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# 고크롬주철의 잔류오스테나이트함량에 미치는 화학조성 및 불안정화열처리의 영향

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# The Effect of Chemical Composition and Destabilization Heat Treatment on the Amount of Retained Austenite in High Chromium Cast Irons

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**초 록** 고크롬주철에 있어서 기지 및 탄화물의 조직제어는 내마모성의 향상을 위해 필수적이다. 특히 기지조직내의 잔류오스테나이트함량은 최적 내마모성을 얻기위해 반드시 조절되어야 한다. 본 연구에서는 3% C-18% (or 25%) Cr-Mo-Ni-Mn 고크롬주철을 800℃, 900℃, 1000℃ 및 1100℃의 질소분위기 하에서 각각 20분 및 60분 불안정화열처리를 행한 후 공냉시켰다. 잔류오스테나이트의 함량은 X선 회절시험을 통해 측정하였으며 회절 peak는 $\alpha_{200}$, $\alpha_{220}$, $\gamma_{220}$ 그리고 $\gamma_{311}$ 을 이용하였다. 화학조성, 불안정화열처리의 온도 및 시간, 그리고 잔류오스테나이트함량간의 관계식을 도출하였다.

***Abstract*** In high chromium cast iron, the control of matrix microstructure as well as carbide structure is important to the performance as a wear resistant material. Particularly, the amount of austenite in the matrix should be controlled to provide an optimum performance for industrial applications. In this study, 18% and 25% Cr white cast irons with constant carbon level of 3% and varying molybdenum, nickel and manganese contents were destabilized at temperatures of 800℃, 900℃, 1000℃ and 1100℃ for 20 and 60 minutes under nitrogen atmosphere, and were followed by air cooling. Then, the volumetric percentage of retained austenite in the matrix($V\gamma$) was measured using a X-ray diffraction method with simultaneously rotating and swinging the sample stage. It was found that $V\gamma$ could be accurately measured by employing the diffraction peaks of $\alpha_{200}$, $\alpha_{220}$ and $\gamma_{220}$, $\gamma_{311}$ for calculation of $V\gamma$. The interrelation among chemical composition, destabilizing condition and $V\gamma$ was clarified.

## 1. Introduction

High chromium cast irons have an excellent resistance to abrasion, corrosion and oxidation because their microstructures consist of chromium-rich primary and eutectic matrix, and eutectic chromium carbides. However, a large amount of austenite is retained in the as-cast state whereby inferior properties are resulted. Therefore, the control of matrix microstructure is important to the performance as a wear resistant material. Particularly, the amount of austenite in the matrix should be controlled to provide an optimum performance for industrial applications.

In this research, the interrelation among chemical composition, destabilization condition and $V\gamma$ was clarified.

## 2. Experimental Procedure

### Preparation of specimen

Specimens were produced using a 15kg silica lined high frequency induction furnace. Melts were super-heated to 1600℃, and transferred into a pre-heated teapot pouring ladle. After removal of any dross or slag, the melts

Table 1. Chemical Analysis for 7 Heats Poured.

| Heat No. | C (%) | Cr (%) | Mo (%) | Ni (%) | Mn (%) | Si (%) |
|---|---|---|---|---|---|---|
| 1 | 2.99 | 18.60 | 0.99 | 0.11 | 1.36 | 2.00 |
| 2 | 3.03 | 20.09 | 0.92 | 1.09 | 1.33 | 2.29 |
| 3 | 3.00 | 19.40 | 1.88 | 0.12 | 1.35 | 1.84 |
| 4 | 3.11 | 20.19 | 1.05 | 0.10 | 2.08 | 1.79 |
| 5 | 3.11 | 21.72 | 1.91 | 2.22 | 1.48 | 1.55 |
| 6 | 3.10 | 26.56 | 1.95 | 1.21 | 1.43 | 1.52 |
| 7 | 3.25 | 26.87 | 2.04 | 0.14 | 2.45 | 1.65 |

were poured at 1550℃ into pep-set molds.

Two sets of castings were made from each melt. One set consisted of cylindrical bars of 10 and 20 mm$\phi$ respectively, having 165 mm in length. Another set was a cylindrical bar of 30 mm$\phi$ × 200 mm h.

### Destabilization heat treatment

The size of specimen used for heat treatment was 10 mm$\phi$ × 10 mm h. These specimens were destabilized at temperatures of 800℃ to 1100℃ for 20 and 60 minutes under nitrogen atmosphere, and subsequently air cooled to room temperature.

### X-ray diffraction method

The $V\gamma$ was measured by using a X-ray diffraction method. The relative intensities of X-ray diffraction peaks from (200) and (220) of ferrite, and those from (220) and (311) of austenite were measured by means of simultaneously rotating and swinging the sample stage.

### Metallographic examination

The specimen was etched, and examined metallographically. The etching solutions used were Murakami's etchant (10 g of potassium ferricyanide, 10 g of potassium hydroxides and 100 ml of distilled water) and Villela's etchant (1 g of picric acid, 5 ml of hydrochloric acid and 100 ml of methyl alcohol).

### Alloy design

Heat series 1 : In order to determine the effect of Mo, Ni and Mn on the $V\gamma$, the hypo-eutectic high chromium cast irons (3.0% C-18.0% Cr) with five different combinations of each alloying element were prepared as follows :

| Mo (%) | Ni (%) | Mn (%) |
|---|---|---|
| 1.0 | 0.0 | 1.0 |
| 1.0 | 1.0 | 1.0 |
| 2.0 | 0.0 | 1.0 |
| 1.0 | 0.0 | 2.0 |
| 2.0 | 2.0 | 1.0 |

Heat series 2 : As in the heat series 1, two different levels of Mo, Ni and Mn were added in the hyper-eutectic high chromium cast irons (3.0% C-25.0% Cr) as shown below :

| Mo (%) | Ni (%) | Mn (%) |
|---|---|---|
| 2.0 | 1.0 | 1.0 |
| 2.0 | 0.0 | 2.0 |

## 3. Experimental Results

### Chemical analysis

A summary of the chemical analysis of the seven heats is shown in Table 1.

### Effect of chemical composition on as-cast microstructures

The microstructures obtained in the as-cast bars are classified into two types : hypo-eutectic microstructure (Heat 1-5) and hyper-eutectic microstructure (Heat 6-7). Fig.1 shows the microphotographs of the specimens

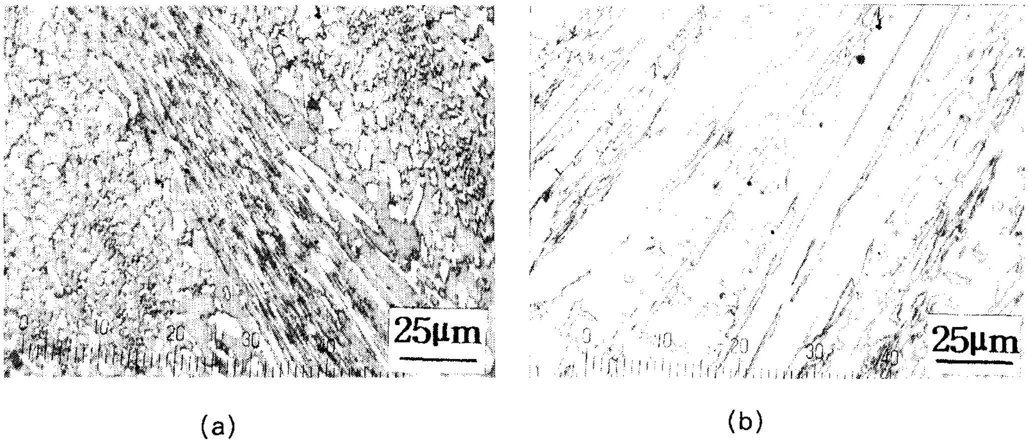


Fig. 1. (a) Microstructure of Heat 2(hypo-eutectic composition) in the as-cast condition. Etched by Villela's reagent (b) Microstructure of Heat 7(hyper-eutectic composition) in the as-cast condition. Etched by Villela's reagent

with 10 mm$\phi$ having Cr/C ratio of 6.5 and 8.7, respectively. As shown in Fig.1, the hypo-eutectic structure was characterized by austenite (primary and eutectic) and eutectic carbides. On the other hand, the hyper-eutectic structure consisted of carbides (primary and eutectic) and eutectic austenite.

By the addition of Mo, Ni and Mn, no pearlitic structure was observed in all specimens. Instead, it can be seen that some martensite may coexist in the austenitic matrix as listed in Table 2. The V$\gamma$ was about 80%–93% with the remainder being martensite. The molybdenum carbide was observed in the specimens of Heat 3, 5, 6 and 7 where 2 mass% Mo was added.

Table 2. V$\gamma$ in the As-Cast Specimen

| Heat No. | V$\gamma$(%) |
|---|---|
| 1 | 88.97 |
| 2 | 83.93 |
| 3 | 79.10 |
| 4 | 86.73 |
| 5 | 91.54 |
| 6 | 92.02 |
| 7 | 92.69 |

### Effect of destabilizing conditions on V$\gamma$

The effect of destabilizing temperature and holding time on the V$\gamma$ is shown in Table 3.

### Effect of destabilizing temperature on V$\gamma$

Relationships between V$\gamma$ and destabilizing temperature at the holding time of 20 and 60 minutes are shown in Figures 2 and 3, respectively. It is clear from the figures that the V$\gamma$ increased in all specimens with an increase in destabilizing temperatures. Especially, a significant increase in the V$\gamma$ was observed when the specimens were destabilized at 1100℃ for 20 or 60 minutes. On the other hand, irrespective of the addition of Mo, Ni and Mn, most of the austenite in the matrix transformed into martensite when the specimens were destabilized at 800℃ and 900℃ for 20 or 60 minutes.

### Effect of chemical composition on V$\gamma$

Effects of Ni and/or Mn in the presence of 1.0% Mo, Mo and Mn without Ni addition, Mo and Ni in the presence of 1.0% Mn on V$\gamma$ were illustrated in Table 3. As has been expected from the composition of the irons, the higher alloy addition produced more V$\gamma$.

## 4. Discussion

### Effect of chemical composition on as-cast microstructures

Table 3. The Effect of Destabilizing Conditions on the Vγ

| Destabilizing Conditions \ Heat No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| 800℃ × 20 min | 0.16 | 0.18 | 0.17 | 0.86 | 0.89 | 0.16 | 0.50 |
| 800℃ × 60 min | 0.20 | 0.61 | 0.68 | 0.24 | 0.49 | 0.18 | 0.18 |
| 900℃ × 20 min | 0.13 | 0.92 | 0.18 | 1.75 | 4.10 | 0.17 | 1.82 |
| 900℃ × 60 min | 0.47 | 0.59 | 1.21 | 3.31 | 4.23 | 6.36 | 0.63 |
| 1000℃ × 20 min | 13.15 | 22.36 | 31.69 | 32.72 | 29.34 | 32.39 | 30.07 |
| 1000℃ × 60 min | 13.40 | 13.17 | 12.76 | 31.26 | 29.68 | 29.24 | 40.83 |
| 1100℃ × 20 min | 42.04 | 71.91 | 61.82 | 58.64 | 76.44 | 69.91 | 70.01 |
| 1100℃ × 60 min | 56.76 | 69.57 | 76.07 | 66.80 | 66.51 | 70.86 | 79.64 |

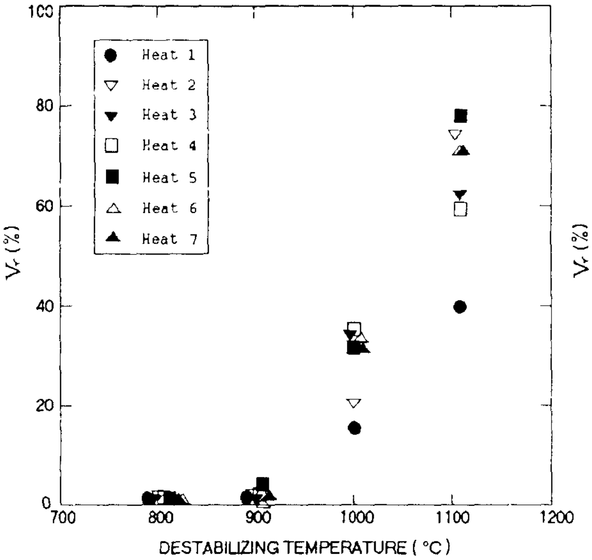


Fig. 2. The effect of destabilizing temperature on the Vγ held for 20 minutes

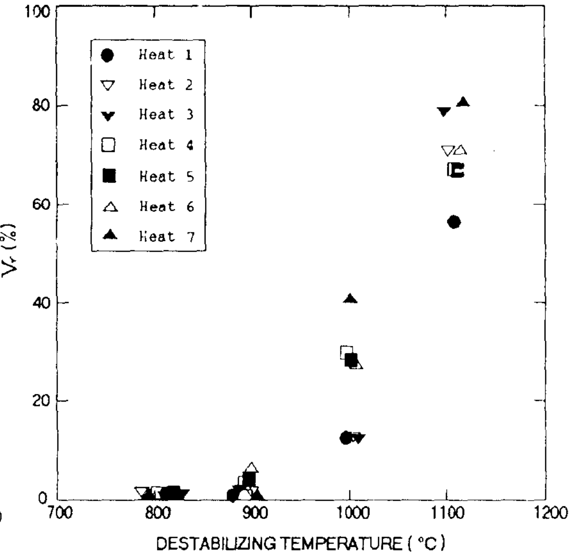


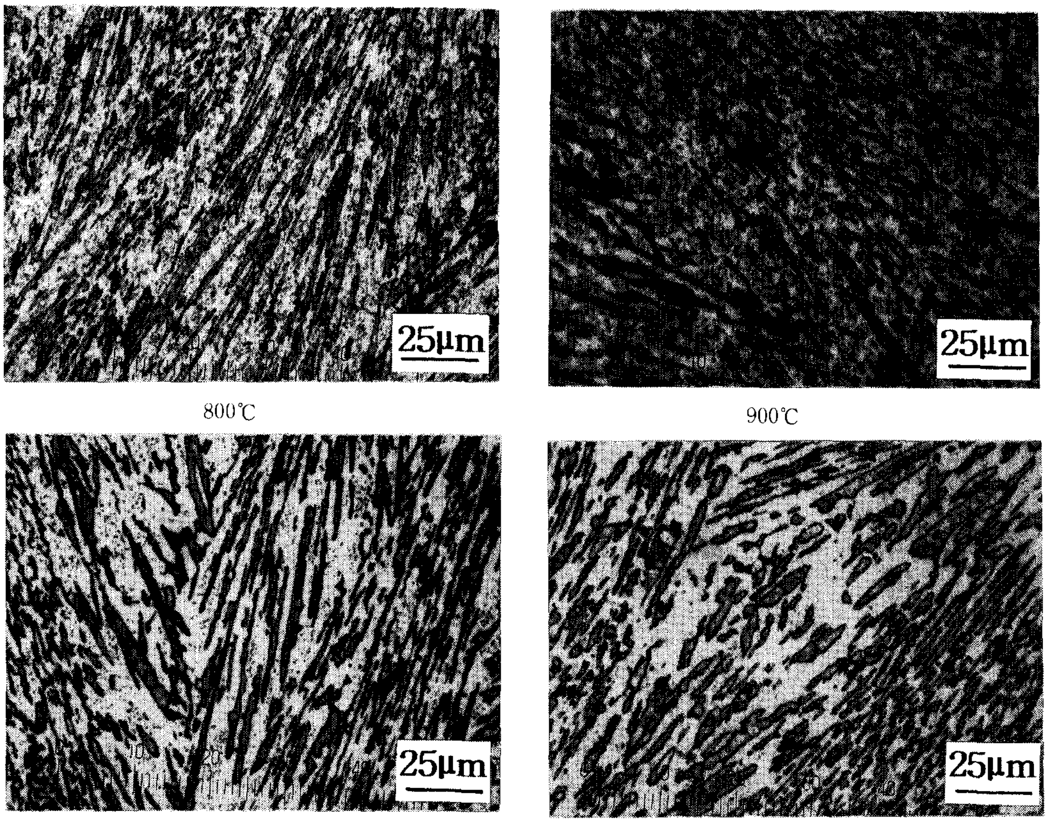
Fig. 3. The effect of destabilizing temperature on the Vγ held for 60 minutes

Effect of Cr on as-cast microstructures

As shown in Figure 1, an increase Cr content from 18.0% to 25.0% characterized the microstructure from hypo-eutectic to hyper-eutectic. With the reference to the liquidus surface diagram of iron-chromium-carbon ternary system[1], the solidification sequence of the hypo-eutectic cast iron (Heat No.1 −5) can be explained by the following procedures: At the end of the crystallization of austenite as primaries, the eutectic reaction of L=γ+ $M_7C_3$ occurrs . On the other hand, the solidification is initiated by precipitating the primary hexagonal carbides, and is followed by the eutectic reaction of L=γ+ $M_7C_3$.

Effect of Mo, Ni and Mn on as-cast microstructures

In the previous study [2], a matrix mixed with 60% Vγ and 40% pearlite resulted when the Mo or Ni-free high chromium cast iron was solidified. But, in this study, no pearlite in the matrix was observed in all irons by the ad-



800℃ 900℃

1000℃ 1100℃

Fig. 4. The effect of the destabilizing temperature on the precipitation of secondary carbides in Heat 1 (hypo-eutectic composition). Etched by Murakami's reagent.

dition of Mo, Ni and Mn. Mo and Ni have an effect to move the CCT curve toward longer time and lower temperatures[3]. Therefore, it can be postulated that on the cooling of iron after solidification, the cooling curve does not pass through the pearlite transformation region, and most of the austenite could be stabilized in stead of being transformed into martensite.

As shown in Table 2, the $V\gamma$ in all specimens is about 80% ~ 93% with remainder of martensite. Therefore, the $V\gamma$ in the as-cast specimens alloyed with Mo, Ni and Mn becomes higher than that of the specimens without the alloying. This might be attributed to the fact that no pearlitic structure is observed in the specimens with alloying Mo, Ni and Mn.

### Effect of destabilizing conditions on volumetric percentage of retained austenite

### Effect of destabilizing temperature on volumetric percentage of retained austenite

As listed in Table 3, the $V\gamma$ is almost negligible when destabilized at 800℃ and 900℃ for 20 or 60 minutes. However, an increase in the $V\gamma$ was observed when the specimens were destabilized at 1000℃ or 1100℃ for 20 or 60 minutes, as shown in Figures 2 and 3.

Because of higher cooling rate after solidification encountered in the as-cast specimens, austenite is supersaturated with C and Cr whereby the $V\gamma$ becomes larger and Ms temperature is lowered. Therefore, the destabilization heat treatment has to be required to reduce C and Cr in the matrix by precipitating the secondary carbides, and subsequently Ms temperature will be raised. The equilibrium concentration of C and Cr in the austenite is determined by Cr/C ratio and destabilizing temperature[4]. At the constant Cr/C ratio, the equilibrium concentration of C in austenite decreases with a decrease in the destabilizing temperature whereby more secondary carbides can be precipitated and higher Ms temperature can be obtained.

The effect of the destabilizing temperature on the precipitation of secondary carbides in Heat 1 is shown in Figure 4. Numerous fine secondary carbides were observed in the specimens destabilized at 800℃ or 900℃ for 20 minutes. Less but coarse secondary carbides were seen in the specimens held for 20 minutes at 1000℃. However, no precipitation of secondary carbides occurred when the specimens were destabilized at 1100℃ for 20 minutes. The same phenomena were also observed in other specimens destabilized for 20 or 60 minutes at 800℃, 900℃, 1000℃ and 1100℃.

### Effect of Mo, Ni and Mn on volumetric percentage of retained austenite

As shown in Table 3 , in the specimens held at 1000℃ or 1100℃ for 20 or 60 minutes, more $V\gamma$ was obtained with an increase in Mo, Ni and Mn . However, regardless of the alloying, the $V\gamma$ in the specimens destabilized for 20 or 60 minutes at 800℃ or 900℃ was almost negligible.

It has been wellknown that Ni and Mn decrease Ms temperature greatly. During solidification, most of Ni is distributed in $\gamma$. Mn also has a high distribution coefficient to $\gamma$. However, Mo is distributed more to carbides than austenite, and sometimes to $Mo_2C$ (with Mo addition more than 2.0 %). Therefore, it can be said that the effect of alloying with Mo, Ni and Mn on $V\gamma$ was diminished when the specimens were destabilized at lower temperatures such as 800℃ or 900℃.

A multiple linear regression was run to show the effect of the principal alloying elements on the $V\gamma$ in the destabilized specimens throughout Heat 1 to 7.

The detailed results of this computer analysis are expressed as :

At 1000℃ $V\gamma=-8.771+4.998\times Mo+3.182\times Ni+13.653\times Mn+0.244\times Cr-0.076\times Time$

At 1100℃ $V\gamma=32.648+6.386\times Mo+4.062\times Ni+5.278\times Mn+0.358\times Cr+0.126\times Time$

As has been expected, the three alloying elements(Mo, Ni and Mn) show a great effect on the $V\gamma$ as compared with Cr.

## 5. Conclusion

1) By the addition of Mo, Ni and Mn, a matrix with pearlite-free structure was obtained and $V\gamma$ of 80−93% resulted.

2) Regardless of alloying with Mo, Ni and Mn, $V\gamma$ was almost negligible when the specimens were destabilized for 20 or 60 minutes at 800℃ or 900℃. At these temperatures, numerous fine secondary carbides were precipitated from the matrix.

3) More $V\gamma$ was obtained with more alloying with Mo, Ni and Mn when the specimens were held at 1000℃ or 1100℃ for 20 or 60 minutes. Less but coarse secondary carbides were observed in the specimens held at 1000℃, and no secondary carbides were precipitated at 1100℃.

4) Following multiple linear regression equations

$V\gamma=-8.771+4.998\times Mo+3.182\times Ni+13.653\times Mn+0.244\times Cr-0.076\times Time$

$V\gamma=32.648+6.386\times Mo+4.062\times Ni+5.278\times Mn+0.358\times Cr+0.126\times Time$

were obtained for the prediction of $V\gamma$ as a function of the alloying elements(Mo, Ni , Mn and Cr) and holding time. From above equations, it is clear the three alloying elements of Mo, Ni and Mn have a great effect on the $V\gamma$.

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