CHAPTER II

LITERATURE SURVEY

2.1 Solidification and Microstructure of High Chromium Cast Iron

High chromium cast iron is basically a Fe-Cr-C ternary alloy of which solidification structure consists of carbides precipitated from liquid and matrix. According to the liquidus surface phase diagram of Fe-Cr-C system shown in Fig.2-1, which was constructed by Thorpe and Chicco [9], the primary phases in the region of high chromium cast iron with 12 to 30%Cr are austenite(γ) in hypo-eutectic and M_7C_3 carbide in hypereutectic compositions, respectively. Later, Thong and Umeda [10] proposed the convenient equations (Eq.2-1 and Eq.2-2) to display the liquidus surface of primary γ and eutectic temperatures. From these equations, the liquidus or primary and eutectic temperatures at various combinations of carbon and chromium contents in hypo-eutectic cast irons can be calculated.

$$T_{Liquidus} = 1554.5 - 89.2 \times C\% - 0.77 \times Cr\% \qquad (Eq.2-1)$$

$$T_{Eutectic} = 1201.7 - 20.3 \times C\% + 5.97 \times Cr\% \qquad (Eq.2-2)$$

In general, the wear resistance and mechanical properties of high chromium cast irons are determined depending on the type, morphology and amount of chromium carbides, and the matrix structure. For alloy with hypoeutectic composition which is widely and commercially produced, the austenite solidifies first from the melt and followed by the (γ+M_7C_3) eutectic reaction as typically shown in Fig.2-2 [11]. In the alloy with hypereutectic composition, M_7C_3 carbide precipitates first from the melt and solidification of (γ+M_7C_3) eutectic structure is followed. In the case of alloy with low
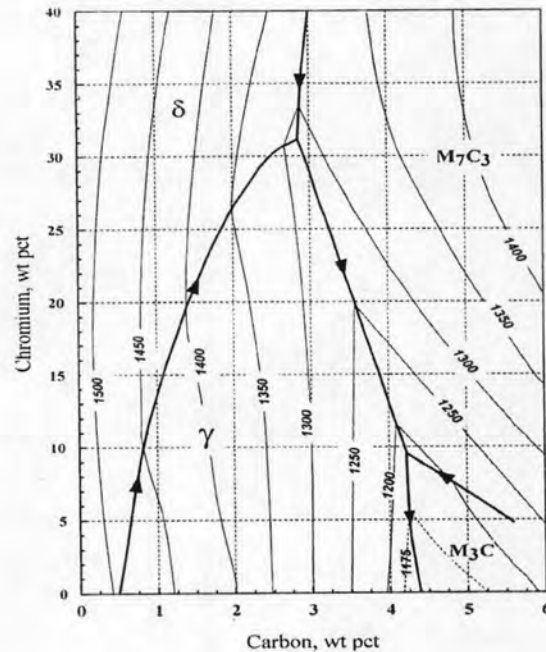
Fig. 2-1 Liquidus surface phase diagram of Fe-Cr-C system [9].

chromium content (less than 10%Cr), $(Fe,Cr)_3C$ or M_3C carbide precipitates as a eutectic, whereas, only $(Fe,Cr)_7C_3$ or M_7C_3 carbide crystallizes as a eutectic in the alloy with chromium contents over about 15% [1,2]. The M_7C_3 carbide is quite different in morphology from M_3C carbide precipitated in low chromium cast iron and Ni-hard iron. The crystal lattice of M_7C_3 carbide is hexagonal while the M_3C carbide is orthorhombic [3].

The hardness of M_7C_3 carbide is 1400-1800 HV and it is much harder than that of M_3C carbide with 800-1100 HV [3]. This difference in hardness improved the wear resistance compared with lower chromium cast irons. Powell [1] observed the carbide morphology of white cast iron by SEM using deep-etched specimen as shown in Fig.2-3. It is noted that the hexagonal M_7C_3 carbides existing in the cast irons with chromium content more than 12% were in rod-like and blade-like morphologies and they were not completely discontinuous. The three-dimensional configuration of $(\gamma+M_7C_3)$

eutectic colonies in high chromium cast iron containing chromium 15% to 20% are illustrated by optical microphotographs. It is pointed out that the eutectic carbides are interconnected and the interconnectivity decreases with an increase in chromium content. With respect to the relationship between microstructure and solidification rate, high solidification rate leads a tendency to promote the selective crystallization of M_3C carbide. Irrespective of the solidification rate, the eutectic carbide of only M_7C_3 type precipitates when the chromium content is more than 15%.

The eutectic colony is clearly revealed by SEM observation and the size of colony is found to change depending on chemical compositions, carbon and chromium contents. The colony size decreases as the carbon content increases when the chromium content is same. It has reported that the colony size is smallest in the iron with 30% Cr [2]. Ogi and Matsubara [27] investigated the growth mechanism of the eutectic cell. The eutectic cell takes a shape of lanky bell and the length of the eutectic cellular projection become larger with an increase in the eutectic freezing range (ΔT_E). On the other hand, the eutectic colony size can be also connected to the ΔT_E and it increases with an increase in the ΔT_E. The rate of radial growth of eutectic cell is closely related to the particle size of eutectic carbides, that is, carbide spacing, particularly in the outside region of eutectic colony.

Base on thermodynamic principle, alloying elements are distributed to both of phases, austenite dendrite and eutectic carbide during solidification. Therefore, the microstructure of high chromium cast iron is greatly influenced by the addition of alloying elements. The volume fraction of carbide (CVF) can be estimated from the initial chemical composition of the cast iron. Maratray [12] demonstrated a following equation that the CVF increases in proportion to the carbon and chromium contents.
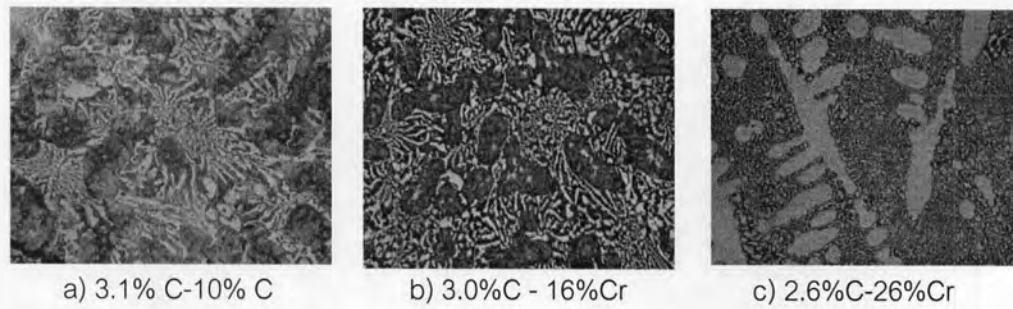
a) 3.1% C-10% C   b) 3.0%C - 16%Cr   c) 2.6%C-26%Cr

Fig. 2-2 Microphotographs of as-cast hypoeutectic high chromium cast irons [11].

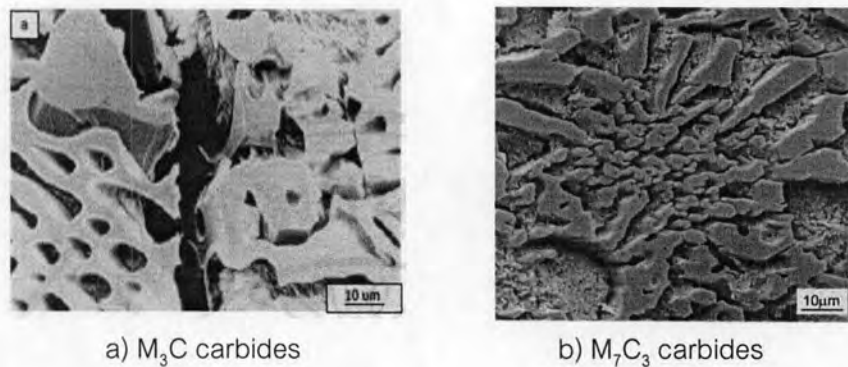

a) M_3C carbides   b) M_7C_3 carbides

Fig. 2-3 Deep-etched microstructures. a) M_3C carbides in 5% Cr and b) M_7C_3 carbides in 17% Cr cast irons, respectively [1].

$$CVF = 12.33(\%C) + 0.55(\%Cr) - 15.2 \qquad (Eq.2-3)$$

High chromium cast irons are sometimes used in the as-cast state where some quantity of γ retains in the matrix. It is said that the hardness is the very important factor affecting the abrasion wear resistance, that is, the wear resistance increases with an increase in the hardness. The hardness of cast iron is determined by the microstructure consisting of kind, amount and morphology of carbide and matrix structure.

In as-cast condition, the matrix of high chromium cast iron often contains

some austenite. It is because the supersaturation of chromium and carbon in matrix occurs during in equilibrium solidification. The carbon content has more effect on the amount of austenite. The more carbon content is, the more austenite retains.

Fully austenitic matrix in as-cast state has positive effect under a certain abrasion wear circumstances which allows austenite to transform into martensite during servicing, and to give a self-replacing wear resistant surface [3,5,7], but the effect is limited in the spalling wear. The high wear performance can be obtained by heat treatment and addition of alloying element because both provide harder and more wear resistant matrix.

Austenite is stable at high temperatures and it will transform to pearlite during cooling under equilibrium condition. However, under non-equilibrium condition, austenite may remain or partially transform into pearlite or martensite depending on cooling rate and chemical composition. Austenite is favored by high cooling rate, high Cr/C ratio, and Ni, Cu and Mo additions [8]. Supersaturation of C and Cr after solidification in the matrix effectively depresses the M_s temperature.

The influence of chromium on the transformation of austenite in the continuous cooling from the as-cast state was investigated by Maratray [12]. Chromium retards the transformation from austenite to pearlite and it lowers M_s temperature. Resultantly, a large amount of austenite exists usually in the as-cast matrix of high chromium cast iron. The as-cast matrix is composed of plural constituents such as pearlite, bainite, martensite and retained austenite. Some martensite appears in the matrix due to the depletion of chromium and carbon around the eutectic carbides. When hardened, the destabilized austenite during austenitization transforms partially into martensite, mixing with retained austenite.

In the most cases, martensitic matrix is preferred to provide high abrasion resistance. For optimum abrasion wear resistance and other mechanical properties, the cast iron with fully martensitic matrix appears to offer the best choice. To obtain the martensitic matrix, the cast iron must be heat-treated. The final microstructure of heat-treated cast iron should consist of eutectic carbides imbedded in the matrix of martensite or tempered martensite mixed with some retained austenite and with secondary carbides precipitated from martensite and retained austenite.

Generally, the alloying elements affect the properties of the cast iron in two ways. First, the element is distributed to the matrix during solidification and the dissolved element determines the matrix structure in the as-cast and the phase transformation behavior in the heat treatment. Resultantly, the properties of matrix can be varied widely by the addition of alloying element. Second, the remained elements are consumed by to form the eutectic carbides, which no longer have any effect on the phase transformation. As for heat treatment of high Cr cast iron, since Cr dissolves preferably in the eutectic carbides, small portion of the total Cr content is retained in the matrix in order to increase the hardenability and improve the heat treatment behavior, supplementary addition of the third alloying elements are needed [3,13]. Normally, the alloying elements such as Mo, Mn, Ni and Cu are added to increase the hardenability and to prevent pearlite transformation. The carbide forming elements such as Mo, V and W used to added when the higher hardness is required [14, 15].

In hypoeutectic cast irons, austenite will tend to reject or to accept certain alloying elements during solidification. The growing austenite dendrite will reject C, Cr, Mo, V and Nb but accept Si, Cu, Ni and Mn. Since Mn is a weak carbide former, it is not strongly rejected by austenite dendrite and it is found that Mn is almost evenly divided in

the austenite and the carbide. When the content of Mo or V exceeds 2%, it can be expected that Mo or V will combine with C to form the special carbides of Mo_2C or VC which has much higher hardness than that of chromium carbide [3]. Because the formation of carbides will consume a large amount of alloying elements, however, low amount of alloy remains in the matrix. At over 3% Mo, the Mo_2C carbide precipitates at the grain boundary [4]. The reason is that the eutectic of $(\gamma + M_7C_3)$ solidifies at high temperature and that of $(\gamma + Mo_2C)$ at low temperature as DTA analysis shows it in Fig. 2.4.
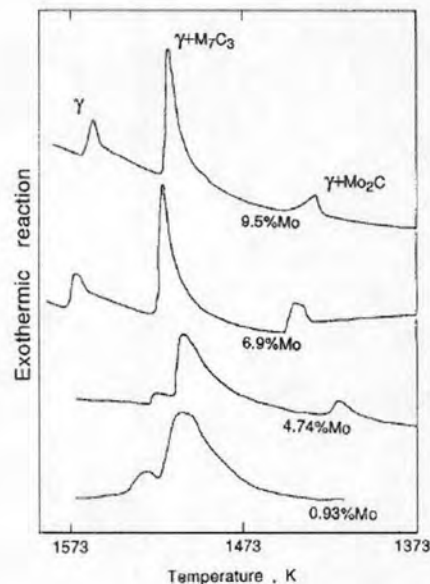

Fig. 2-4 DTA cooling curves of 3% C-20% Cr cast iron with different Mo content [4].

The tramp elements like P and S are limited. It is because P and S strongly segregate into liquid and they form brittle phosphide and sulfide eutectic which cause cracking or hot tearing during solidification. However, these brittle phases have a little effect on the mechanical and wear resistance of the cast irons compared with the effect of the brittlement of eutectic carbide itself.

In order to improve the mechanical properties, the trails to control or to modify the shape of M_7C_3 eutectic carbide were done by the adjustment of alloy composition. The carbide has been modified by the adding of carbide forming elements, such as Nb, V and Ti [3]. The presence of such elements affects significantly the strength of matrix structure, composition and dispersion of carbides [3]. Rickard [16] studied the effect of Ti inoculation on ferritic high chromium cast iron with 1.5%C and 30%Cr. The results showed that TiC carbides precipitated first and followed by delta ferrite (δ) in the solidification process and resultantly finer grained microstructure was obtained. This suggests that TiC acts probably as nucleation sites for the primary δ ferrite during solidification. He also showed the tensile test data indicating that the grain refinement increased the tensile strength from 45 MPa to 54 MPa. The effect of rare earth on the morphology of eutectic carbide was reported by Liang et al. [17]. The mischmetal was added into the low and high chromium cast irons, 3.7%Cr and 18%Cr, respectively, and considerable modification of eutectic carbide was seen in the low chromium cast iron but little change was obtained in high chromium cast iron. This is because eutectic M_7C_3 carbide grew fast as a characteristic configuration of like lath or rod. However, they suggested that the carbide morphology might be changed by adding some elements which could hinder the growth of eutectic during solidification. Powell and Randle [18] observed a reduction in the carbide connectivity when 1.3% Si was added to 18 %Cr iron. Laid and Powell [19] reported that Si inhibits the nucleation of the M_7C_3 carbide in 18% Cr iron. On the contrary, Shen and Zhou [20] reported that an increase in the number of carbide nuclei is due to Si. The reason is that Si was found to refine the dendrite crystallization and increase the volume fraction of eutectic carbide. When the addition of Si was over 3%, transformation of austenite to pearlite occurred in referent to

martensite. B addition to 13%Cr cast iron and to 28%Cr cast iron [30] have changed the carbide morphology from being coarse and interconnected to being isolated in a parallel distribution. [21] The other way to control the size of eutectic is to make the melt cool fast by using chill mold or permanent mold. Matsubara et al. [22] investigated the influence of alloying element on the eutectic structure of high chromium cast iron and clarified that the size of eutectic colony and carbide particle could be controlled by the addition of the third alloying elements which vary the temperature of eutectic solidification range, being extended by Mo, Al and reduced by V. The former case enlarges both the eutectic colony and size of carbide particle and the later case refines them. The addition of Ti refined the eutectic structure that is the sizes of colony and carbide particle, because of its inoculation effect.

2.2 Heat Treatment of High Chromium Cast Iron

As–cast high chromium cast iron has usually some volume fraction of austenite which decreases the hardness. High hardness, better abrasion resistance and resistance to spalling are said to be obtained in the case of martensitic matrix. Generally, the as-cast state does not display the maximum hardness. However, the high chromium cast iron is seldom used in the as-cast condition with some retained austenite, because the austenite can transform into martensite under a certain wear condition and it results in an increase of the abrasion wear resistance. Under the certain wear circumstances, therefore, the martensitic matrix is requested for superior wear performance. In order to obtain more martensite, the cast iron must be heat-treated.

The primary purpose of heat treatment is to destabilized stable austenite to allow the transformation of martensite. Another purpose of heat treatments such as

tempering is aimed to reduce the amount of retained austenite in the matrix and the residual stress caused by hardening. The important thing in the heat treatment of alloyed cast iron is that the transformation behaviors of the alloy have been clarified and understood. It tells us how is the behavior of alloying elements in the matrix, i.e. how they form secondary carbides. In as-cast state, for example, since the matrix is austenitic due to supersaturation of carbon and chromium, a destabilization treatment of austenite is introduced.

2.2.1 Destabilization treatment

Austenitic matrix in the as-cast state can be destabilized by holding at an elevated temperature. So-called destabilization used to be carried out at 1273 – 1323 K for 1 – 6 hours when the as-cast iron has considerable amount of austenite. During holding, the precipitation of secondary carbides occur, the secondary carbides in high chromium cast iron are M_7C_3 and/or $M_{23}C_6$ depending on chemical composition and condition of heat treatment, and they reduce chromium and carbon contents [3, 5, 19]. Powell[19] reported that the precipitation of secondary carbide in austenitic matrix can occur in two stages. The $M_{23}C_6$ carbides precipitate first and then transform to M_7C_3 at the longer holding time.

The typical IT diagram of 20% Cr - 1% Mo cast iron is shown in Fig. 2.5 (a) for the as-cast cast iron while Fig. 2.5 (b) for the cast iron after destabilizing at 1000 °C [3]. The secondary precipitation curve displays the "C" curve in a) and the nose of curve is around 1000 °C. At the higher temperatures, 920 to 1060 °C, the austenite is destabilized and the reaction can be described as;

$$\gamma \quad \rightarrow \quad \text{secondary carbides } (M_3C, M_7C_3, M_{23}C_6) + \gamma^*$$
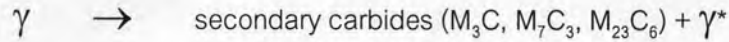
where the γ^* is austenite with a lower alloy content than the austenite with original high alloy content.

This reaction depletes C and Cr in austenite. At the lower tempering temperature in Fig.2-5(b), if enough holding time is given, the austenite is fully destabilized and transforms into pearlite. It is found from Fig.2.5(b) that the pearlite transformation is shifted to the long time side. Due to the precipitation of carbides during destabilization, the alloy concentration in austenite reduces and therefore, Ms temperature goes up above the room temperature, in other word, martensite transformation appears. Hence, during cooling to the room temperature, the retained austenite transforms to martensite. This is one of reasons why retained austenite in the as-hardened state contributes to increase hardness by tempering.

In 25% to 30% Cr cast irons, the $M_{23}C_6$ carbides are formed, and M_7C_3 and $M_{23}C_6$ carbides are found in 15% to 20% Cr cast irons [25]. The M_3C carbides can also form in low Cr cast iron [1, 26, 27]. Powell and Laird [23] predicted the types of secondary carbides to precipitate by using the isothermal section at 1000 °C of C-Cr-Fe ternary shown in Fig.2-6, and they reported that after destabilization of three cast irons with 10% Cr, 18% Cr and 30% Cr at 1000 °C, the main types of secondary carbides precipitated are M_3C in 10% Cr, M_7C_3 in 18% Cr and $M_{23}C_6$ in 30% Cr cast irons, respectively.

The destabilization temperature has a major effect on the transformation of austenite into martensite and controls the final hardness. Maratray and Poulalion [28] suggested that the important factors controlling the amount of retained austenite are
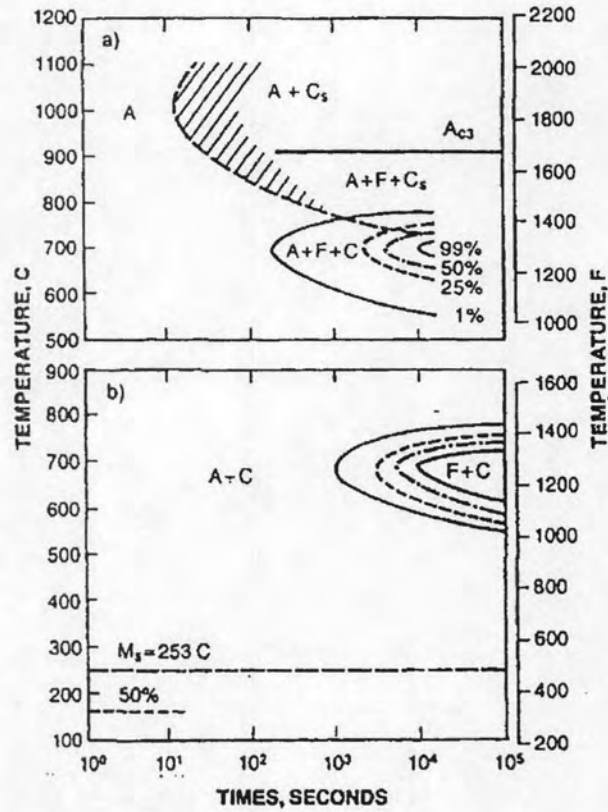
Fig.2-5 Isothermal transformation diagrams of high Cr cast iron with 2.5%C - 20%Cr - 1%Mo; a) before and b) after destabilizing austenite: A= austenite; C= pearlite; F= ferrite; Ms= martensite start; Cs= secondary carbide.   [3]
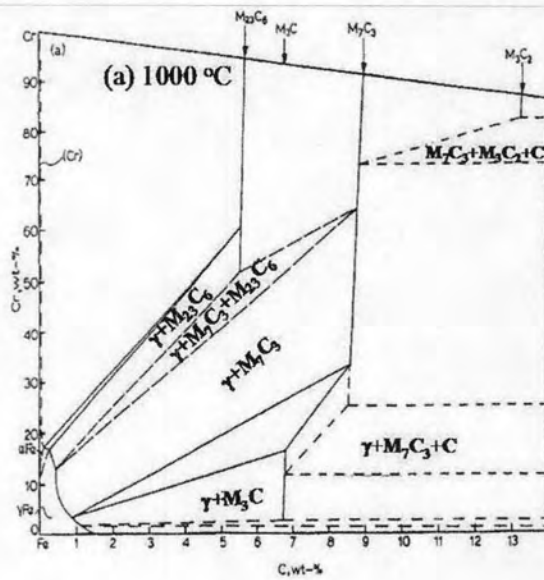

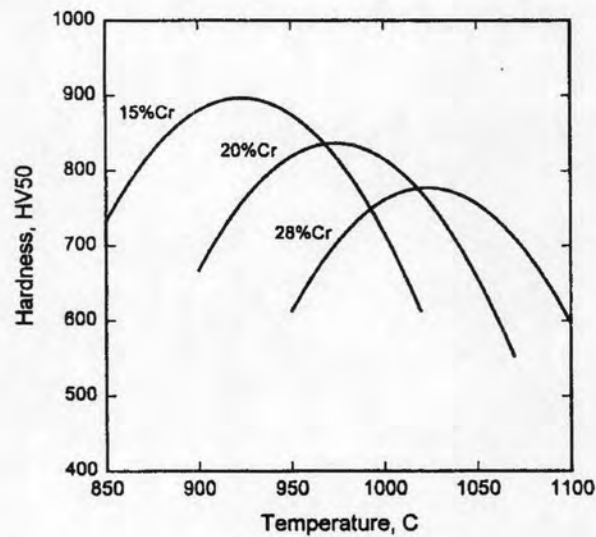Fig.2-6 Solid-state isotherms of C-C-Fe system at 1000 °C.   [23]

Fig.2-7 Influence of Cr content on the optimum hardening temperature in high chromium cast irons.   [28]

chemical composition, destabilization temperature and cooling rate. Chromium content has a significant influence on the optimum hardening or austenitizing temperature and the relationship between austenitizing temperature and hardness is shown in Fig.2-7 [28]. It is found that the higher level of chromium content needs the higher austenitizing temperature to obtain the maximum hardness. The maximum hardness is obtained at the austenitizing temperature between 930 to 1030 $^\circ$C. With an increase in the austenitizing temperature, the solubility of C in austenite increases and resultantly, hard martensite is obtained on subsequent cooling. However, the higher C content in the matrix lowers the M_s temperature and results in the production of more retained austenite which caused a decrease in the hardness.

Since chromium is a strong-carbide forming element, the volume fraction of carbide increases as the carbon content rises. Here a parameter of Cr/C value has been introduced to understand the effect of both the chromium and carbon contents of

the cast iron. It has been reported that in alloy-free cast irons, the volume fraction of retained austenite (V_γ) increases with an increase in Cr/C value up to 4.0 [11]. When the Cr/C value rises over 4.0, the V_γ inversely decreases with increasing the Cr/C value. The V_γ in austenitization at 1050°C is higher than that at 1000°C austenitization. It is also reported that the maximum hardness in as-hardened state was obtained at the Cr/C value of 7.0.

Martensite formation in high chromium cast iron usually occurs at low temperature and then the matrix contains high quantity of retained austenite in the as-hardened state. According to the effect of alloying elements on the Ms temperature of carbon steel, carbon has a greatest effect followed by the other of V, Cr, Ni, Cu and Mo, respectively. A following equation has been proposed experimentally [29]:

$$Ms(^\circ C) = 550 - 350(\%C) - 35\%(V) - 20\%(Cr) - 17(\%Ni) \qquad \text{(Eq.2-4)}$$
$$- 10\%(Cu) - 7(\%Mo)$$

The alloying elements such as Mo, Ni, Cu and Mn are usually added to high Cr cast iron in order to improve the hardenability. They delay the transformation of austenite into pearlite. Most of them decrease the Ms temperature and tend to stabilize the austenite. S. Inthidech et al. [8,11] have been studied widely on the effect of the third alloying elements on heat treatment behavior of high chromium cast irons. Inthidech reported that the V_γ in the as-hardened state increased greatly with increasing Ni, Cu and Mo contents but decreased with V content. However, the hardness reduces remarkably with increasing Ni and Cu contents. [8] The reason is considered that too much austenite is retained. These results agree well with the Eq.2-4.

According to Eq.2-4, it seems that the M_s temperature is dependent on the austenitizing temperature. However, the magnitude of the martensite transformation depends on the amount of secondary carbides precipitated. At a certain destabilization temperature, the amount of martensite increases with increasing the amount of secondary.

2.2.2 Tempering

It has been reported that the spalling resistance decreased when the matrix transformed fully into martensite. [3] This could be due to too high hardness. To overcome this weakness, the tempering or subcritical heat treatment is given. Tempering is necessary after destabilization to transform retained austenite to martensite and to control the hardness to suitable for the service. [3] The tempering temperature and holding time must be carefully chosen so that the martensite must not be over-tempered, or in other words, the tempered martensite can remain greatly in the matrix. Over-tempering leads to a decrease in hardness and resultantly to decrease in the strength of the matrix.

The precipitation of the secondary carbides by tempering decreases both of C and Cr content. The M_s temperature of the destabilized austenite rises as the holding time increases. Maratray [28] reported that in the range of tempering temperature from 753K to 923K (480 to 650°C), $M_{23}C_6$ carbide is more stable than M_7C_3 carbide. Biss [30] showed that the tempering at 923K (625°C) produced $M_{23}C_6$ carbide and he also found the some martensite in the matrix. I.R. SARE et al. [31] reported that in alloyed white cast iron, the hardness does not change until the tempering temperature was risen to 723K (450°C) but over 723K (500°C), it gradually decreases as the tempering temperature increases.

The effect Mo content on tempering behavior of 16% Cr cast irons as shown in Fig.2-8, has been studied by Inthidech et al. [8]. The hardness varies depending on amount of retained austenite, Mo content and tempering temperature. The hardness curves show a clear secondary hardening due to the precipitation of molybdenum special carbides with higher hardness than chromium carbides. The degree of the secondary hardening increases with increasing of Mo content. The maximum hardness by tempering over 800HV30 is obtained at the tempering temperature of 773 - 823K. At the temperature over the maximum point, the hardness is decreased due to the coarsening of secondary carbides, or almost decomposition of austenite to pearlite. According to Fig. 2.8, it suggests that in the cast irons with larger amount of retained austenite, the secondary hardening by tempering gives a higher hardness.

2.3 Abrasion Wear Resistance

In the field of mining, iron and steel, electric power plant and cement industries, various kinds of machines are used for digging, crushing or milling and pulverizing. Abrasion wear usually occurs in these parts by colliding the abrasive particle or fragments on machines surface of materials. The abrasion wear can be classified into three types [3],
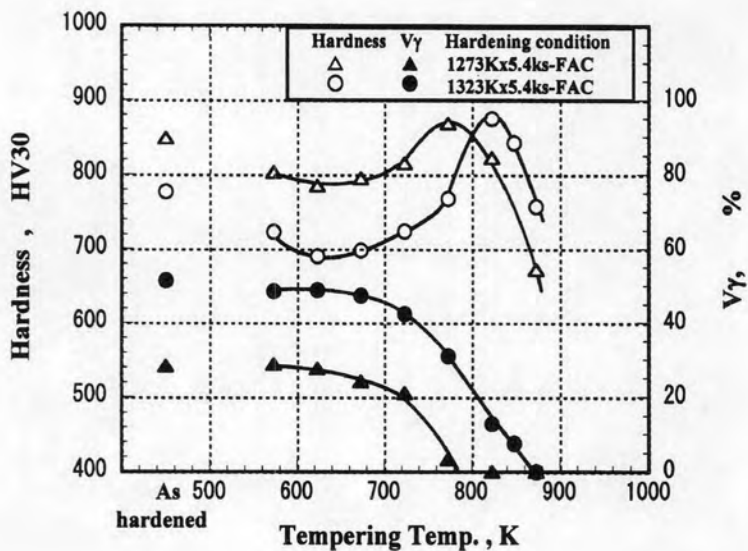
(1) Gouging abrasion which arises when the surface of materials is scooped out by the large mass of abrasives such as ores or stones with heavy impact load e.g. hammer materials in an impact crusher.

(2) Grinding or high-stress abrasion which takes place when mineral or cement clinker is pulverized between two moving metals in ball mill, e.g. wear in mill
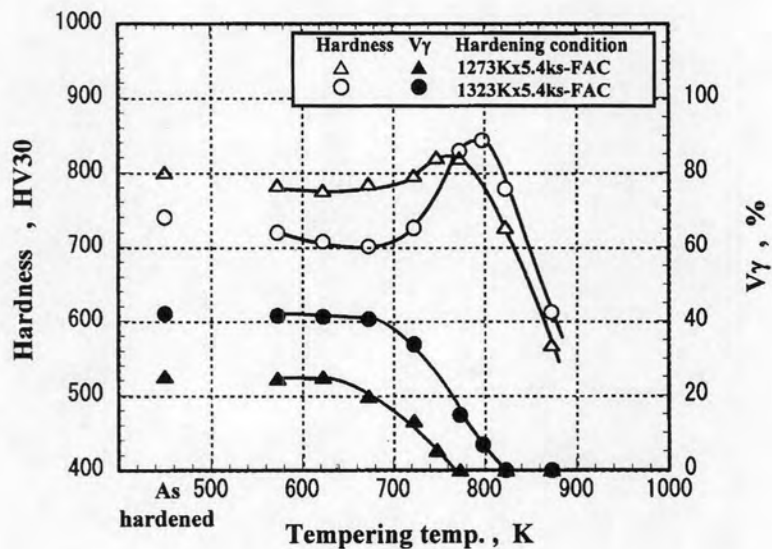
a) 1% Mo

b) 3% Mo

Fig.2-8 Relationship among hardness, volume fraction of retained austenite and tempering temperature of 16% Cr cast irons with Mo. a) 1% Mo and b) 3% Mo [8].

liners and grinding media, and crushing discs and roll.

(3) Scratching abrasion or low-stress abrasion which occurs when the small abrasives are touching or scratching on the surface of working parts and when low stress is sufficient to crush or grind the abrasives, i.e. wear in sand milling, sand and shot blasting, slurry pump.

In general, the combination wear of two or three types occurs on the surface of parts during service. As we know, wear resistance of high chromium cast iron is related to the microstructure, that is, morphology and amount of carbide and the matrix structure, which are factors to determine the macro-hardness of cast iron. These factors may also determine mechanical properties, particularly strength and toughness of the cast iron. As the eutectic carbide change little in both the quantity and morphology after solidification, the matrix structure becomes an important factor to improve the wear property.

As above-mentioned, wear resistance of high chromium cast irons depends on the both of eutectic carbides and matrix structure. High chromium cast iron contains the M_7C_3 carbide as the eutectic carbide, which has higher hardness than that of the abrasive commonly used in the mining industry such as quartz and garnet. Therefore, this irons shows excellent wear resistance. The addition of the strong carbide formers such as V, Mo, Nb and Ti can improve the abrasion wear resistance due to increases the relative hardness [32-35]. It has been reported that the rate of wear increases with increasing the hardness of the abrasive [32-34] and with the size of abrasive particle [36]. Dogan et al. [37,38] reported that carbides aligned parallel to the wear surface produced the higher wear resistance in pin abrasion test.

The wear resistance is determined by the hardness and the toughness of

the cast iron which connected to the amount of carbides. The carbide volume fraction (CVF) has been shown to strong influence in the wear resistance. It was reported somewhere that the carbon increases both the hardness and the CVF as a result in the improvement of the wear resistance [3]. Zum Gahr and Done [39] found that the maximum abrasion wear resistance is obtained at 30% CVF. I.R. Share [7] also showed that an increase in CVF had a little effect upon the spalling rate but the increasing of CVF provides some improvement in abrasion wear resistance.

Abrasion wear resistance of 15% and 26% Cr cast iron in the as-cast condition was investigated by O.N. Dogan [37] and it was discussed by connecting it to CVF. In his paper, an equation (2.5) of CVF vs. carbon and chromium content which was proposed by Maratray[14] was used for calculation of the CVF [11]. The relationship between hardness and CVF is shown in Fig.2-9. At the same chromium content, the hardness increases with an increase in carbon content, and higher hardness is obtained at high chromium content. The relation between CVF and wear rate is shown in Fig.2-10. The wear rate decreases as the CVF increases and the decreasing rate is larger in 15%Cr cast iron, but the wear rate of 15% Cr cast iron is three times as much as that of 26%Cr cast iron. As shown in Fig.2-11, the wear rate decreases roughly in proportion to the hardness. From above reviews, it can be concluded that the abrasion wear resistance of 26%Cr cast iron, which has more austenitic matrix and high CVF, is greater than that of 15%Cr cast iron with bainitic and pearlitic matrix and lower volume fraction of carbide. However, it must be noted that the wear resistance of 15%Cr cast iron can be improved by the addition of alloying elements.

Although wear resistance is generally increased with increasing the CVF, the wear behavior is varied depending on the wear system. Under high stress abrasion,
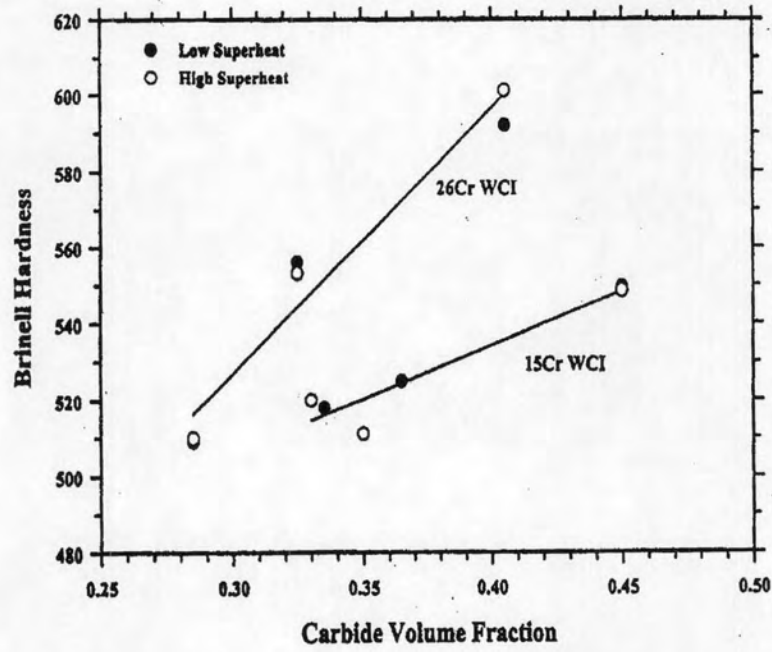
Fig.2-9 Effect of volume fraction of carbide on the overall hardness of white cast irons with different matrix structures [37].
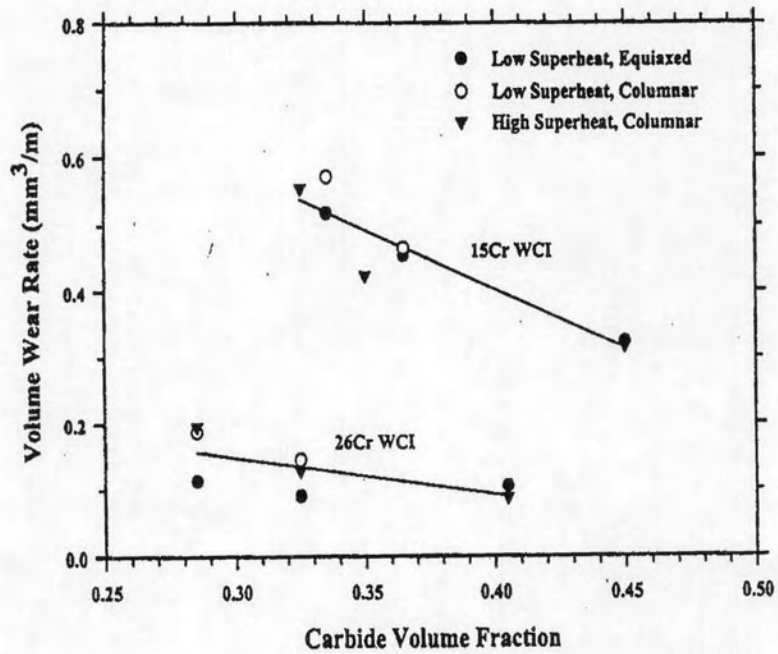

Fig.2-10 Effect of volume fraction of carbide on the abrasion rate of high chromium cast irons [37].
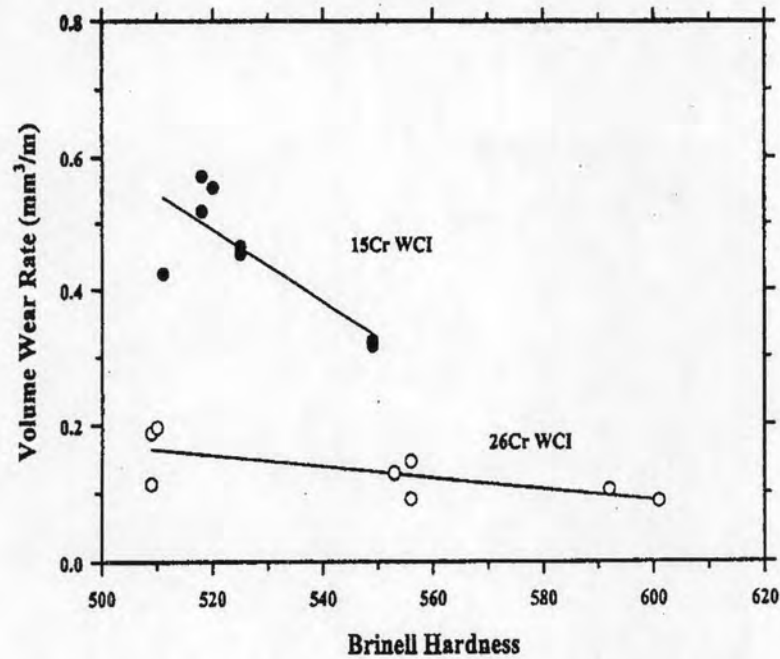
Fig.2-11 Relationship between abrasion resistance and hardness of the two high chromium white cast irons [37].

such as pin-on-disk wear test, large massed carbide provides better abrasion wear resistance [40]. In the case that the abrasive materials are softer than the eutectic carbides, the wear resistance would be expected to increase with an increase in the CVF. When the abrasive materials are harder then eutectic carbides, on the other hand, an increase in the CVF has little effect on the wear resistance. This suggested that the harder abrasive materials rapidly removed the matrix leading to spalling, and therefore greater wear rate become greater. In the case of the abrasive with low hardness, the eutectic carbides protect the matrix and results in a lower wear rate, as the CVF increases [33,34]. Under a low stress abrasion, the increasing of CVF improved the wear resistance [14].

Fracture toughness of high chromium cast iron also depends on the matrix structure and eutectic carbide. In general, M_7C_3 eutectic carbides in

discontinuous morphology have higher toughness than M_3C carbides in continuous morphology. The fracture toughness increases by reducing the CVF. However, the reduction of CVF decreases wear resistance. It was reported that in hypoeutectic cast irons, the CVF of approximately 30-35 vol% shows the optimization or good balance between wear resistance and toughness [4,41].

As mentioned earlier, the wear resistance depends on both the eutectic carbide and matrix structure. Generally, the higher matrix hardness provides the higher abrasion wear resistance. Therefore, the heat-treated cast irons with fully martensitic matrix must have higher abrasion resistance. However, they have lower toughness than austenitic or pearlitic matrix [33,34,42,43]. The wear resistance of high chromium cast iron in the as-cast state is studied by Dogan et al. [37, 38]. The results showed that pearlitic matrix has extremely poor wear resistance compared with the matrix structure mixed with austenite and martensite. Many researches were reported that the large volume fraction of retained austenite was preferable to the abrasion wear resistance against the heavy abrasive load or high stress abrasion condition, whereas in a light abrasion, martensitic matrix is preferred [5,7,37,38]. Even to an impact abrasive load, a certain amount of retained austenite is considered to be effective [37]. It is well known that the retained austenite may often lead to cracking when it is used, because of the great expansion by the stress-induced martensite transformation. This phenomenon is solved by using heat treatment which decomposes the retained austenite to a low level. I.R. Sare [7, 31] reported that the level of retained austenite which gives the optimum wear resistance is, for example, 10% for repetitive-impact condition and 30-40% for gouging abrasion, respectively.

It can be said from the reports mention above that, the parameters being

able to determine the wear property are not the amount of eutectic carbide and matrix structure. Many literatures reported that the small amount of retained austenite in the matrix is not effective to the spalling resistance in applications under the impact loading [3,7,37,38,43]. This is because the transformation of austenite into martensite under repetitive impacts induces the subsurface tensile stress and deteriorates the toughness of the surface layer. In order to overcome this problem, the cast iron should be given the heat treatment which tends to destabilize the retained austenite by further secondary carbide precipitation and allows it to transform into martensite. Gudlace and Parks [32] reported that the abrasion wear resistance of the in heat-treated cast iron which has martensitic matrix is higher than that of as-cast iron which has austenitic matrix[3]. Share et al. [31] studied on pin-on-disk wear test of 27% Cr cast iron and the result was shown that the highest wear resistance is obtained in the as-hardened state containing retained austenite more than 20%. The effect of heat treatment on the gouging abrasion resistance or the high stress abrasion resistance of alloyed white cast iron was investigated by Share and Arnold [5] using a jaw crusher. They found that lowest wear loss or highest wear resistance is obtained at the intermediate level of retained austenite like 30-40%, as shown in Fig.2-12. The relationship between hardness and weight loss is shown in Fig.2-13. Though the data are scattered, it can be said that the weight loss decreases as the hardness increases. In high-stress abrasion, the effects of austenitizing temperature on the wear losses in the as-hardened and tempered cast irons are shown in Fig.2-14. It is usually said that the abrasion resistance after tempering is reduced and the highest abrasion resistance is obtained in the as-hardened state. In tempered state as shown in Fig.2-15, the wear loss decreases gradually as the tempering temperature rises to 723 K (500 $^\circ$C). This can be explained by that over the 798 K (525°C), carbides
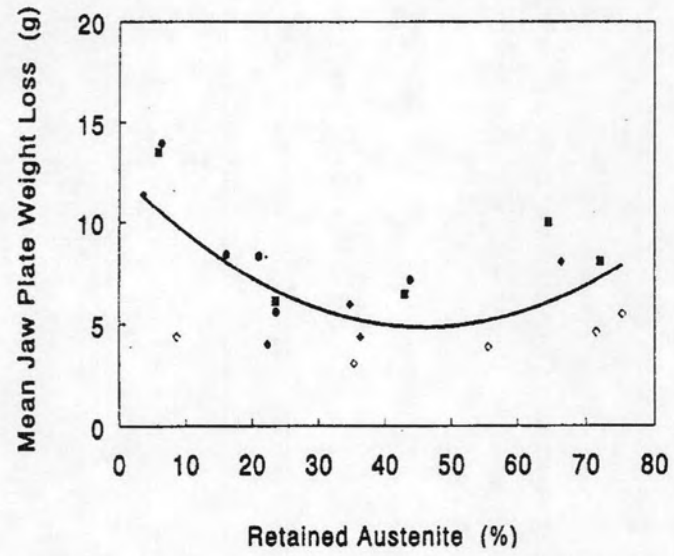
Fig.2-12 Relationship between mean jaw-plate weight loss(g) and volume fraction of retained austenite [31].
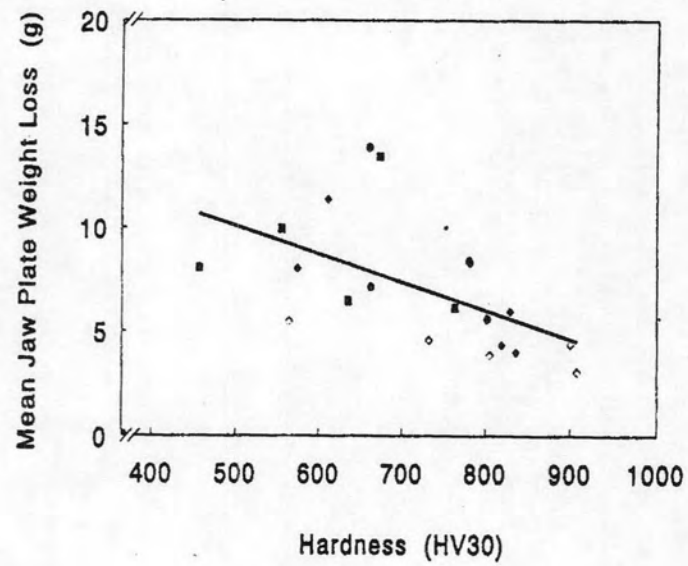

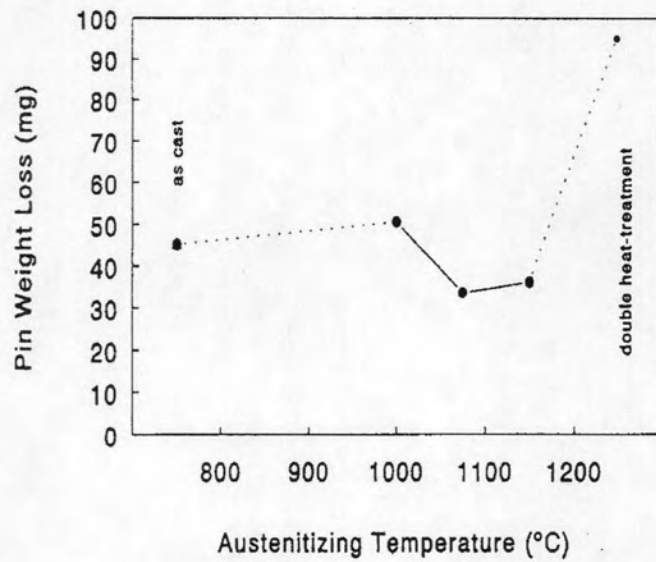Fig.2-13 Relationship between Jaw-plate weight loss and hardness [31].

Fig.2-14 Relationship between mean high-stress abrasion pin weight loss (mg) and austenitizing temperature($^{\circ}$C) of 27%Cr cast iron. Data are also shown in the as-cast and as-tempered condition [31].
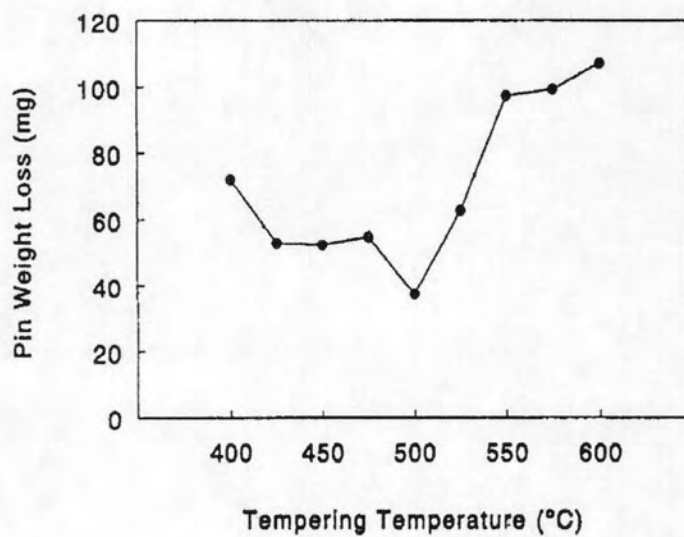

Fig.2-15 Relationship between mean high-stress abrasion pin weight loss(mg) and tempering temperature($^{\circ}$C) of 27%Cr cast iron [31].

formed by tempering starts to agglomerate and to be coarsened. Result of pin-on-disk wear test is shown in Fig.2-16. It is clear that the wear resistance in tempered state is in good accordance with the macro-hardness and it decreases as the hardness increases. To obtain high hardness, the tempering temperature must be chosen by considering the amount of retained austenite in the matrix. Matsubara et al. [44] reported that the abrasion resistance increases in the order of annealed, as-cast, tempered and hardened states. In annealed state, the abrasion wear resistance is lowest because all the austenite were decomposed to coarse pearlite.

Inthidech et al. [8, 11] has clarified the relations in high chromium cast irons that the higher tempering temperature should be adopted as the volume fraction of retained austenite becomes higher to decompose to martensite. S.K. Yu et al. [5] investigated the effect of volume fraction of retained austenite (V_γ) on the rate of abrasion wear (R_w) in hypoeutectic high chromium white cast iron. As shown in Fig.2-17, the R_w decreases with increasing the V_γ because of the transformation of retained austenite to martensite during the abrasion test. Ikeda et al. [4] had studied on the effect of Mo on hot wear resistance in the as-cast 3%C-20%Cr cast irons and the results are shown in Fig.2-18. It is found that hot wear resistance increases with increasing Mo content because the precipitation of Mo_2C carbides prevents the propagation of cracking. However, he suggested that the CVF should be controlled less than 35%.

The cooling rate of hardening also affects the hardness and wear resistance. M. IÇzciler and H. CËelik [45] investigated the effect of cooling rate of boron alloyed high chromium cast iron on the Pin-on-disc and Rubber wheel abrasion wear tests. The comparison of wear rate between Pin-on-disc and Rubber wheel abrasion wear tests of specimen with different cooling rate is shown in Fig.2-19. It is found that the
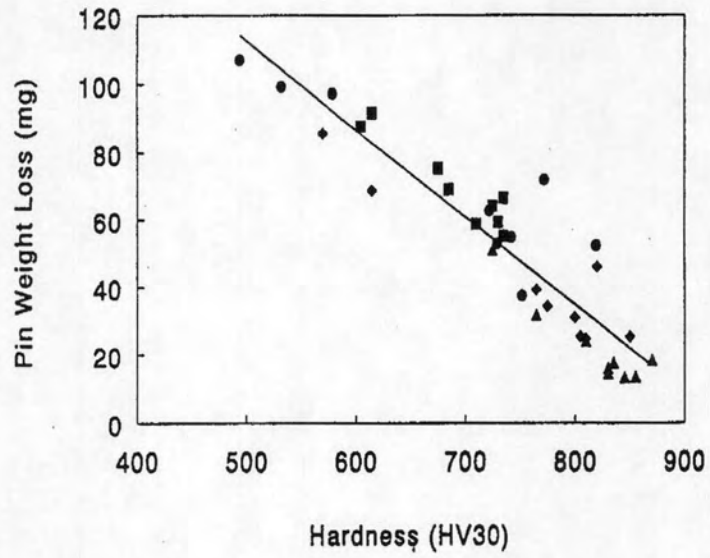
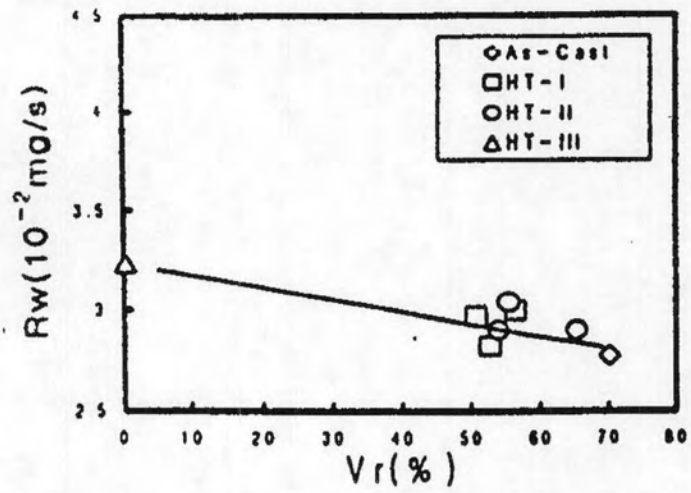Fig.2-16 Relationship between pin weight loss and hardness [31].

Fig.2-17 The relationship between wear rate and volume fraction of retained austenite (V_γ) of hypoeutectic 26% Cr cast irons. [5]
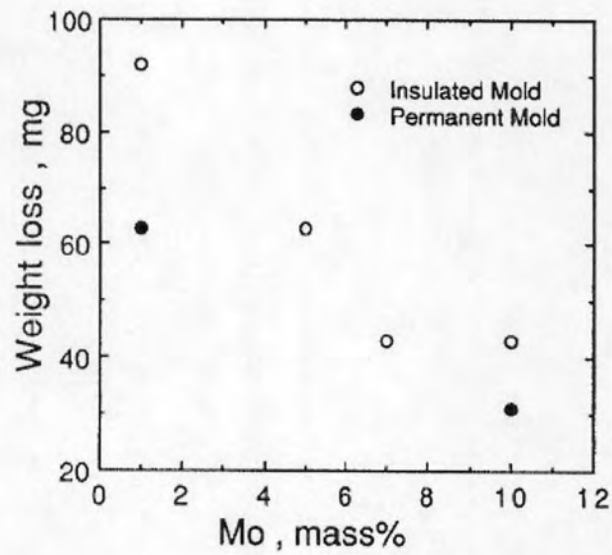
35

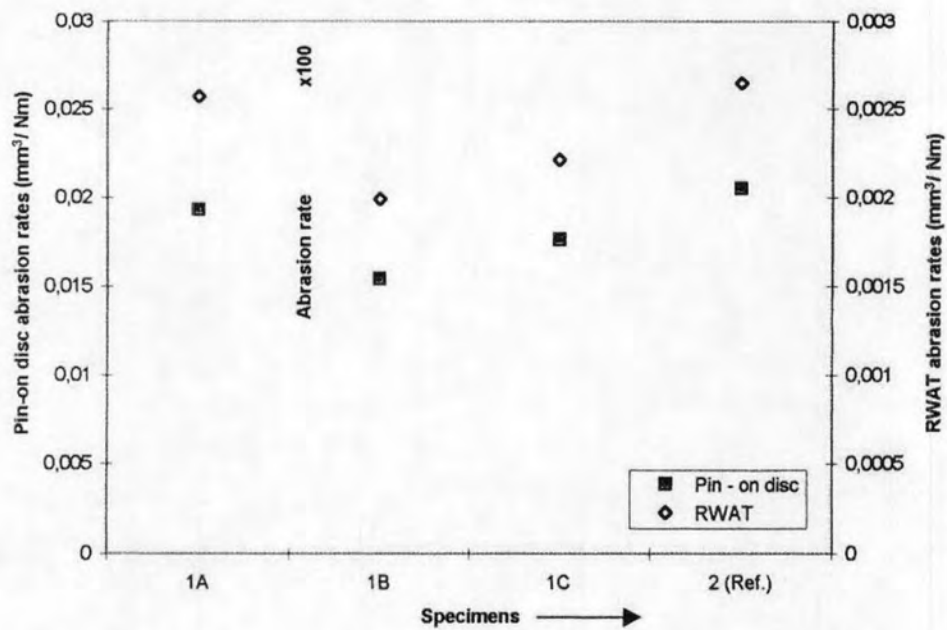Fig.2-18 Weight loss after the wear test 773 K of 3%C-20%Cr cast irons with various Mo contents. [4]

Fig.2-19 Comparison of the abrasion performance results of specimens with different cooling method, fan-air-cooling(1A), oil-quenching(1B) and water-quenching(1C) on Pin-on-disc and Rubber abrasion wear tests. Pin-on-disc: 80 grit SiC abrasive paper, 53.7N load, 5.95m sliding distance; Rubber wheel abrasion wear test: 60 grit SiC abrasive particles, 56N load, 1270 revolutions test duration. [45]

smallest wear rate or the best wear resistance in both abrasion wear tests is obtained in oil-quenched specimen and the largest wear rate or the worst is obtained in specimen cooled by fan air.

The normal heat treatment of high chromium cast iron is cooled down to the room temperature for hardening. Since the temperature at which the martensitic transformation finishes is usually below the room temperature, However, the subzero treatment is generally introduced to reduce the retained austenite and increase the hardness. Hong-Shan Yang et al. [46] investigated the effect of subzero treatment on the matrix structure and abrasion resistance of white cast iron. He reported that the hardness of specimens treated with subzero treatment are greater than those of the specimens by general hardening. The retained austenite in the specimens with subzero treatment was all lower and the wear resistance also was greater. The results are shown in Fig.2-20(a) to (c). It is clear that the subzero treatment can contribute to improve the hardness and wear resistance by increasing the amount of martensite and by decreasing the retained austenite.

The sizes of abrasive particles also have an effect on the abrasion wear. G. Pintaude et al. [47] investigated the effect of the size of granite particle on abrasion wear of mill balls made by high chromium white cast iron. As shown in Fig.2-21(a) and (b), it is apparent that the fine granite gives the highest wear rate or the worst wear resistance in both the dry and wet wear conditions
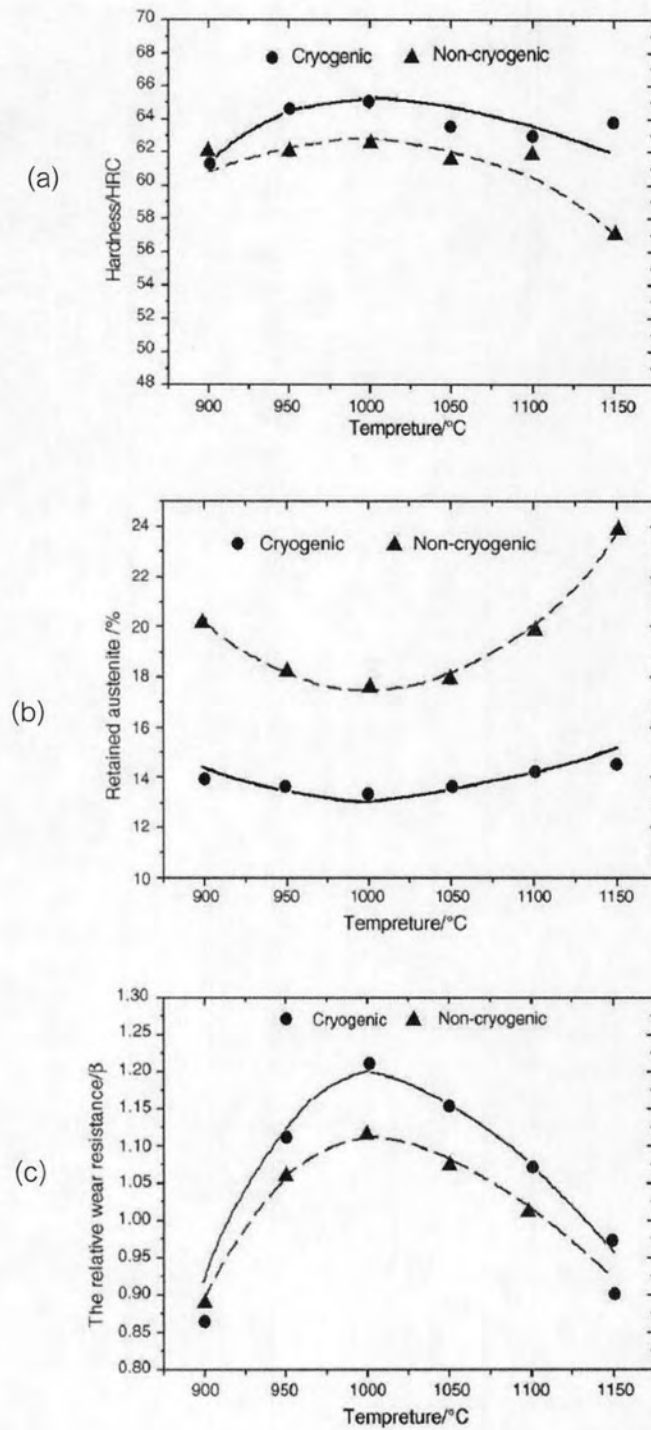
Fig.2-20 Relationship between hardness, retained austenite, wear resistance and the austenitizied temperature of specimen with cryogenic treatment and with non-cryogenic treatment. [46]

Dry condition
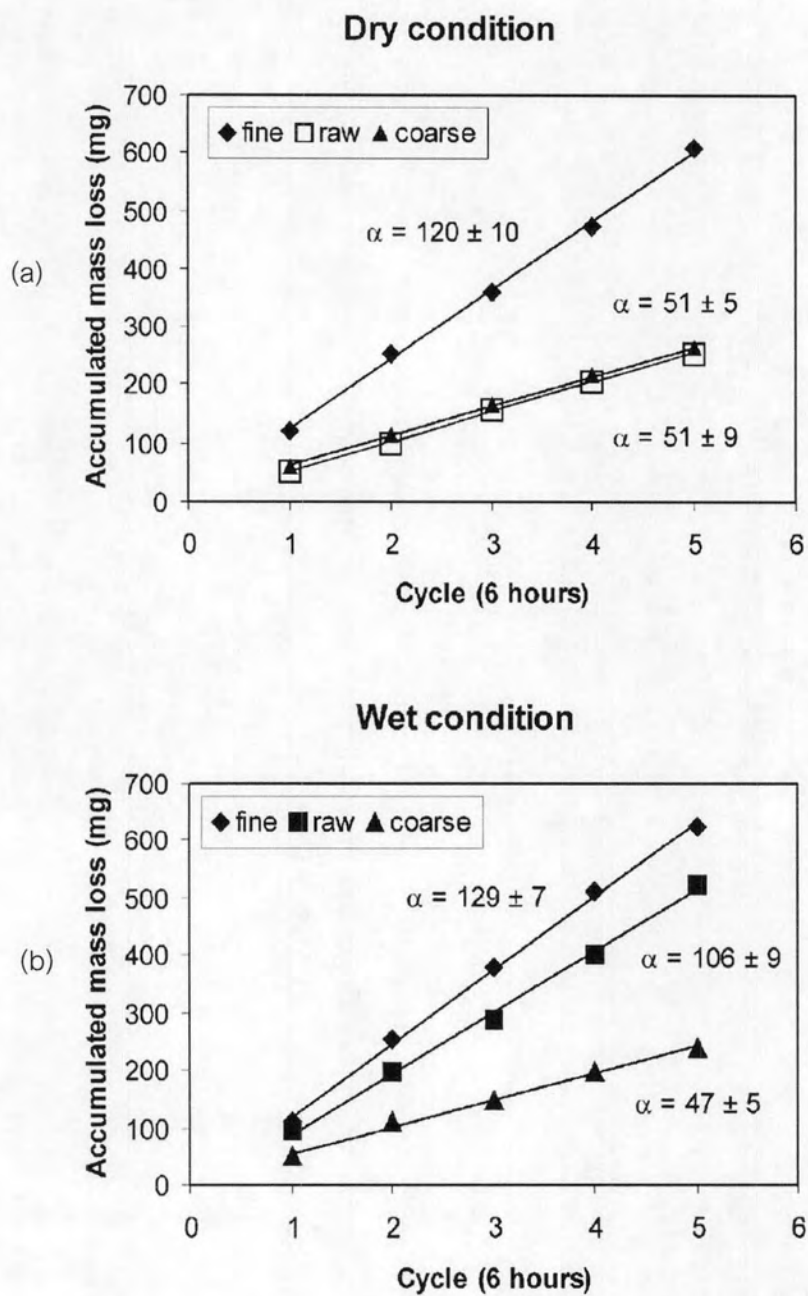

(a)

Wet condition

(b)

Fig.2-21 Accumulated ball mass losses under
(a) dry-grinding condition and (b) wet-grinding condition   [47]