

## Chapter 3

### Experimental Procedure

#### 3.1 Preparation of Specimens

##### 3.1.1 Alloy Design

The chemical composition of the multi-component white cast iron for cold work roll must be designed to satisfy the properties mentioned in the Background Section of Chapter 1. Also, it is important that the properties of the cast iron can be widely changed by heat treatment. The preservation of the roll surface roughness to control the slipping between roll and sheet and the wear resistance, which are more important properties, are undertaken by fine eutectic carbides with high hardness. The MC and  $M_2C$  carbides that are formed respectively by V and Mo and W can be expected for this purpose. However, it will be better that W is eliminated because it has a tendency to make the eutectic  $M_2C$  carbide massive and to promote the segregation of light MC carbide in the roll production by centrifugal casting process<sup>2)</sup>. Cr is needed to improve both the hardenability and oxidation resistance. The C content should be lower than that of multi-alloyed white cast iron for hot work roll because of the high strength and toughness. From these standpoints, the basic alloy composition of Fe-5%Cr-5%Mo was decided, and C and V were varied in the range of 0.5 to 1.5% and 1 to 3%, respectively.

##### 3.1.2 Mold Design and Test Piece

The shape and dimension of the  $CO_2$  mold is shown in Fig. 3-1(a). The exothermic powder was covered on the top of melt just after pouring

to prevent the freezing of the melt from top surface. As illustrated in Fig. 3-1(b), the cast specimen was sliced to obtain the disk-shaped test pieces with 7 mm in thickness.

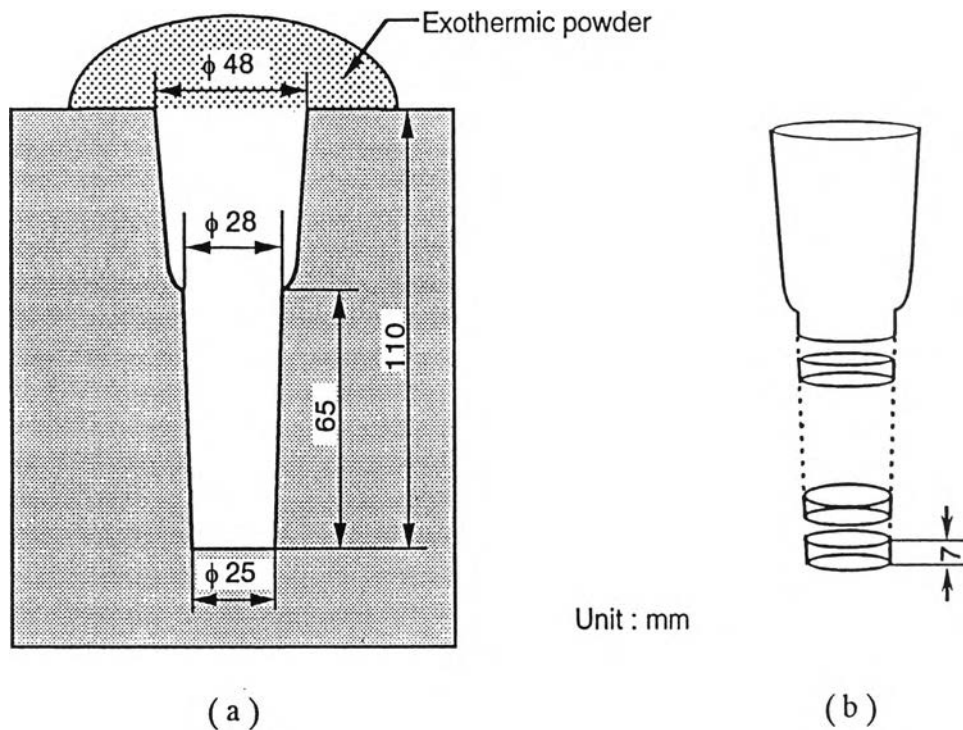


Fig. 3-1 Schematic drawings of CO<sub>2</sub> mold (a) and test piece (b).

### 3.1.3 Production of Specimens

Various kinds of charge materials such as mild steel scrap, high purity pig iron, ferroalloys, pure metals were used to make the specimens. The chemical compositions of charge materials are shown in Table 3-1. Charge calculation for the aimed composition was carried out for total mass of 10 kg. The raw materials were melted down in a 10 kg-capacity high frequency induction furnace with alumina (Al<sub>2</sub>O<sub>3</sub>) lining and

superheated up to 1853 K (1580 °C). The melt was poured into preheated CO<sub>2</sub> molds at the pouring temperature of 1773-1793 K (1500-1520 °C) and then immediately covered with dry exothermic powder. The chemical compositions, the carbon balance ( $C_{bal}$ ) and the type of eutectic carbides precipitated in the specimens are given in Table 3-2.

Table 3-1 Chemical composition of charge materials

Charge Material	Element (mass%)						
	C	V	Cr	Mo	Si	Mn	Fe
Mild steel scrap	0.12				0.02	0.28	bal
Pig iron	4.30				0.20	0.12	bal
Metallic Cr			98.60				
Metallic Mn						99.97	
Fe-Cr (HC)	8.12		60.54		1.80		bal
Fe-Cr (LC)	0.08		67.44		0.37		bal
Fe-Mo	0.05			62.87	0.70		bal
Fe-V	0.09	82.31			1.07		bal
Fe-Si	0.05				77.80		bal

Table 3-2 Chemical composition, carbon balance ( $C_{bal}$ , mass%) and type of carbide in specimens

Specimen	Element (mass%)						$C_{bal}^*$	Type of Carbide
	C	V	Cr	Mo	Si	Mn		
No. 1	0.54	1.03	5.05	4.99	0.51	0.54	-0.32	MC and $M_2C$
No. 2	0.51	1.99	4.90	4.91	0.54	0.53	-0.56	
No. 3	0.99	1.06	4.97	4.84	0.43	0.46	0.14	
No. 4	0.97	1.95	4.92	4.81	0.43	0.45	-0.09	
No. 5	0.97	2.92	4.95	4.79	0.48	0.44	-0.32	
No. 6	1.42	1.06	4.95	4.90	0.47	0.48	0.57	
No. 7	1.42	1.94	4.90	4.84	0.42	0.43	0.37	
No. 8	1.43	2.98	4.96	4.91	0.48	0.48	0.12	

$C_{bal}^*$  was calculated by the equation (2.1) and (2.2).

### 3.2 Heat Treatment Procedure

To investigate the heat treatment behavior of these multi-component white cast irons, three processes of heat treatment listed in Table 3-3 are introduced.

#### 3.2.1 Annealing

The test pieces were pasted with a reagent of oxidation prevention

to prevent the decarburization and charged into an electric furnace. Cold charge were heated up and held at 1223 K (950 °C) for 18 ks (5 hour) to homogenize the micro-segregation of elements. After holding, test pieces were cooled in the furnace. After the furnace cooled down to room temperature, test pieces were taken out and ground by a belt grinder to eliminate the oxide layer.

Table 3-3 Heat treatment process

Heat Treatment Process	Temperature (K)	Holding Time (ks)	Cooling Condition
Annealing	1223	18	F.C
Hardening	1273	3.6	F.A.C
	1373		
Tempering	623	12	A.C
	673		
	723		
	748		
	773		
	798		
	823		
	848		
	873		
	923*		

\* The tempering temperature 923 K was adopted for only specimens No. 7 and 8 which were hardened at an austenitizing temperature of 1373 K.

### **3.2.2 Hardening**

Annealed specimens were set on alumina boat and put into a computerized electric furnace (Model KDF-009G). The specimens and furnace were simultaneously heated up with a heating rate of 20 K/min to 1273 K (1000 °C) or 1373 K (1100 °C) under an argon (Ar) atmosphere (5kg/cm<sup>2</sup>) and held for 3.6 ks (1 hour), and then followed by forced air cooling (FAC) to the room temperature.

### **3.2.3 Tempering**

The hardened specimens were arranged on alumina boat and held at various temperatures for 12 ks (200 minutes). Subsequently, specimens were cooled to the room temperature in the still air. The condition of tempering is also shown in Table 3-3.

## **3.3 Observation of Microstructure**

### **3.3.1 Etching Reagents**

The etchants used in this study are specified as type A, B and C as listed in Table 3-4.

### **3.3.2 Optical Microscopy**

To investigate the microstructure of specimen by means of an optical microscope (OM), the specimen was polished using emery papers in the order of 180, 320, 400 and 600 mesh and finally by a buff cloth with 0.3 micron alumina powder. Type A etchant was generally used to reveal the microstructure. For the identification of the type of precipitated

carbides, the type B etchant was adopted because carbides are colored differently after etching. This result was reconfirmed by alloy concentration in the precipitated carbides measured by means of Electron Probe Microanalyser (EPMA).

Table 3-4 The list of etchants<sup>9)</sup>

Type	Etchant	Etching Method	Observation
A	Picric acid 1 g HCl 5 cc Ethanol 100 cc	Immersion at room temperature	Reveal carbide and matrix structures
B	Murakami reagent KOH 10g K <sub>3</sub> Fe(CN) <sub>6</sub> 10g Distilled water 100ml	Immersion at 60 °C for 1 minute	M <sub>2</sub> C and M <sub>7</sub> C <sub>3</sub> : black M <sub>6</sub> C: colored MC: light etched
C	Nital reagent HNO <sub>3</sub> 5 cc Ethanol 95 cc	Immersion at room temperature	Reveal matrix structure

### 3.3.3 Scanning Electron Microscopy

The microstructure and secondarily precipitated carbides were observed in detail using a Scanning Electron Microscope (SEM) of Hitachi Model S2380 N. A polished specimen was etched using the type C etchant to reveal the microstructure. The microphotographs mainly focusing on carbide morphology were taken using 25 kV for more discussions.

### **3.3.4 Electron Probe Microanalysis**

In order to affirm the type of precipitated carbide revealed by the etching method, the alloy concentration of phases in as-cast specimen was analyzed quantitatively by using an Energy Dispersive X-ray Spectrometer (EDS) of Electron Probe Microanalyser (EPMA) and adequacy of the identified carbide type by etching was certified.

## **3.4 Hardness Measurement**

### **3.4.1 Macro-hardness**

The measurement of macro-hardness was performed by a vickers hardness tester (Akashi Model AVK) with the load of 300 N (30 kgf). Five indentations were taken at random and the average value was availed.

### **3.4.2 Micro-hardness**

Measurement of micro-hardness was carried out in the matrix using a micro-vickers hardness tester (Akashi Model MVK-G1) with 100 gf load and the average value of five measurement was adopted.

## **3.5 Measurement of Volume Fraction of Retained Austenite**

### **3.5.1 Theory for Measurement of Retained Austenite by X-ray Diffraction Method**

The volume fraction of retained austenite ( $V_\gamma$ ) in roll materials is one of the important factors which should be kept at the minimum because the retained austenite has low hardness and becomes a cause of change in



dimension due to post transformation. In the case of roll, the retained austenite leads to the cracking during service because of the volume change by the stress-induced martensite transformation. One of the measurement methods for the amount of retained austenite is X-ray diffraction which shows the diffraction intensity closely related to the amount of retained austenite.

The basic equation of diffraction intensity of a phase<sup>10-12)</sup> is expressed as

$$I_{hkl} = K(FF^*)(LPF)me^{-2M}A(\theta)V_i/v_i^2 \quad \text{-----}(3.1)$$

where,

- K = proportionality constant
- FF\* = structure factor of the unit cell of the phase of interest, equal to  $4f^2$  and  $16f^2$  for diffraction lines of  $\alpha$  (martensite/ferrite) and  $\gamma$  (austenite), respectively, where  $f$  is the atomic scattering factor of the atom species which make up the unit cell :  $f$  relates to  $(\sin \theta)/\lambda$
- LPF = Lorenz Polarization Factor,  $(1+\cos^2 2\theta)/\sin^2 \theta \cos \theta$
- m = multiplicity factor, the number of {hkl} planes in a unit cell
- $e^{-2M}$  = Debye –Waller temperature factor where  $M = (B \sin^2 \theta) / \lambda^2$  : B is a material constant
- A ( $\theta$ ) = absorption factor, independent of  $\theta$  if sample is flat
- $V_i$  = volume fraction of the phase

and

- $v_i$  = volume of unit cell

Let,

$$K' = K \times A(\theta) \quad \text{and}$$

$$R_{hkl} = [FF^*(LPF)me^{-2M}]/v_i^2$$

Substitutes  $K'$  and  $R_{hkl}$  in the equation (3.1) to be equation (3.2),

$$I_{hkl} = K'R_{hkl}V_i \quad \text{-----}(3.2)$$

When several peaks in the diffraction pattern participate in the calculation, the above equation becomes

$$\Sigma I_{hkl} = K'(\Sigma R_{hkl})(V_i) \quad \text{-----}(3.3)$$

Therefore, peaks of ferrite and/or martensite ( $\alpha$ ) and peaks of austenite ( $\gamma$ ) are respectively shown as

$$\Sigma I_{\alpha} = K'(\Sigma R_{\alpha})(V_{\alpha}) \quad \text{-----}(3.4)$$

$$\Sigma I_{\gamma} = K'(\Sigma R_{\gamma})(V_{\gamma}) \quad \text{-----}(3.5)$$

Besides,

$$V_{\alpha} + V_{\gamma} + V_c = 1 \quad \text{-----}(3.6)$$

Where,

$V_c$  is the volume fraction of other phase.

Assume only  $\alpha$  and  $\gamma$  phases exist in the specimen, the equation (3.6) is,

$$V_{\alpha} + V_{\gamma} = 1 \quad \text{-----}(3.7)$$

The relationship between  $V_{\alpha}$  and  $V_{\gamma}$  from the equation (3.4) and (3.5) can be expressed as the equation (3.8)

$$V_{\alpha} = [\Sigma I_{\alpha} \cdot \Sigma R_{\gamma} / \Sigma I_{\gamma} \cdot \Sigma R_{\alpha}] \times V_{\gamma} \quad \text{-----}(3.8)$$

Finally solving the equation (3.7) and the equation (3.8) to obtain the volume fraction of austenite which relates to the diffraction intensity and R values as

$$V_{\gamma} = 1 / [1 + (\Sigma I_{\alpha} \cdot \Sigma R_{\gamma} / \Sigma I_{\gamma} \cdot \Sigma R_{\alpha})] \quad \text{-----}(3.9)$$

For the determination of the amount of retained austenite, R values can be obtained by the calculation, and simultaneously I values can be obtained by measuring the area under the diffraction peaks of  $\alpha$  and  $\gamma$ . Resultantly, the volume fraction of retained austenite ( $V_{\gamma}$ ) is attained numerically.

### 3.5.2 Equipment and Measuring Condition

The measurement of  $V_{\gamma}$  is carried out using X-ray diffractometer.

The measuring condition is demonstrated in Table 3-5. The measurement was performed using the method which developed by R.L. Miller and proved by C. Kim<sup>12)</sup> being applied to high chromium white cast irons. With respect to Miller's technique, the effect of preferred orientation in the cast iron is cancelled by simultaneously rotating and swinging the sample stage. For this investigation, the specimen was prepared by grinding with alumina grinding wheel and followed by polishing with 180, 320, 400, 600mesh emery paper and 0.3 micron alumina powder to obtain the surface like a mirror. Mo-K $\alpha$  characteristic line with a wavelength of 0.711 Å<sup>11)</sup> was used as a source of X-ray beam.

Table 3-5 X-ray diffraction condition for measurement of volume fraction of retained austenite

Target	Mo
Tube Voltage · Current	50 kV · 30mA
Slits	Divergence Slit: 1° Receiving Slit: 1.5 mm Scattering Slit: 1°
Filter	Zr
Scanning Range	24-44 deg
Scanning Speed	0.5 deg/min
Step/Sampling	0.01 deg

### 3.5.3 Calculation of the Volume Fraction of Retained Austenite

In this investigation, the peaks which involves in the calculation are (200) and (220) of ferrite or/and martensite and (220) and (331) of austenite because these four peaks are independent or have no interference

from the peaks of carbide phases<sup>12)</sup>. As examples, the diffraction patterns of three specimens with different  $V\gamma$  of 1.7, 29.9 and 72.5% are shown for comparison in Fig. 3-2. Reason why the  $\alpha(211)$  peak is not taken into account is that this peak is overlapped with strong peak of carbide. The integrated areas under these peaks were measured using an image analyzer (Nireco Model Luzex IIIU). The calculation of  $V\gamma$  was done by a computer for three combination of peaks,  $\alpha(200) - \gamma(311)$ ,  $\alpha(200) - \Sigma\gamma(220,311)$  and  $\Sigma\alpha(200,220) - \gamma(311)$ . The data used as the result are an average of values calculated from the three combinations.

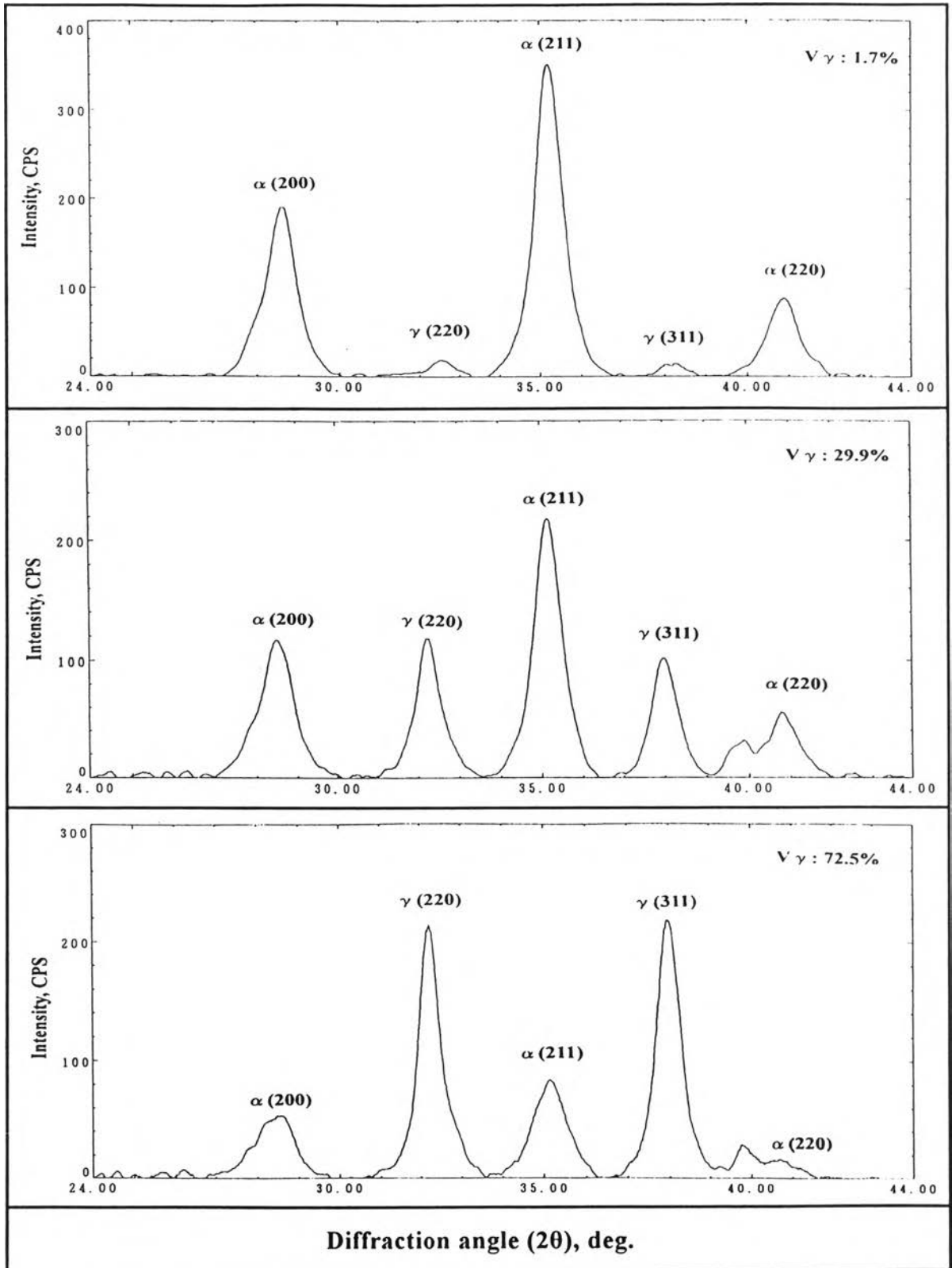


Fig. 3-2 X-ray diffraction patterns of specimens with different volume fraction of retained austenite ( $V_\gamma$ )  
 $V_\gamma$  : (a) 1.7%, (b) 29.9% and (c) 72.5%