> means that the surplus carbon is dissolved in the matrix instead of being combined with any carbides forming elements, while a negative value of C<sub>bal</sub> indicates that the surplus carbides forming elements are dissolved in the matrix because of the lack of carbon to be combined with them. These facts explain the drastic increase in the volume fraction of carbides when the value of C<sub>bal</sub> changed from negative to positive.

A deep-etched specimen was also prepared for the identification of the type of carbides by X-ray diffraction. The peaks of each carbide (MC, M<sub>2</sub>C and M<sub>7</sub>C<sub>3</sub>) in Heat No. 6 are shown in Fig. 2.

The result of X-ray diffraction in the as-cast iron was corresponded to the solidification reactions clarified by thermal analysis method[4]. From the X-ray diffraction experiment and microstructural observation, different types of the carbides were precipitated with varying carbon content. At the carbon level of 0.5%, flaky MC carbide and traces of lamellar M<sub>2</sub>C carbides were precipitated at the grain boundary. In the specimens with carbon content of 1.0, 1.5 and 2.0%, flaky MC and more of lamellar M<sub>2</sub>C carbides were coexisted along the grain boundary. On the other hand, in the specimens with more than 2.0% C, rectangular and flaky MC, lamellar M<sub>2</sub>C and cellular M<sub>7</sub>C<sub>3</sub> carbides

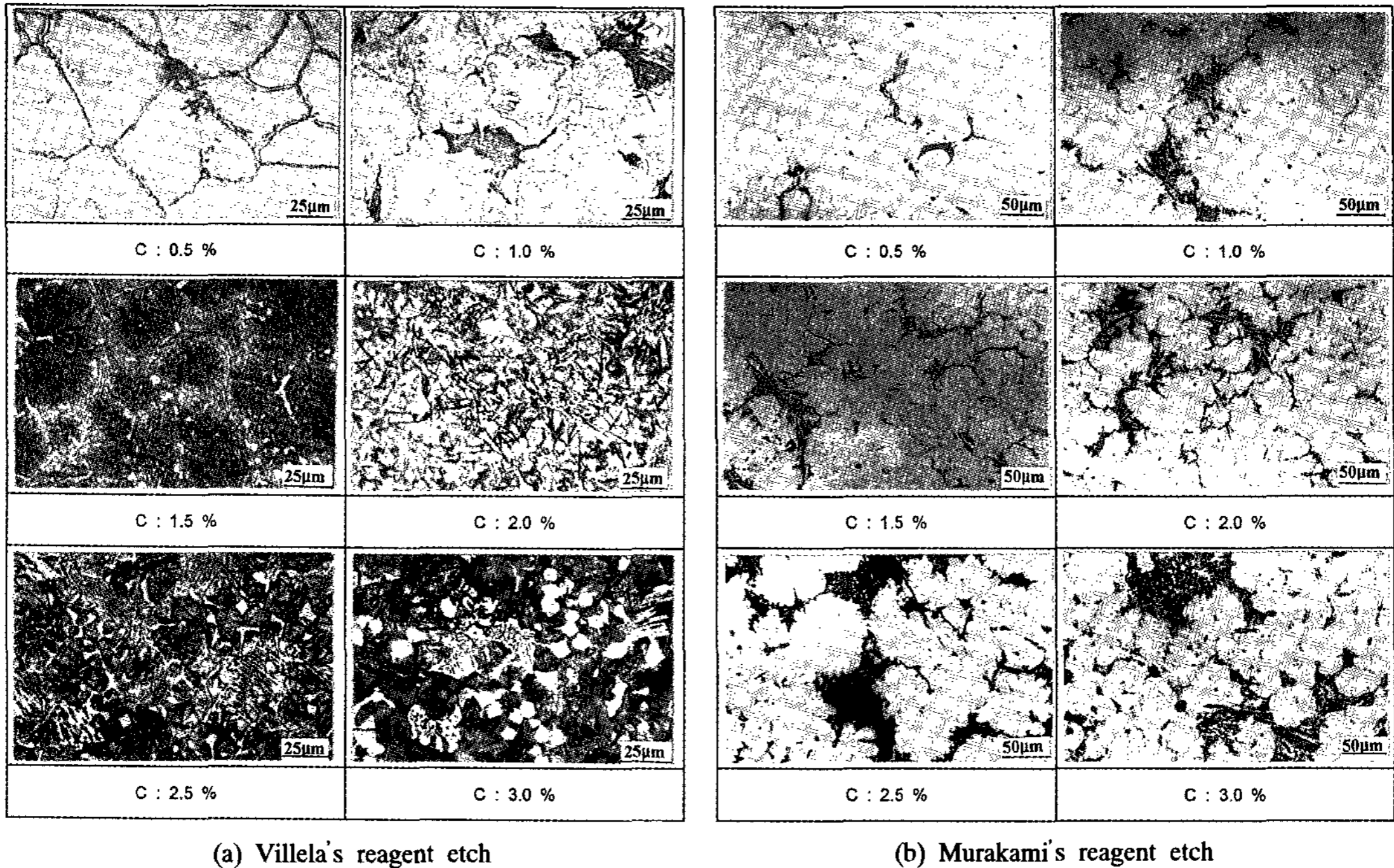


Fig 1. Effect of carbon content on the carbide structure in as-cast specimens.

were observed not only in the grain boundary but also in the matrix. According to the cooling curves of Fe-5%Cr-5%V-5%Mo-5%W-X%C (X=0.5, 1.0, 1.5, 2.0, 2.5, 3.0) multi-component white cast irons[4], at the carbon level of 0.5 or 1.0%, the eutectic reactions of  $L \rightarrow \gamma+MC$  and  $L \rightarrow \gamma+M_2C$  are preceded by  $L \rightarrow \delta$  and  $L+\delta \rightarrow \gamma$  reactions. With increasing the carbon content,  $L \rightarrow \gamma$  or  $L \rightarrow MC$  reaction is followed by the eutectic reactions of  $L \rightarrow \gamma+MC$ ,  $L \rightarrow \gamma+M_2C$  and  $L \rightarrow \gamma+M_7C_3$ .

3.2.2 For the case of heat-treated specimen

The change in carbide structure with various carbon content in the specimens which were forced air cooled from the austenitizing temperature of 1373 K is shown

Table 1. Volume fraction of carbides in 6 specimens

Heat No.	Volume Fraction (%) of Carbide	C <sub>bal</sub> (%)
1 (C=0.5%)	1.36	-1.455
2 (C=1.0%)	4.61	-0.955
3 (C=1.5%)	7.75	-0.455
4 (C=2.0%)	17.01	0.045
5 (C=2.5%)	21.12	0.545
6 (C=3.0%)	24.02	1.045

in Fig. 3.

General morphology of carbides were similar to that observed in the as-cast specimen. The interesting fact to be noted is that fine secondary carbides were precipitated in all specimens, even including those with negative value of C<sub>bal</sub>. From this fact, it can be thought that some amount of carbon and carbide forming elements were still dissolved in austenite because of nonequilibrium solidification due to the higher cooling rate encountered in as-cast specimen. Therefore, during austenitizing at 1373 K for 5.4 ks, the dissolved carbon

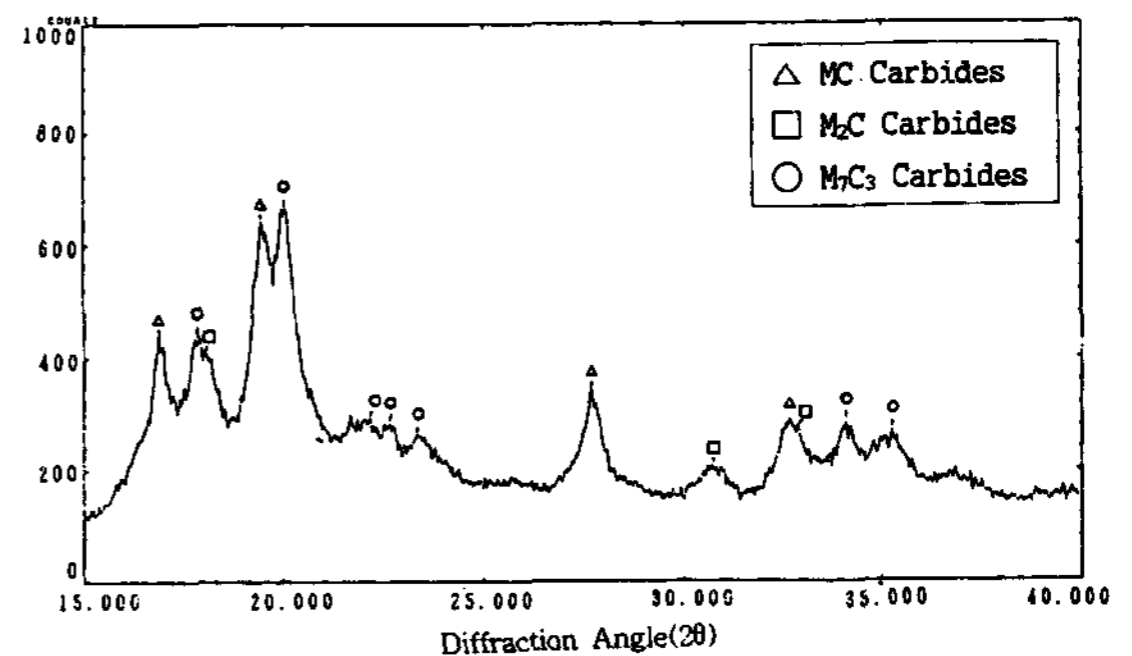


Fig. 2. X-ray diffraction pattern of carbides in the specimen of Heat No. 6.

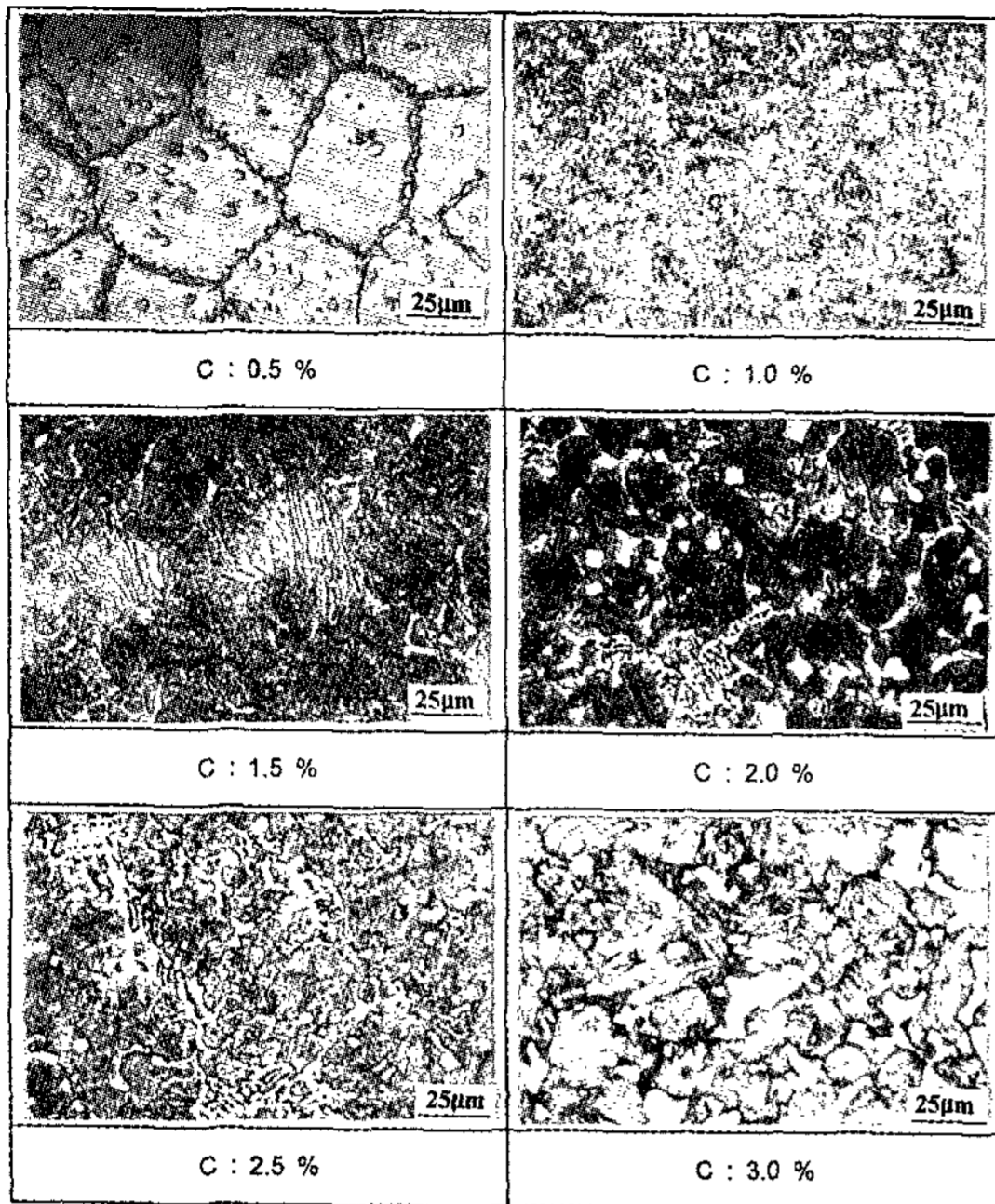


Fig. 3. Effect of carbon content on the carbide structure in forced air cooled specimens. (Vilella's reagent etch) (Austenitizing temperature: 1373 K)

and carbide forming elements were combined and precipitated as secondary carbides. The same phenomenon was also observed in the specimens which were forced air cooled from the austenitizing temperatures of 1273 and 1323 K for 5.4 ks. With an increase in the austenitizing temperature, less but coarser secondary carbides were observed. This can be explained by the fact that the diffusion rate of carbon and carbide forming elements was accelerated by raising the austenitizing temperatures, and coalescence of fine carbides precipitated was occurred during austenitizing. Fig. 4 shows the microstructural variation of specimens with the carbon content in the specimens which were forced air cooled from 1373 K and followed by tempering at 573 K. The type and morphology of the carbides were almost same as those observed in the as-cast and forced air cooled specimens. Even if the tempering temperature was raised to 773K, the carbide structure was almost same, but that of matrix was changed.

### 3.3 Effect of Carbon Content on the Amount of Austenite in the Matrix

#### 3.3.1 For the case of as-cast specimen

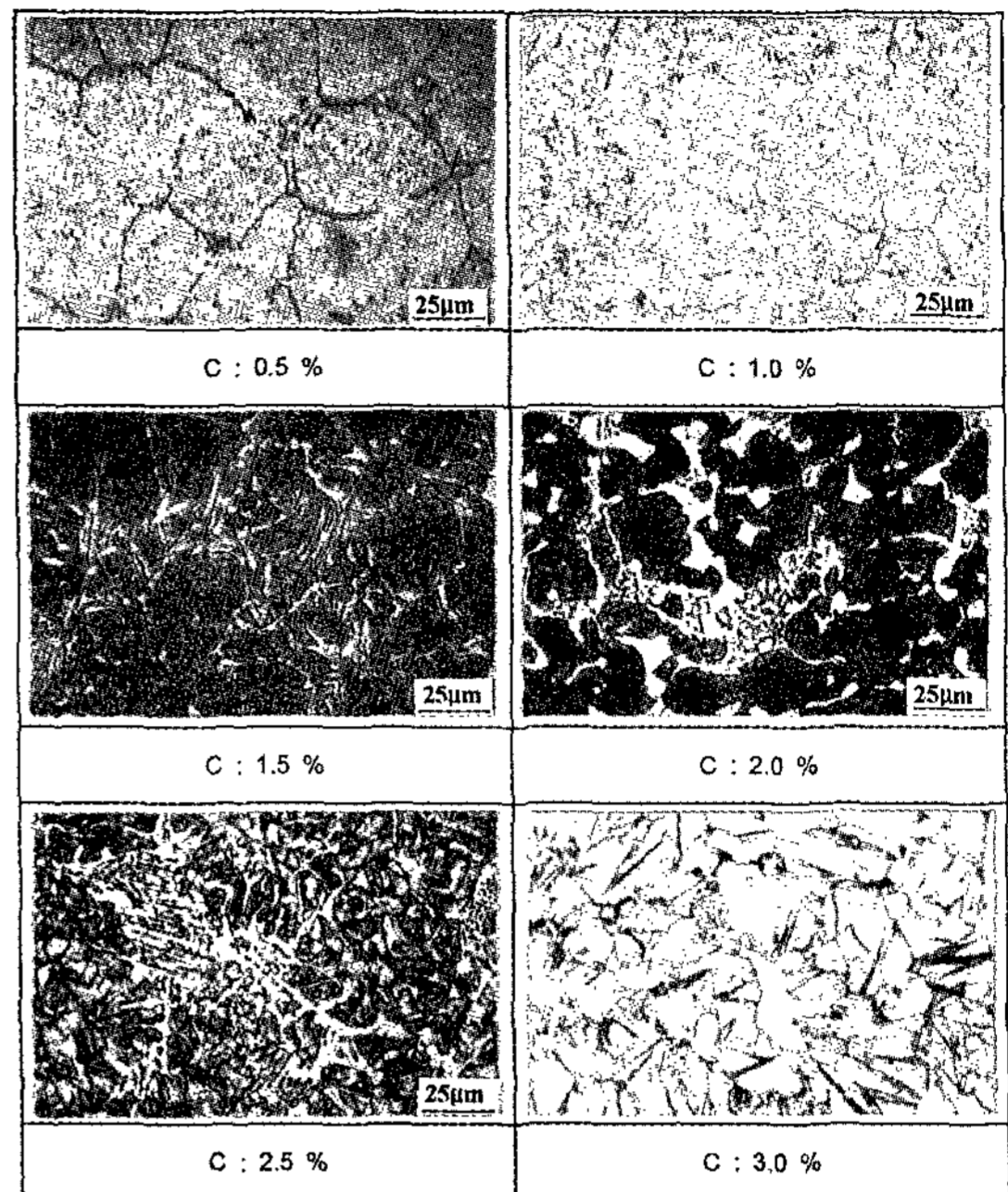


Fig. 4. Effect of carbon content on the carbide structure in tempered specimens. (Vilella's reagent etch) (Austenitizing temperature: 1373 K, tempering temperature: 573 K)

$V_{\gamma}$  as a function of carbon content is shown in Fig. 5. As was shown in Fig. 1, almost all of the matrix were ferrite in the specimens with 0.5 and 1.0% C, which can account for very low values of  $V_{\gamma}$  in these specimens. Then,  $V_{\gamma}$  increased as the carbon content increased up to 2.5% at which the maximum  $V_{\gamma}$  of 84.8% was obtained, but it decreased again at 3.0% C. By increasing the carbon content from 1.5 to 2.5%, more part of the matrix was occupied by austenite with the remainder of the matrix being martensite. This can be attributed to the fact that  $M_s$  temperature decreased with an increase in carbon content. In high chromium white cast iron as well as carbon steel, carbon is known to decrease  $M_s$  temperature whereby more austenite is formed with increasing the carbon content. As for the 3.0% C specimen, fully pearlitic structure was obtained instead of austenite-martensite mixed structure and a large amount of rectangular primary MC carbide was observed. Therefore, it is considered that much of the added carbon was consumed for the formation of primary MC carbide, and the resulting matrix microstructure became pearlite because the carbon content in

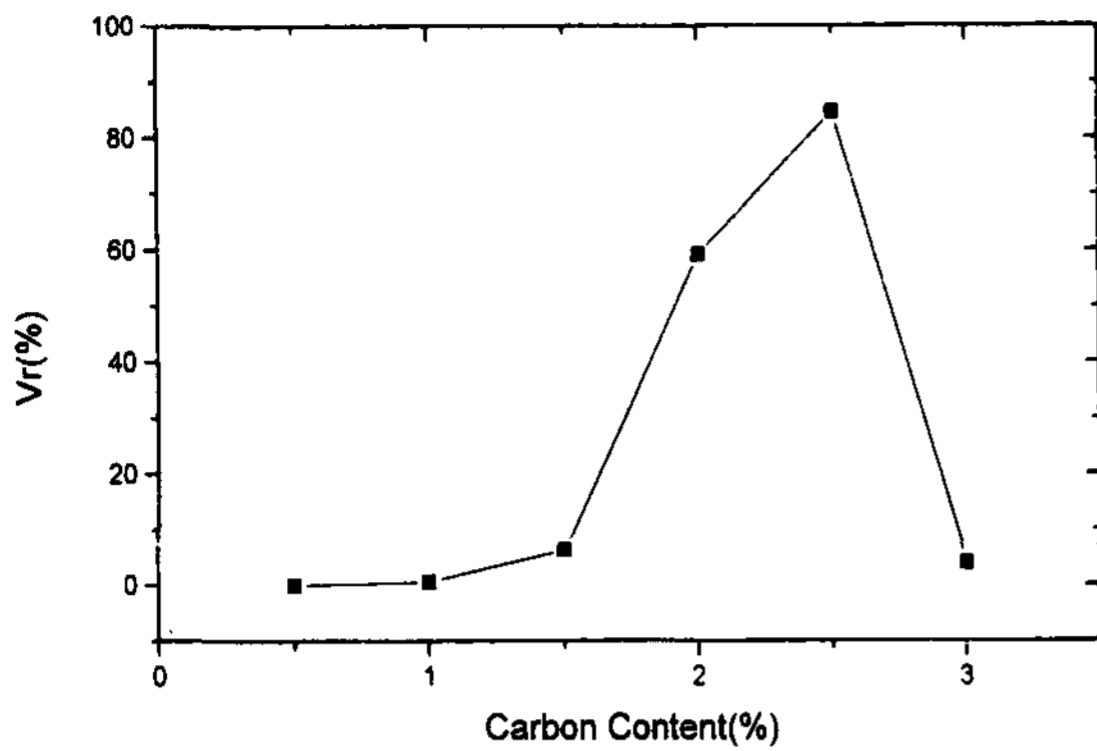


Fig. 5. The relationship between carbon content and V<sub>γ</sub> in as-cast specimens.

the matrix was lowered.

3.3.2 For the case of forced air cooled specimen

The relation of carbon content vs. V<sub>γ</sub> in the specimens forced air cooled from three different austenitizing temperatures is shown in Fig. 6. In contrast to the situation observed in the as-cast specimens, V<sub>γ</sub> continued to increase with increasing the carbon content from 1.5% to 3.0%. Although fully pearlitic structure was obtained in the as-cast specimen with 3.0% C, austenite-martensite mixed structure resulted in with forced air cooling. At the same carbon level, the higher austenitizing temperature, the more austenite was retained.

Because of nonequilibrium solidification in the as-cast specimens, austenite is supersaturated with carbon and carbide forming elements whereby M<sub>s</sub> temperature is lowered and V<sub>γ</sub> becomes high. Thus, the heat treatment is required to reduce carbon and carbide forming elements in the matrix by precipitating it as the second

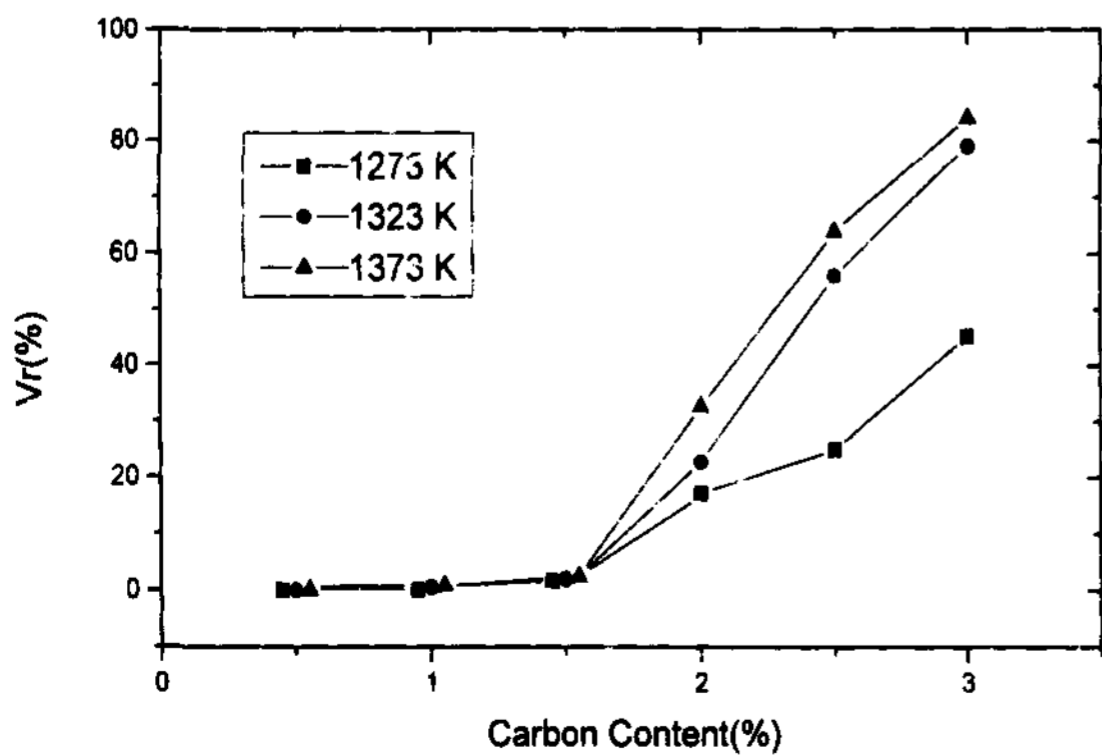
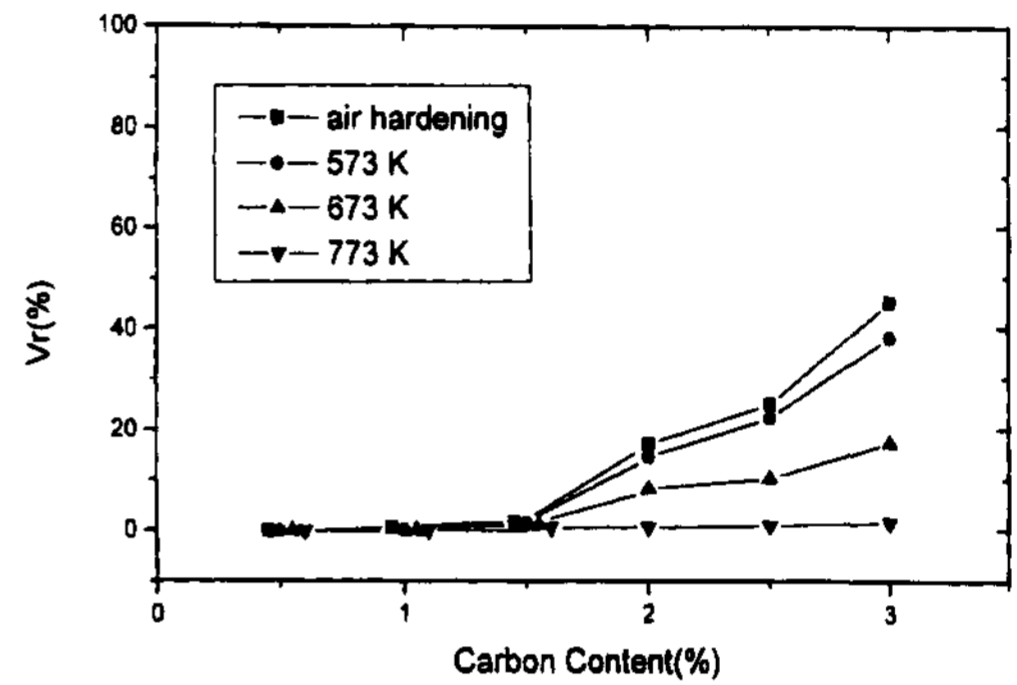


Fig. 6. The relationship between carbon content and V in forced air cooled specimens.

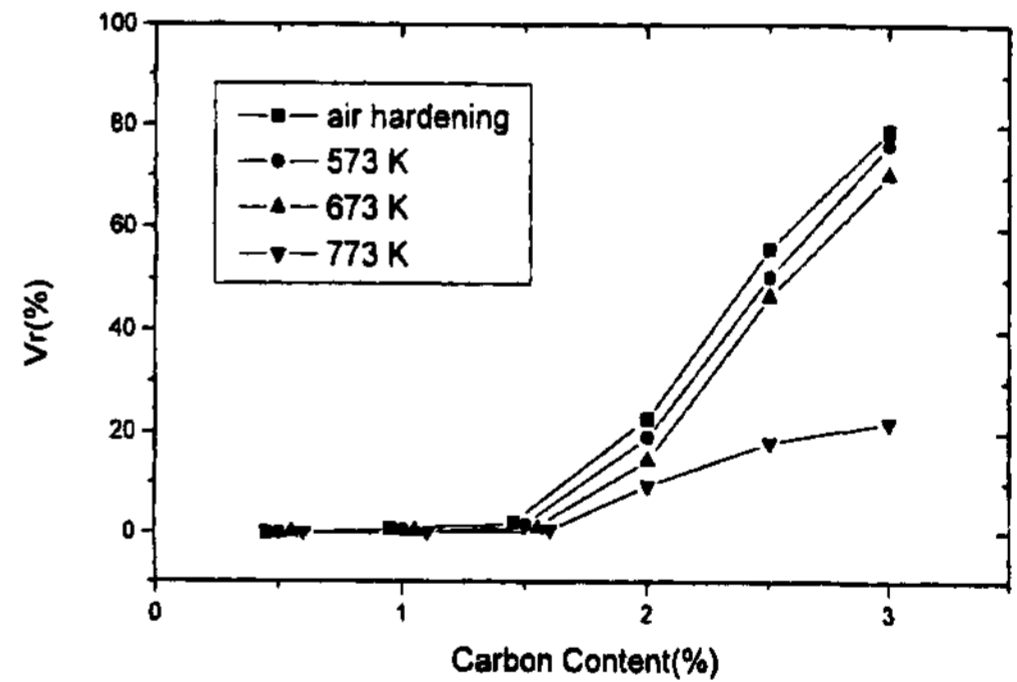
ary carbides, by which M<sub>s</sub> temperature is raised and the matrix is transformed into martensite. The solubility of carbon as well as the third alloying element in austenite increases with the increase in austenitizing temperature whereby less secondary carbides are precipitated and more V<sub>γ</sub> is retained in the matrix.

3.3.3 For the case of tempered specimen

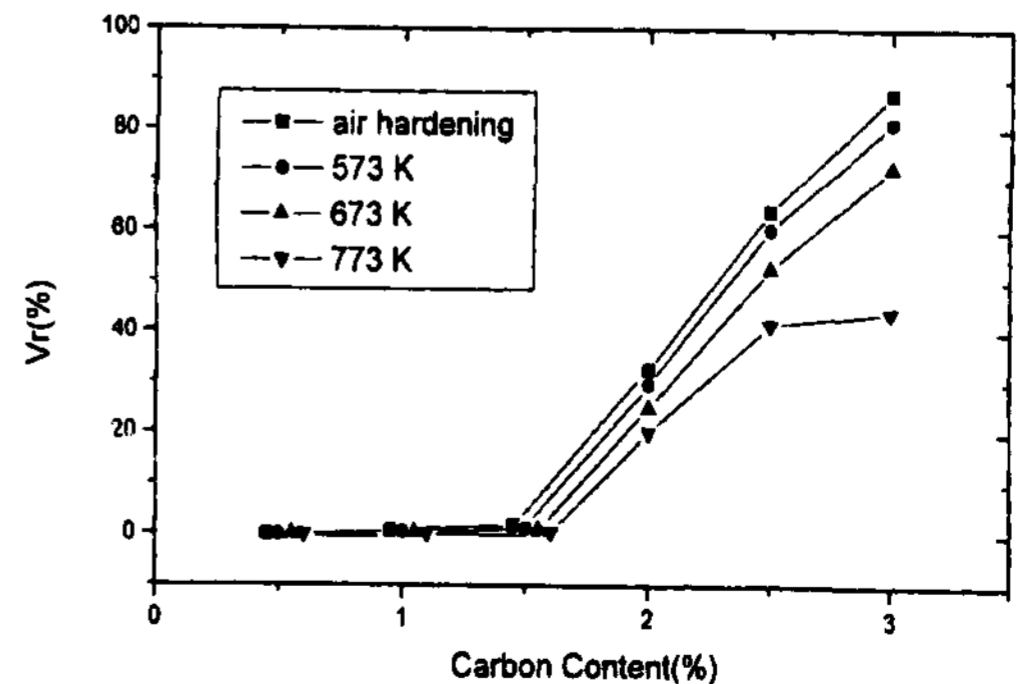
The effect of carbon content on V<sub>γ</sub> in the specimens which were forced air cooled from austenitizing tem-



(a) (Austenitizing temperature = 1273 K)



(b) (Austenitizing temperature = 1323 K)



(c) (Austenitizing temperature = 1373 K)

Fig. 7. Effects of Carbon Content on the Amount of Austenite in the Matrix (Tempered Condition).

peratures of 1273(a), 1323(b) and 1373(c) K, and followed by tempering at 573, 673 and 773 K is shown in Fig. 7. The values of  $V\gamma$  in the tempered specimens were lower than those measured in the forced air cooled specimens(Fig. 6), which proves that the retained austenite was decomposed to tempered martensite or sorbite. At the same carbon level, more austenite was retained in the specimen which was tempered at lower temperature.

#### 4. Conclusions

Multi-component white cast irons with basic alloy composition of Fe-5%Cr-5%V-5%Mo-5%W and with different carbon levels were prepared, and the mutual relationship among carbon content, type and morphology of carbides, and  $V\gamma$  in as-cast and heat-treated conditions was investigated. The results are summarized as follows:

1) In as-cast specimen, the volume fraction and the type and morphology of carbide varied with change in carbon content. Up to the carbon content of 2.0%, only flaky MC and lamellar  $M_2C$  carbides were coexisted in the grain boundary region. On the other hand, in the specimens with more than 2.0% C, rectangular and flaky MC, lamellar  $M_2C$  and cellular  $M_7C_3$  carbides were distributed throughout the matrix. The amount of austenite in the matrix ( $V\gamma$ ) increased with an increase in carbon content up to 2.5% where a maximum  $V\gamma$  of 84.8% was obtained, and then it decreased to less than 10% at 3.0% C.

2) In forced air cooled specimen, fine secondary car-

bides were precipitated during austenitizing, but the type and morphology of the eutectic carbides were similar to those observed in the as-cast specimen. The  $V\gamma$  continued to increase with an increase in carbon content up to 3.0%. It was found that the higher austenitizing temperature, the more austenite was retained in the matrix at the same carbon levels.

3) In tempered specimen, the type and morphology of the carbides were little different from those of the forced air cooled specimen, but the  $V\gamma$  was reduced when compared with that in the forced air cooled specimen. At the same carbon level, more austenite was retained in the specimen which was tempered at lower temperature.

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