

CHAPTER II

LITERATURE REVIEWS

2.1 Alloyed white cast irons for abrasive wear resistance materials

Abrasive wear resistant materials are extensively needed in heavy industries such as mining, mineral and steel-making. Ferrous wear resistant alloys involving steels and white cast iron show well-established mechanical and wear properties. Among ferrous alloys, white cast iron demonstrates generally good wear resistance as shown in Figure 2.1. Among all candidate materials, alloyed white cast irons are the most common and high performing ferrous alloys employed to reduce the wear. As compared with steels having high toughness but low abrasive wear resistance, alloyed white cast iron has an excellent wear resistance even at the offering of toughness by bearing hard carbide in the microstructure. Therefore, alloyed white cast iron is employed widely in steel-making, cement and mining industries, and they can be classified as follows,

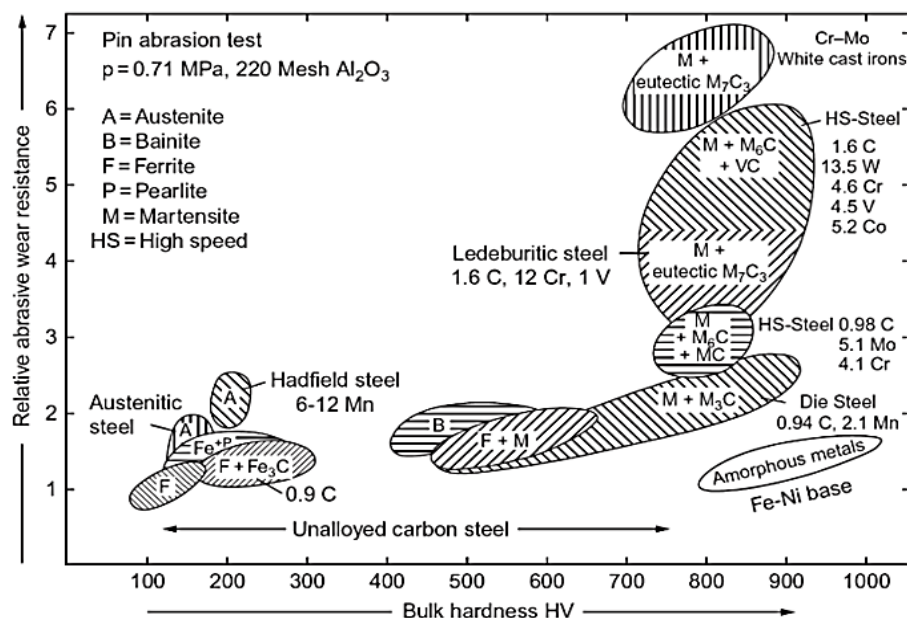


Figure 2.1 Relative abrasion resistance of different classes of alloys and bulk hardness (Zum Gahr, 1987).

2.1.1 Low-alloyed or pearlitic white cast iron

Low-alloyed or pearlitic white cast iron contains low silicon content to prevent graphitization. A small amount of chromium is frequently added to low-alloyed white cast iron to promote the chill tendency and suppress the graphitization during solidification. The solidification structure of low-alloyed white cast iron consists of eutectic in ledeburitic morphology with a pearlitic matrix. The chill layer depends upon the carbon and silicon content of the cast iron. However, the toughness of low-alloyed white cast iron is quite low because it contains a large fraction of ledeburite structure which has a continuous network. The tough matrix of pearlite or other transformed products from austenite is separated by the continuous carbides. Therefore, this group of cast iron is limited to being utilized where high wear resistance and toughness are not severely required.

2.1.2 Ni-hard cast iron

Ni-hard cast iron is alloyed white cast iron with nickel and chromium which was developed by the INCO Company. The first development generation is known as Ni-hard I and II. Nickel prevents pearlite and bainite transformation and promotes martensite transformation in the as-cast condition. Chromium suppresses the graphitizing tendency resulting from nickel and therefore, the carbide is stabilized. It can be expected to improve the abrasive wear resistance due to the formation of M_3C carbide (M: carbide forming elements) with higher hardness than Fe_3C . However, Ni-hard cast iron with some graphite in the structure has been used where strong impact or heavy load is applied. Generally, some austenite is still retained in as-cast condition because the M_s temperature drops together with the M_f temperature due to dissolving the alloying elements in the matrix. Therefore, the fully martensitic matrix cannot be obtained in the as-cast condition. Redundant retained austenite reduces not only the wear resistance but also causes a risk of crack failure resulting from the volume expansion accompanied by the strain-induced martensite during service. Therefore, the subzero treatment is generally applied to modify the matrix structure. However, the toughness is still low because M_3C carbide in ledeburitic cannot be modified.

From above problems, Ni-hard IV cast iron had been developed. This type of Ni-hard cast iron contains 8 to 10%Cr, 4 to 6%Ni and 1.5 to 2.2%Si. Addition of more chromium and silicon results in the transition of eutectic carbide type from M_3C

to M_7C_3 . The M_7C_3 carbide has finer and lesser continuity compared with M_3C carbide. By comparing with Ni-hard I and II cast irons, however, the Ni-hard IV cast iron may show lower abrasive wear resistance in the as-cast condition due to higher amounts of carbon and chromium dissolving in the matrix which reduce the amount of martensite. Typically, the destabilization and the subzero heat treatment processes are given to achieve better wear resistance.

2.1.3 High chromium cast iron

High chromium cast iron was developed in Europe in the late 1970's. This type of cast iron contains a high level of 12 to 30%Cr. The as-cast microstructure consists of hard M_7C_3 carbides with less continuity embedded in the matrix of austenite, martensite, pearlite or bainite depending on alloying elements and cooling rate. Several research studies have been done on the high Cr cast iron to control or modify the solidification structure, heat treatment behavior and mechanical properties (Laird et al., 2000). It is pointed out that the excellent performance as abrasive wear resistant material had been proved. In addition to wear resistance, high Cr cast iron also provides good heat and corrosion resistance due to the highly dissolved Cr in the matrix. Since a supersaturation of chromium and carbon in the matrix, the M_s and M_f temperatures reduce significantly. Resultantly, a large fraction of austenite remains in the as-cast condition. In order to attain more martensite fraction, the cast iron must be heat-treated by the "destabilization treatment". The stable austenite matrix is destabilized by precipitation of secondary carbides during holding at high temperatures. Then, the M_s temperature goes up over the room temperature and therefore, austenite becomes ready to transform into martensite. It is also necessary to add other alloying elements such as molybdenum, nickel and copper to improve the behavior of heat treatment. It was reported that high Cr cast irons showed better abrasive wear resistance than Ni-hard cast iron (Laird et al., 2000).

2.2 Alloyed white cast iron for roll materials

The steel-making process normally provides the most common application of hot rolling operations. Hot rolling mill rolls are tools for forming steel products and a typical roll for hot steel rolling is shown in Figure 2.2. The work process starts out as the thick slab is placed in a furnace until it has reached a uniform temperature so that the metal will flow consistently during rolling. The desired temperature for hot rolling

is about 1100 – 1300°C. After soaking, the slab is moved to the rolling mill where it is rolled into strips. In practical terms as shown in Figure 2.3, the finishing hot rolling mill consists of 6 or 7 stands with work rolls which are placed side by side, and the hot slab is rolled continuously to reduce the thickness. Continuous rolling under high pressure and rolling volume rate are increased due to the high strength of the rolled material. The temperature of the roll surface increases up to 500 – 700°C depending on the kind of steel and roll in the stand (Yarita, 1984).

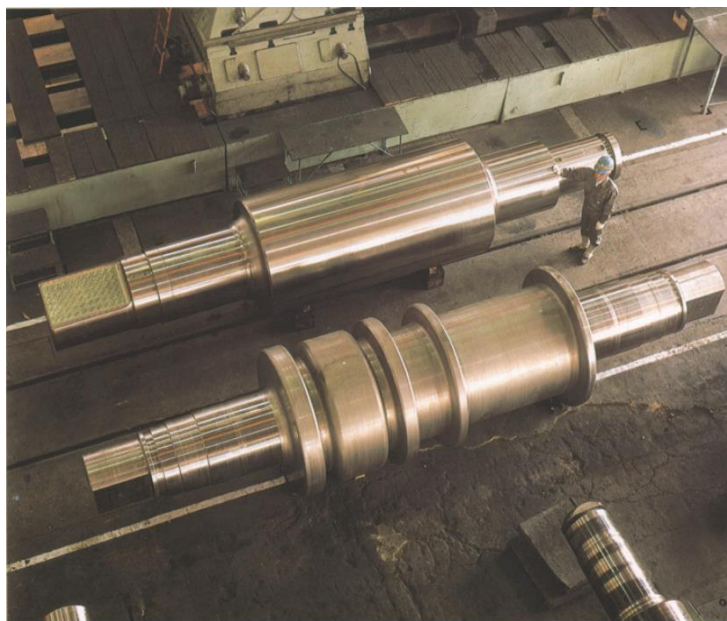


Figure 2.2 Example of rolls for steel rolling (Hashimoto, 2008).

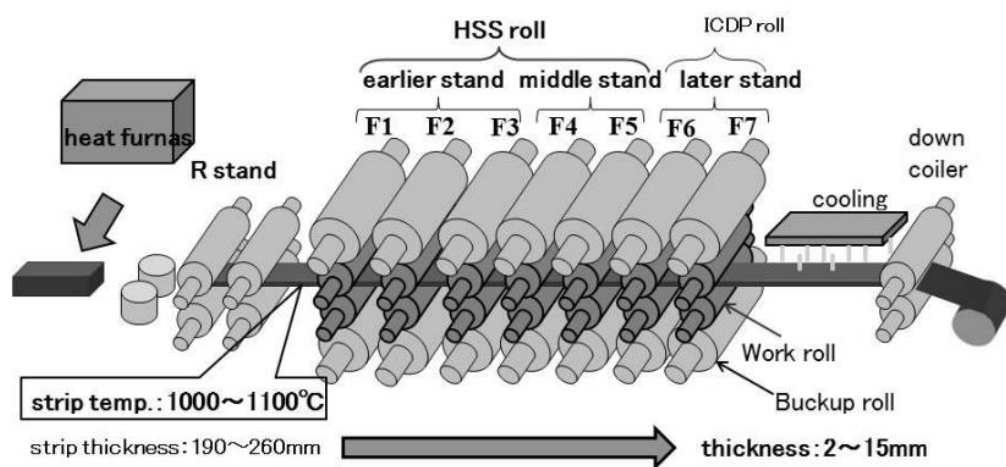


Figure 2.3 Finishing mill layout (Morikawa et al., 2014).

During hot rolling, the work roll makes direct contact with the slab which results in a deterioration of roll surfaces. Major wear mechanism in rolls is abrasive wear, in which micro-cutting, surface plastic deformation and crack initiation simultaneously occur depending on the shape and hardness of abrasive particles (Spuzic et al., 1994). Additionally, thermal fatigue due to cycle heating and cooling of a roll surface, oxidation wear, fatigue wear and sticking of a rolled material onto a roll surface affect the roll wear performance as well. For this reason, there is an increasing demand for quality improvement such as wear resistance, surface deterioration resistance, and crack resistance of hot work roll materials. The main requirements of a hot work roll are high hardness, high softening resistance and high wear resistance at elevated temperature. In the viewpoint of roll material microstructure, the amount and distribution of plural eutectic carbides with high hardness and the strengthened matrix with tempered martensite, secondary carbides and very less retained austenite are very important factors (Boccalini, 2011; Morikawa et al., 2014).

In most cases, work rolls for the finishing stands of hot-strip mills are composite components made of an outer shell of wear resistant material and a core of tough materials like ductile iron or forged steel. Historically, the evolution of the outer shell material is based on selecting wear resistant alloys commonly used in other manufacturing processes such as crushing, grinding or rolling. The development of materials for hot work roll is shown in Figure 2.4. The roll materials started with low-alloyed white cast iron through hyper-eutectoid alloyed steel (adamite), Ni-hard (indefinite chill cast iron) and high Cr cast irons which are very popular as practical applications, respectively. These families belong to the Fe-C-X system, where X represents carbide forming elements such as Cr, Mo or V. Although high Cr cast iron has superior abrasive wear resistance (Laird et al., 2000), a large fraction of eutectic carbide reduces the toughness of the roll. Therefore, new type of roll materials with much higher performance than Ni-hard and high Cr cast irons have been increasingly demanded.

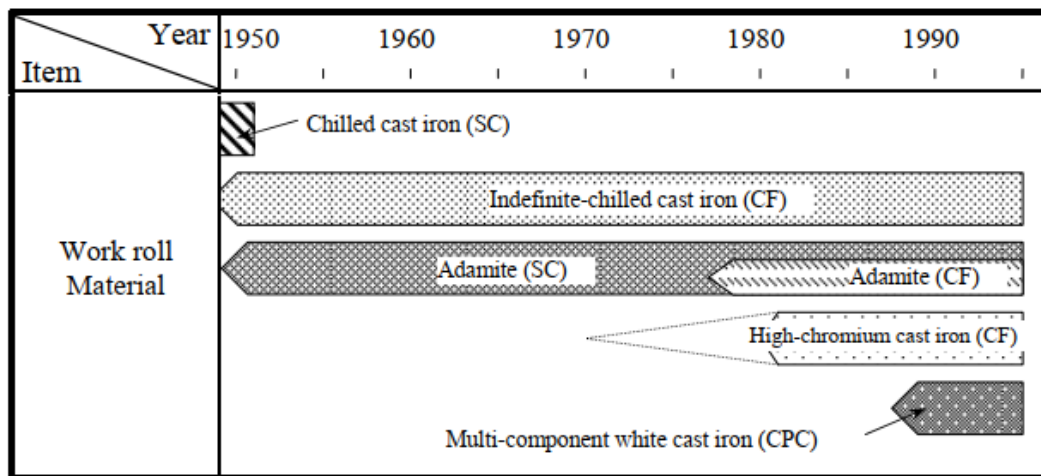


Figure 2.4 Development of roll materials (Hashimoto, 2008).

2.3 Multi-alloyed white cast iron

As previously mentioned, the hot work rolls with higher performance than Ni-hard and high Cr cast irons are required to improve productivity and quality of strip. To achieve this purpose, it is considered that other types of carbides with much higher hardness and much better morphology than those the Cr carbides have to be produced in the solidification structure. There are many alloying elements capable of forming carbide such as molybdenum, tungsten, vanadium and niobium in the order of carbide forming ability. The type and the hardness of carbides and those of matrix structure are listed in Table 2.1. The special or pure carbides of VC, NbC, WC, Mo₂C and W₂C with higher hardness than Cr carbides of Cr₇C₃ and Cr₂₃C₆ are considered to be available. Most of them contain iron and other elements as expressed by MC, M₂C and M₇C₃ or M₂₃C₆. The MC and M₂C or M₆C carbides that are main carbides in high speed steel are expected to improve the abrasive wear resistance. However, the M₇C₃ and M₂₃C₆ carbides have also shown satisfactory abrasive wear resistance in high Cr cast irons. Since chromium dissolves into the matrix and improves the hardenability, it is an indispensable element for alloyed white cast iron as well. Cobalt is not a carbide forming element but it enhances high temperature properties. The new type of alloyed white cast iron containing several carbide forming elements was developed in Japan by Prof. Dr. Yasuhiro Matsubara and it is termed as “**Multi-alloyed white cast iron**” (Matsubara et al., 1994).

Table 2.1 Hardness of carbide and matrix structure in multi-alloyed white cast iron (Wu, 2000).

Carbide / matrix	Hardness (HV)
$\text{Fe}_3\text{C} / \text{M}_3\text{C}$	800-1000
$(\text{Cr}, \text{Fe})_7\text{C}_3 / \text{M}_7\text{C}_3$	1200-1800
$(\text{Cr}, \text{Fe})_{23}\text{C}_6 / \text{M}_{23}\text{C}_6$	1100
$(\text{Mo}, \text{Fe})_2\text{C} / \text{M}_2\text{C}$	1800
$(\text{Mo}, \text{Fe})_6\text{C} / \text{M}_6\text{C}$	1800-2000
WC / MC	2400
$(\text{W}, \text{Fe})_2\text{C} / \text{M}_2\text{C}$	3000
$(\text{W}, \text{Fe})_6\text{C} / \text{M}_6\text{C}$	1900-2100
$(\text{V}, \text{Fe})\text{C} / \text{MC}$	2800
NbC	2400-3000
Ferrite	200-270
Pearlite	250-450
Austenite	250-500
Martensite	300-800

2.3.1 Alloying elements in multi-alloyed white cast iron

In such a multi-alloyed system, several types of eutectic carbides such as MC, M_2C and M_7C_3 can be expected to crystallize in the solidification structure. The carbide forming elements are not only forming their eutectic carbides with extremely high hardness but also dissolve into matrix. They promote the precipitation of secondary carbide and the transformation of retained austenite to martensite during heat treatment (Hashimoto et al., 1995; Wu, 2000). The role of alloying elements in multi-alloyed white cast iron can be summarized as follows,

Chromium (Cr). Cr is the main element in Ni-hard and high Cr cast irons. Cr forms complex carbides of M_3C $[(\text{Fe}, \text{Cr})_3\text{C}]$, M_7C_3 $[(\text{Fe}, \text{Cr})_7\text{C}_3]$ and M_{23}C_6 $[(\text{Fe}, \text{Cr})_{23}\text{C}_6]$. Cr is a stronger carbide former than Fe. When the Cr content is greater than about 10 – 12%, the M_7C_3 eutectic carbides form instead of M_3C carbides. The M_7C_3 carbide contributes directly to the excellent abrasive wear resistance and satisfactory toughness because of its high hardness and discontinuous rod-like morphology.

Moreover, Cr also dissolves into iron matrix and improves the hardenability. However, Cr content must be limited in order to be regarded as the crystallization of other harder carbides (Laird et al., 2000; Wu, 2000).

Molybdenum (Mo). Mo is a strong carbide forming element that combines with C to form eutectic carbides of M_2C [(Mo, Fe) $_2C$], M_6C [(Mo, Fe) $_6C$] types. The M_2C and M_6C carbides have generally higher hardness than the M_7C_3 carbides. The Mo dissolving in the matrix increases hardenability and promotes the precipitation of secondary carbides from austenite during heat treatment. Tungsten (W) has a similar carbide-forming ability to Mo. In the case that both Mo and W are added to the cast iron, complex carbides of M_2C and M_6C crystallize as eutectic carbides. It is the fact that Mo has an efficiency twice of tungsten because atomic density of Mo is about half to that of W. Since Mo shows similar behavior to W, it is recommended to consider the synergy of these two elements by the term of “Tungsten equivalent (W_{eq})” as following equation,

$$W_{eq} = \%W + 2\%Mo \quad (2.1)$$

Vanadium (V), V is the most effective carbide forming element. V forms VC or MC carbides and greatly encourages secondary carbide formation from austenite during heat treatment. MC carbides have higher hardness than M_2C and M_6C carbides and have been suggested to offer better wear performance at room and high temperature. V increases the M_s temperature and promotes increased martensite and reduced retained austenite (Boccalini, 2011; Wu, 2000).

Cobalt (Co), Co is not a carbide forming element but it is added to multi-alloyed white cast iron to improve the corrosion, oxidation, strength and wear resistance at elevated temperatures. It is well known that Co increases eutectic reaction temperature and decreases the degree of grain coarsening (Boccalini, 2011; Theisen, 2008; Wu, 2000).

Carbon (C), C is one of the main constituents of the carbide phases in steel and cast iron. In alloyed white cast iron, a large proportion of the C is consumed by carbide formers to form eutectic carbides and the remainder is distributed into the matrix. C increases hardness by increasing total carbide fraction. Moreover, the hardness of martensite is directly related to the C content of the matrix. In multi-

alloyed white cast iron, there are multiple types of eutectic carbides crystallized during solidification. Since the C dissolving in the matrix is very difficult to determine, a parameter of carbon balance (C_{bal}) which is defined by the next equation is introduced to express the behavior of C dissolving in the matrix.

$$C_{bal} = \%C - \%C_{stoich} \quad (2.2)$$

Where $\%C$ is total carbon content in the cast iron and $\%C_{stoich}$ is the amount of C which combines with carbide forming elements to form plural eutectic carbides.

In multi-alloyed white cast iron with basic alloy composition, the C_{stoich} can be calculated from the following equation in the case that the MC and M_2C crystallize in the microstructure.

$$\%C_{stoich} = (0.060\%Cr) + (0.063\%Mo) + (0.033\%W) + (0.235\%V) \quad (2.3)$$

The next equation can be used to calculate the C_{stoich} when MC, M_2C and M_7C_3 carbides co-exist,

$$\%C_{stoich} = (0.099\%Cr) + (0.063\%Mo) + (0.033\%W) + (0.235\%V) \quad (2.4)$$

In the case of multi-alloyed white cast iron containing Nb, if the MC and M_2C carbides crystallize as eutectic carbides, the C_{stoich} can be calculated from the following equation,

$$\%C_{stoich} = (0.060\%Cr) + (0.063\%Mo) + (0.033\%W) + (0.235\%V) + (0.129\%Nb) \quad (2.5)$$

In the case that the MC, M_2C and M_7C_3 carbides coexisting, the next equation can be adopted,

$$\%C_{stoich} = (0.099\%Cr) + (0.063\%Mo) + (0.033\%W) + (0.235\%V) + (0.129\%Nb) \quad (2.6)$$

The C_{bal} value is a very important parameter to determine transformation of matrix during heat treatment. A positive C_{bal} value indicates that there is an extra C

remaining in the matrix. On the other hand, a negative value of C_{bal} means that the C in the matrix is lacking. However, the C_{bal} value is a theoretical parameter that is calculated from an equilibrium state. In practice, the solidification sequence is far from an equilibrium state and therefore, the calculated C_{bal} value may not be exactly the precise value. However, the calculated value could be the present parameter for alloy design of multi-alloyed white cast iron. For these reasons, the C_{bal} value is a very significant factor to determine not only the carbide structure but also the heat treatment behavior of the multi-alloyed white cast iron. It was reported that the martensitic matrix is obtained when the C_{bal} value is in the range between -1.0 and +1.0 (Hashimoto, 2011; Matsubara et al., 1994).

2.3.2 Solidification sequence

Thermodynamic calculation is quite useful for predicting the solidification sequence of multi-alloyed white cast iron. However, it requires some knowledge on the solidification behavior of the alloy. Figure 2.5 shows the equilibrium solidification diagram of multi-alloyed white cast iron with basic alloy composition calculated by means of the ThermoCalc program. The high C content induces the primary crystallization of austenite and the decomposition of the residual interdendritic liquid may lead to the formation of eutectics: ($\gamma + MC$), ($\gamma + M_2C$) and ($\gamma + M_7C_3$). The ($\gamma + MC$) eutectic always crystallizes first, owing to the high V content of the alloys, while the sequence by which ($\gamma + M_2C$) and ($\gamma + M_7C_3$) or ($\gamma + M_3C$) depend on the chemical composition. In practice, however, the solidification is under non equilibrium and has led to unexpectedly high levels of disagreement with the calculated results.

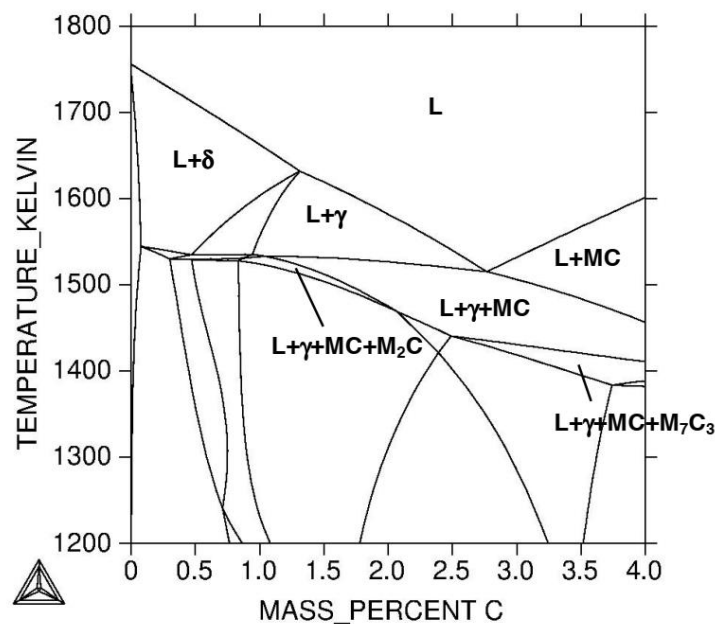


Figure 2.5 Quasi-binary phase diagram of Fe-5%Cr-5%W-5%Mo-5%V-5%Co-C system calculated using ThermoCalc program.

The solidification sequence of multi-alloyed white cast iron was clarified by Prof. Dr.Yasuhiro Matsubara research group (Matsubara et al., 1994) using thermal analysis and the quenching method. A thermal analysis curve and microstructure of multi-alloyed white cast iron basic alloy composition are shown in Figure 2.6. By means of quenching test, the microstructure of cast iron before and after each eutectic reaction is obtained. The quasi-binary phase diagram of the basic alloy composition and liquidus surface diagram of the iron M-V-C alloy are shown in Figure 2.7 (a) and (b), respectively. It is obvious that the high temperature part of quasi-binary phase diagram (Figure 2.7 (a)) exhibits a simple eutectic system between austenite and MC carbide. As the eutectic point less near the C content about 2.8%, the cast iron with the basic alloy content bears hypo-eutectic microstructure. This diagram also tells that after the eutectic reaction ($L \rightarrow \gamma + MC$), the melt may be followed by two other eutectic reactions, ($L \rightarrow \gamma + M_7C_3$) and/or ($L \rightarrow \gamma + M_2C$). These eutectic reactions occur corresponding to the C content. On the other hand, quasi-ternary liquidus surface diagram (Figure 2.7 (b)) shows a liquidus surface construction when C and V content are varied individually. Crystallization of primary delta ferrite, austenite, MC carbide as well as M_7C_3 and M_3C carbide are displayed on the diagram as well, while

the reaction of ($L \rightarrow \gamma + M_2C$) cannot be expressed on this diagram. The solidification sequence of multi-alloyed white cast iron with different chemical composition are shown in Table 2.2 (Wu et al., 1996).

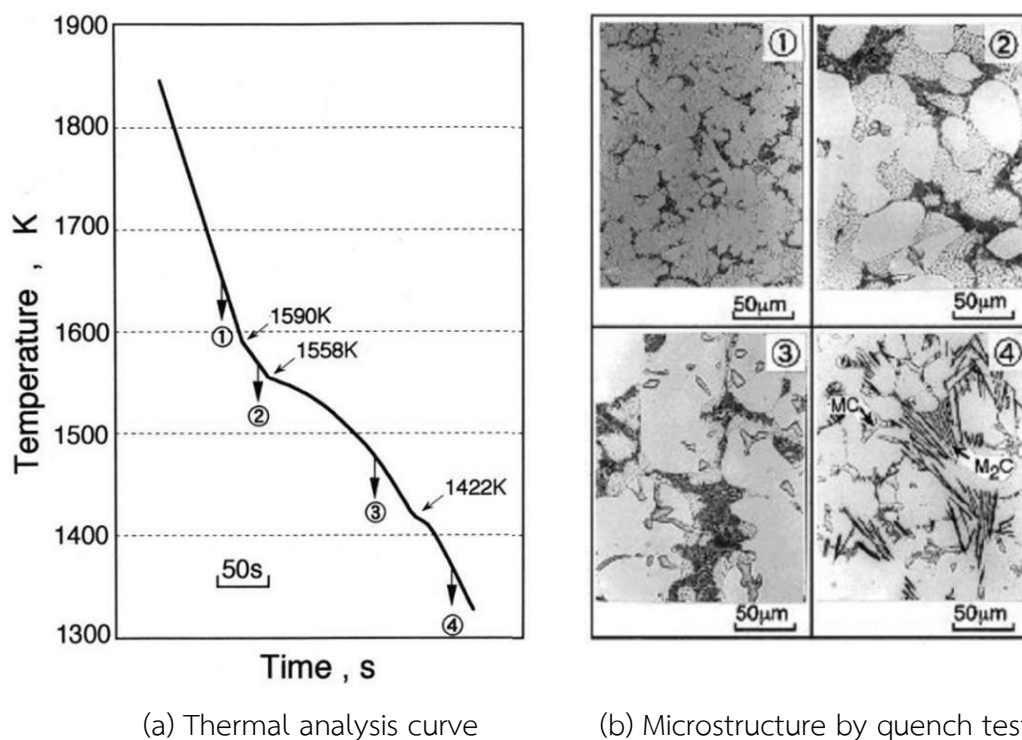
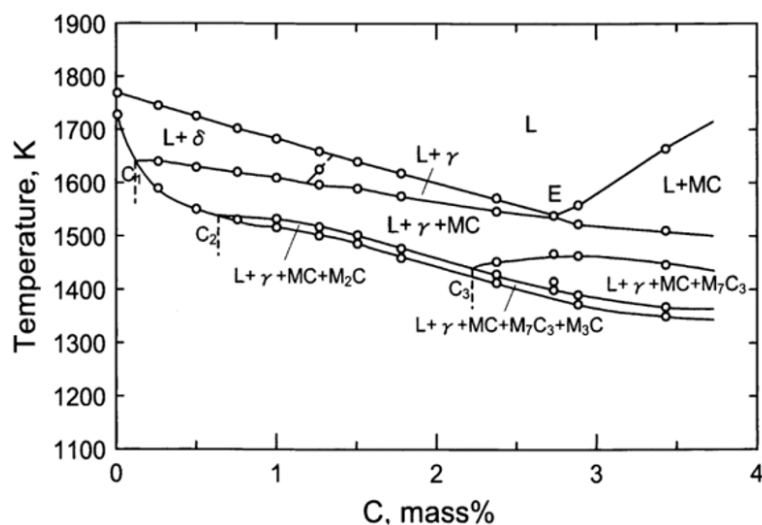
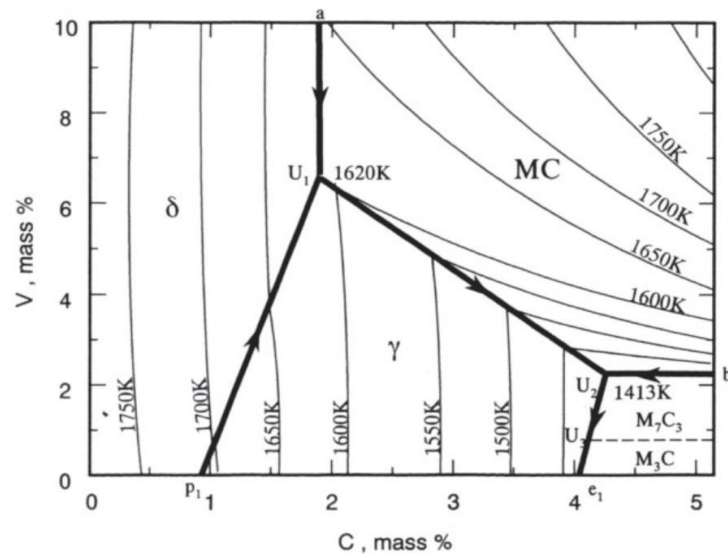


Figure 2.6 Solidification sequence of multi-alloyed white cast iron with basic composition (2%C-5%Cr-5%Mo-5%W-5%V-5%Co), (a) Thermal analysis curve and (b) Transition of microstructure by quench test (Wu et al., 1996).





(b) (Fe-5%Cr-5%Mo-5%W-5%Co)-V-C

Figure 2.7 Quasi-binary section diagram of multi-alloyed white cast iron, (a) (Fe-5%Cr-5%Mo-5%W-5%V-5%Co)-C and (b) (Fe-5%Cr-5%Mo-5%W-5%Co)-V-C (Wu et al., 1997).

Table 2.2 Solidification sequence of multi-alloyed white cast iron with different chemical composition (Wu et al., 1996).

Chemical composition	Combination of carbides	Solidification sequences	
2%C-5%Cr-2%Mo-2%W-9%V-5%Co	Coral-like MC, Fine lamellar M_2C	$L_0 \rightarrow \gamma_P + L_1$	at 1378°C
		$L_1 \rightarrow (\gamma+MC)_E + L_2$	at 1358°C
		$L_2 \rightarrow (\gamma+M_2C)_E$	at 1225°C
3%C-5%Cr-2%Mo-2%W-5%V-5%Co	Nodular MC, Rod-like M_7C_3	$L_0 \rightarrow \gamma_P + L_1$	at 1283°C
		$L_1 \rightarrow (\gamma+MC)_E + L_2$	at 1242°C
		$L_2 \rightarrow (\gamma+M_7C_3)_E$	at 1179°C
3%C-5%Cr-2%Mo-2%W-9%V-5%Co	Coral-like MC, Rod-like M_7C_3	$L_0 \rightarrow (MC)_P + L_1$	at 1459°C
		$L_1 \rightarrow (\gamma+MC)_E + L_2$	at 1277°C
		$L_2 \rightarrow (\gamma+M_7C_3)_E$	at 1180°C

2.3.3 Type and morphology of carbide

Since multi-alloyed white cast iron contains plural types of strong carbide forming elements, several types of eutectic carbide precipitate in the solidification structure, and they show diversities of morphology according to the chemical composition. Within the range of chemical composition of multi-alloyed white cast iron, three types of carbides (MC , M_2C and M_7C_3) have been crystallized. The concentration of alloys in each carbide type and as-cast matrix is analyzed by EDS technique, and it is shown in Table 2.3 (Matsubara et al., 1994; Wu et al., 1995).

Table 2.3 Alloy concentration in carbides and matrix of multi-alloyed white cast iron with basic chemical composition (Wu et al., 1995).

Carbides and matrix	Chemical composition, (wt%)					
	Cr	Mo	W	V	Co	Fe
MC	3.0 – 4.1	4.2 – 10	4.3 – 8.3	49 – 65	0.6 – 1.0	16 – 18
M_2C	10 – 15	26 – 30	19 – 22	6.4 – 12	0.8 – 1.3	20 – 26
M_7C_3	17 – 24	5.3 – 9.0	3.6 – 5.4	3.2 – 6.2	2.2 – 3.2	59 – 66
Matrix	3.5 – 4.2	0.2 – 1.3	1.8 – 3.1	1.0 – 2.4	0 – 14	82 – 85

2.3.3.1 MC carbide

The MC carbide contains more than 50%V and it crystallizes as a eutectic during solidification. The MC carbide can be classified as petal-like, nodular and coral-like morphologies as shown in Figure 2.8. Petal-like MC carbide crystallized in a low carbon content where the crystallization of austenite dendrite proceeds before eutectic of ($\gamma + MC$) forms. Nodular MC carbide crystallizes in the cast iron with high carbon content. Coral-like MC carbide consists of primary MC crystals in the center and eutectic MC carbides growing in radial direction from the primary MC. The coral-like MC carbide crystallizes in the cast iron with high vanadium content and can coexist with M_7C_3 carbide or small amounts of M_2C carbide depending on the carbon content of the melt. Hardness of MC carbide is about 2800 HV. The MC carbide may be very effective to wear resistance of the cast iron, and the nodular morphology of MC carbide may also improve the toughness of the cast iron because of less notch effect. When the chemical composition changes, however, nodularity of MC carbide may deteriorate to chunky or flaky morphology.

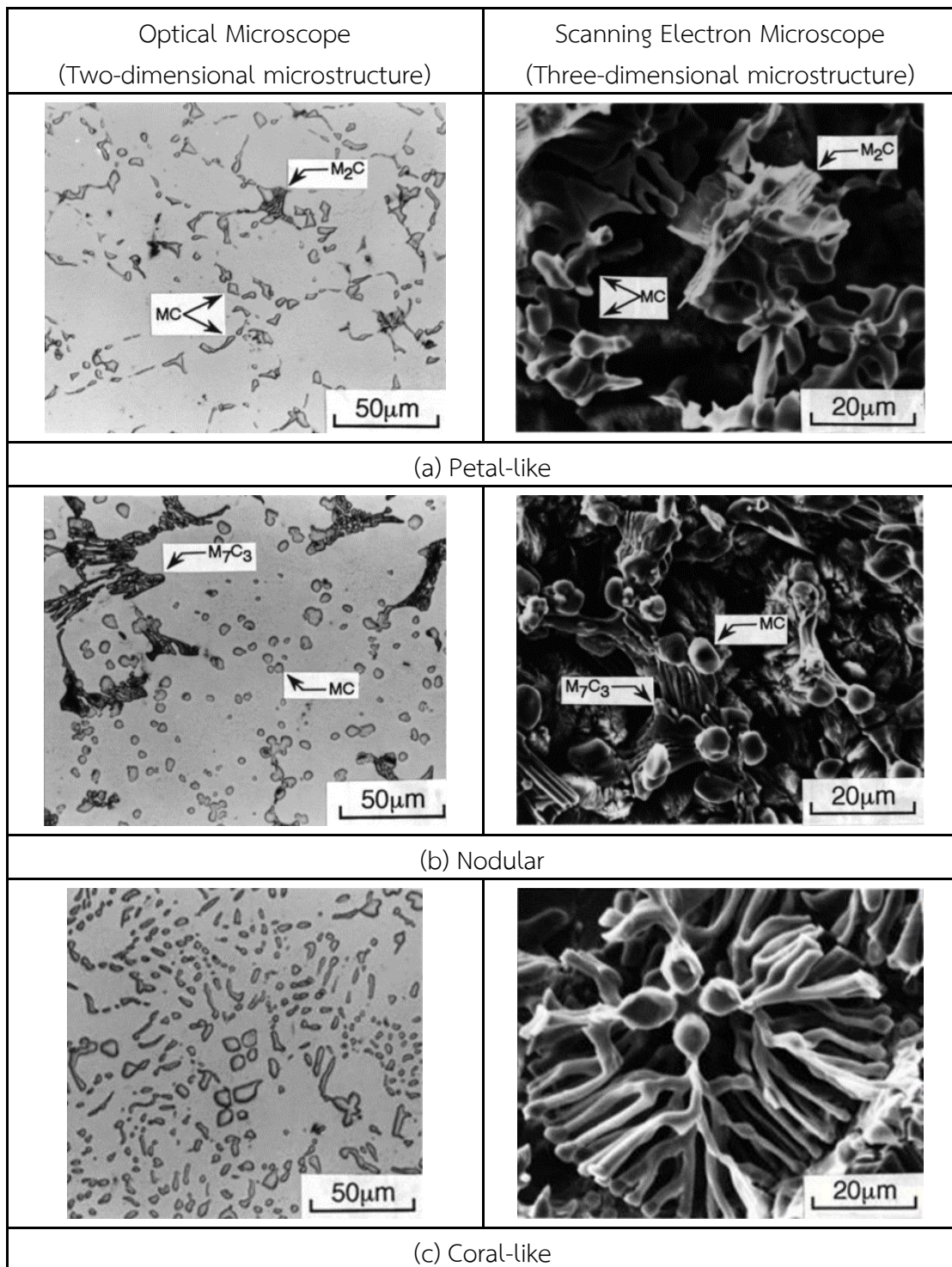


Figure 2.8 Comparison of two-dimensional and three-dimensional microstructure of MC carbide in multi-alloyed white cast iron by OM and SEM (Wu et al., 1995).

The effect of vanadium and carbon content on the morphology of carbides in multi-alloyed white cast iron is shown in Figure 2.9. It is found that the MC carbide crystallizes in all the compositions. The petal-like MC carbide crystallizes in cast iron with less than 1.8%C. The nodular MC carbide appears up to 6%V and carbon content more than 1.4%. The coral-like MC carbide crystallizes in the range of 8 and 15%V (Wu et al., 1995; Wu et al., 1997).

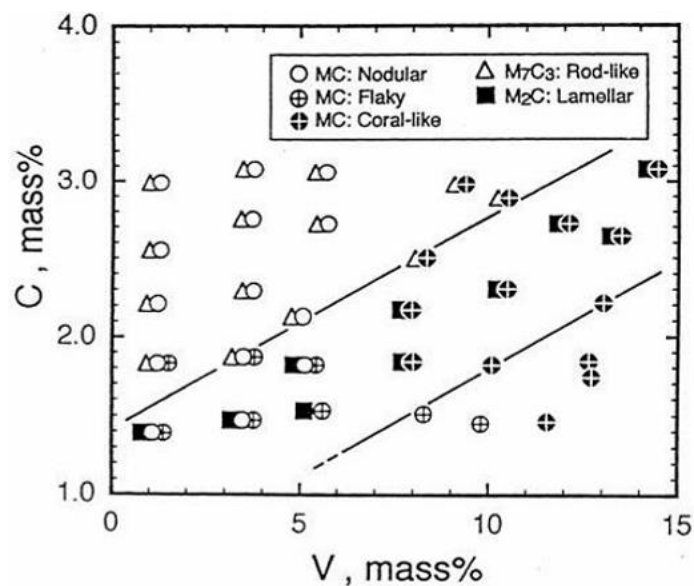


Figure 2.9 Effect of V and C contents on type and morphology of carbides crystallized from melt in multi-alloyed white cast iron (Wu et al., 1995).

2.3.3.2 M_2C carbide

The M_2C carbide is Mo and W rich carbide. It takes fine lamellar or coarse plate-like morphology as shown in Figure 2.10 depending on the chemical composition. The hardness of M_2C carbide is about 1800 HV. Lamellar eutectic M_2C carbide exists in isolation, and this indicates that the M_2C carbide crystallizes in the last stage of solidification. The plate-like M_2C carbide consists of large and thick plates. This type of carbide can be usually seen in the cast iron with high W_{eq} value. In the cast iron with high carbon content, the plate-like M_2C carbide exists together with M_7C_3 carbide. The influence of W_{eq} value and carbon content on type and morphology of carbides in multi-alloyed white cast iron is shown in Figure 2.11. It is found that the lamellar M_2C carbide can be observed when W_{eq} is less than 15% but plate-like M_2C appears at over 15% W_{eq} (Wu et al., 1995).

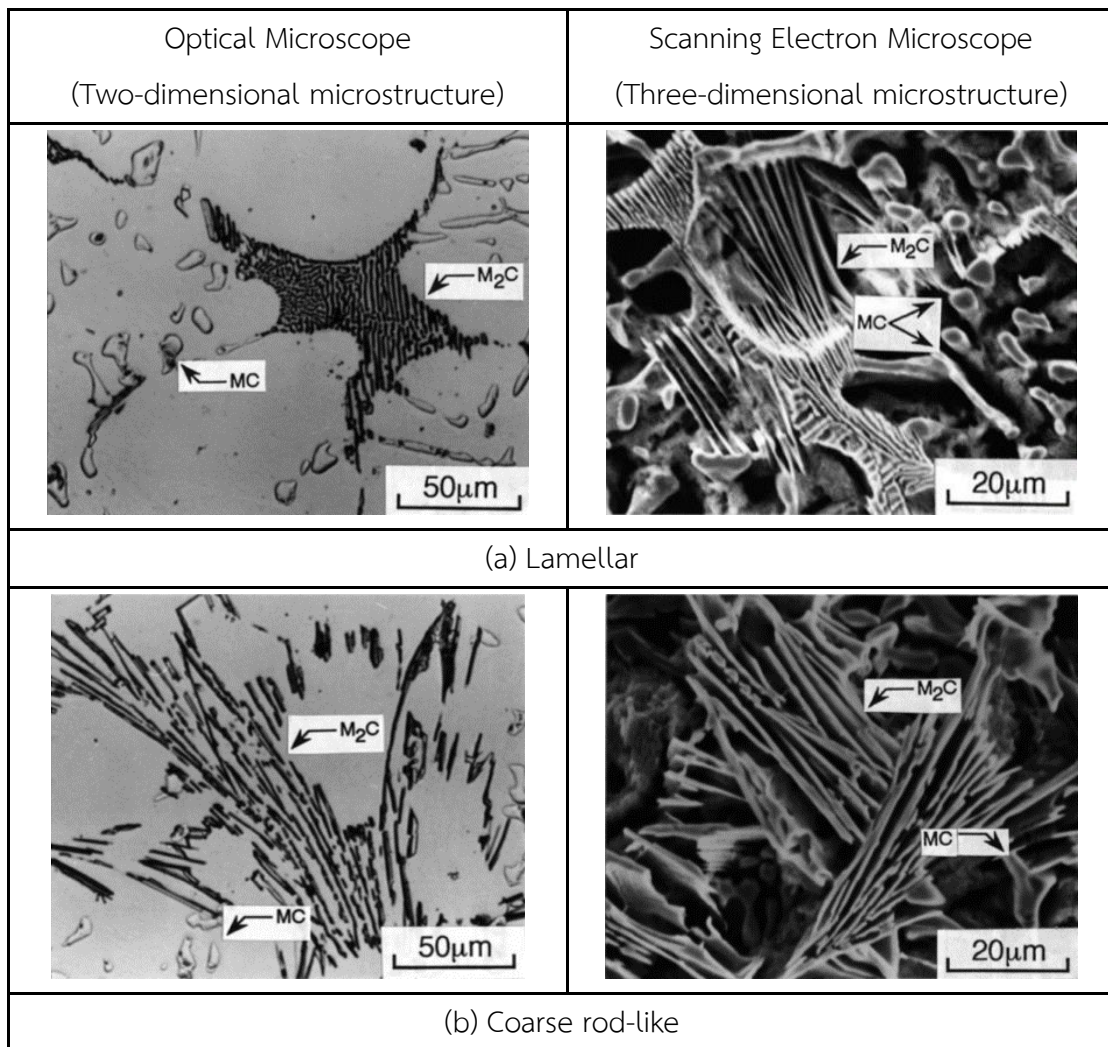


Figure 2.10 Comparison of two-dimensional microstructure of M_2C carbide in multi-alloyed white cast iron by OM and SEM (Wu et al., 1995).

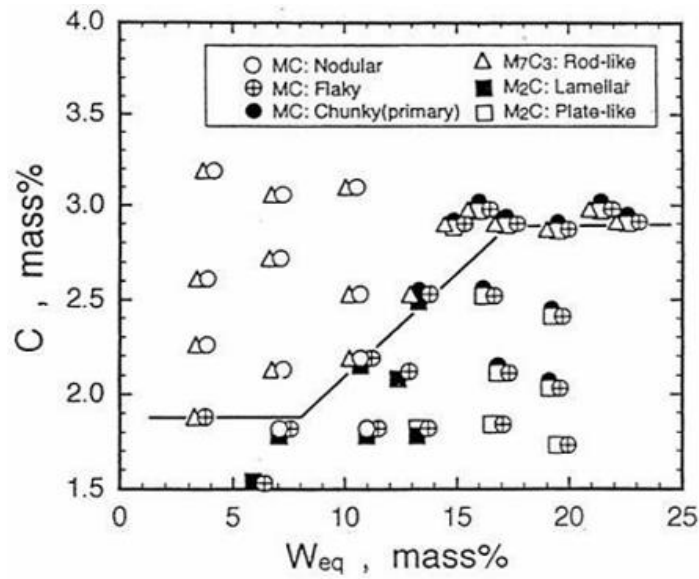
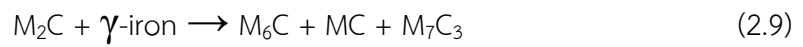


Figure 2.11 Effect of W_{eq} value and carbon content on type and morphology of carbides crystallized from melt in multi-alloyed white cast iron (Wu et al., 1995).

It was reported that the M_2C carbide transforms into M_6C carbide at high temperature for a long time (Hashimoto et al., 2004b; Lee et al., 1998). Figure 2.12 shows the decomposition of M_2C eutectic carbide. The decomposition processes are schematic expressions in Figure 2.12 and the reactions can be displayed by the following equations (Lee et al., 1998).



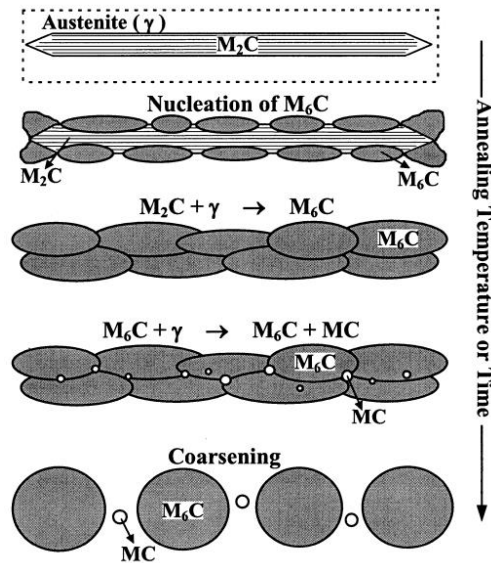


Figure 2.12 Schematic expression for decomposition processes of M_2C carbide to M_6C carbide (Lee et al., 1998).

2.3.3.3 M_7C_3 carbide

The M_7C_3 carbide contains high chromium levels and the morphology is rod-like or blade-like structure. The rod-like or ledeburitic morphology appears in iron with higher W_{eq} value and higher carbon content. It sometimes co-exists with MC and M_2C carbides as shown in Figure 2.13. The hardness of M_7C_3 carbide is in the range of 1200 – 1800 HV.

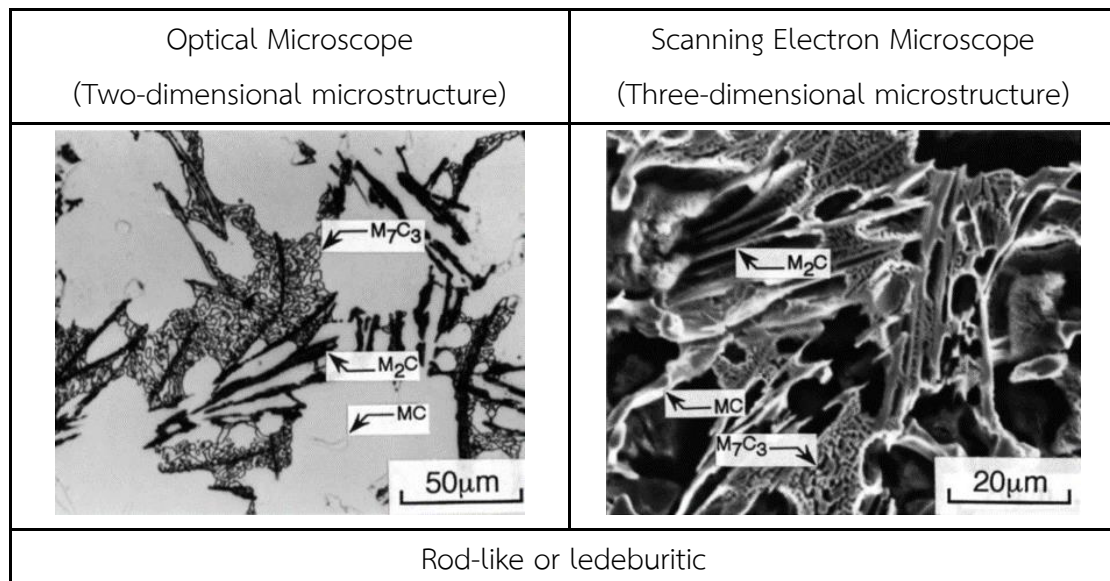


Figure 2.13 Comparison of two-dimensional microstructure of M_7C_3 carbide in multi-alloyed white cast iron by OM and SEM (Wu et al., 1995).

2.3.4 Effect of solidification rate on type and morphology of carbide

The type of crystallized carbide in multi-alloyed white cast iron is controlled by the chemical composition and the solidification rate. The effect of carbon content and solidification rate on type carbides in multi-alloyed white cast iron is shown in Figure 2.14. Although the morphology of carbide is varied, the MC and M_2C carbides are observed regardless of carbon content and solidification rate. As the solidification rate decreases, the size of MC carbide increases but the amount of decrease. The M_7C_3 carbide is found to crystallize in the range of high carbon content and low solidification rate.

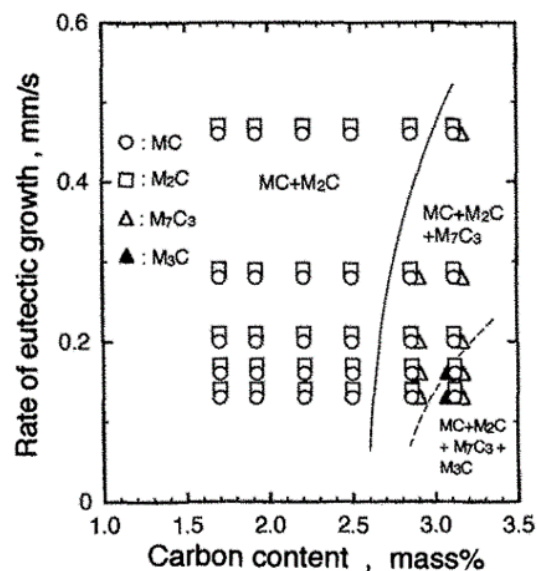


Figure 2.14 Type of crystallized carbides corresponding to solidification rate and carbon content (Matsubara et al., 1994).

2.3.5 Carbide fraction

The volume fraction of carbide (V_c) in multi-alloyed white cast iron with basic alloy composition is shown in Figure 2.15. The result shows that V_c of both MC and M_2C carbides increases linearly with an increase in the carbon content. The V_c of MC carbide becomes doubled when carbon content of the cast iron changes from 1.70 to 2.86%. When carbon content becomes higher than 2.50%, V_c of M_2C carbide dramatically decreases while M_7C_3 carbide begins to crystallize. This tells that crystallization of M_7C_3 carbide affects the crystallization of M_2C carbide. However, the

total V_c increases constantly with increasing the carbon content and it may be over 20% when carbon content reaches 3.0%.

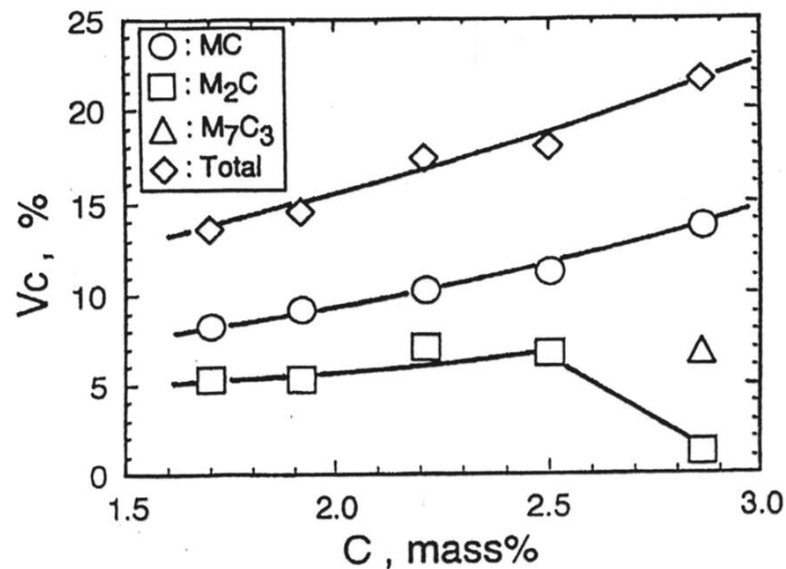


Figure 2.15 Effect of carbon content on carbide volume fraction (V_c) of multi-alloyed white cast iron with basic alloy composition (Wu, 2000).

2.3.6 As-cast matrix of multi-alloyed white cast iron

In the same manner as carbides, the matrix structure also plays an important role on wear resistance during services. Therefore, the matrix structure must have not only high hardness but also high toughness and strength. The matrix structure of multi-alloyed white cast iron in the as-cast condition can be ferrite, pearlite, bainite, martensite and/or austenite depending on the chemical composition and cooling rate (Theisen, 2008). The retained austenite in as-cast condition has very importance in the heat treatment process. The retained austenite can be transformed into martensite by stress-induced mechanism in services (Laird et al., 2000).

2.3.7 Solid state transformation

The carbide forming elements also distribute into matrices according to their distribution coefficient to austenite and give effects on the matrix transformation. As mentioned before, the wear resistance and the mechanical properties of multi-alloyed white cast iron are controlled by not only the type and morphology of eutectic carbide but also the matrix structure. Since the matrix in the as-cast condition has very low hardness and poor wear resistance, the heat treatment processes must be provided to the cast iron before services. For multi-alloyed white cast iron, the heat

treatment process is the same manner as high Cr cast iron and tool steels (Laird et al., 2000), that is, general heat treatment of hardening and tempering. The solid state phase transformation during heat treatment comprises the decomposition of austenite and the precipitation of secondary carbides.

In order to get instructions of the heat treatment condition providing the cast iron with desired properties, it is necessary to clarify the transformation behavior of the matrix. The continuous cooling transformation diagrams (CCT) of the basic multi-alloyed white cast iron with 1.95% and 2.81%C had been reported by Matsubara et al. as displayed in Figure 2.16 (Matsubara et al., 1999). The cast irons were hardened from 1273K (1000°C) and 1373K (1100°C) austenitizing by fan air cooling. In spite of the difference in carbon contents and austenitizing temperatures, pearlite and bainite transformations separate to the top and the bottom independently. The nose temperatures of both the pearlite and bainite transformations range from 920K (647°C) to 980K (707°C) and 570K (297°C) to 610K (337°C) for low carbon cast iron, and 900K (627°C) to 950K (677°C) and 590K (317°C) to 640K (367°C) for high carbon cast iron, respectively. With respect to transformation time or nose time, the low carbon cast iron shows great difference in nose time of pearlite and bainite transformation at 1273K (1000°C) austenitizing and the pearlite transformation is located at the long time side more than 3 times as much as the bainite transformation. When the austenitizing temperature is increased to 1373K (1100°C), both transformations are delayed approximately twice. It is clear that the M_s temperature appears but the M_f temperature does not appear in this kind of cast iron. In 1273K (1000°C) austenitizing, the M_s temperature is 475K (202°C) to 495K (227°C) in the low carbon cast iron and 375K (102°C) to 380K (107°C) in the high carbon cast iron. The reason for M_s temperature to rise is explained by that as the cooling rate reduces, the alloy concentration in the matrix decreases due to an increase in the precipitation of secondary carbides. The reason for M_s temperature to lower can be explained by that the enrichment of carbon in austenite takes place due to the discharge of carbon by the proceeding of bainite transformation.

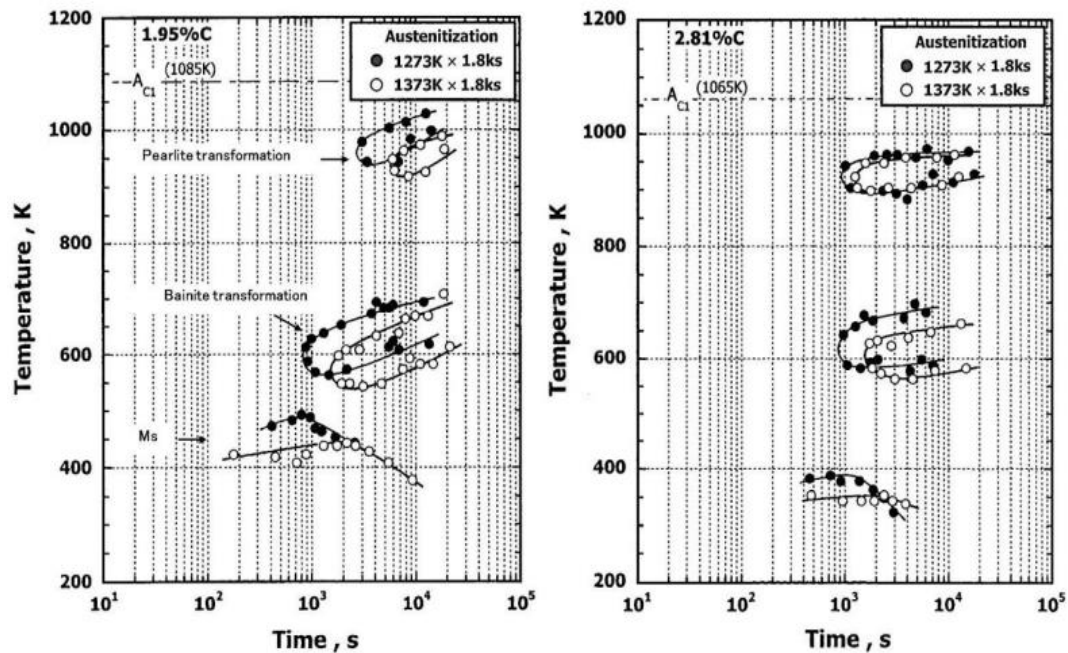


Figure 2.16 The CCT diagrams of multi-alloyed white cast iron with different carbon content (Fe-5%Cr-5%Mo-5%W-5%V-2%Co-C alloys) (Matsubara et al., 1999).

2.3.8 Heat treatment behavior

The heat treatment processes of hardening and tempering are applied to multi-alloyed white cast iron in the same manner as steel. However, the transformation behavior is quite different from heat treatment of steel because several kinds of carbide forming element are dissolved in as-hardened matrix. Particularly, the tempered hardness shows obvious secondary hardening due to the precipitation of secondary carbides and the transformation of retained austenite to martensite. The precipitation of carbides reduced alloy concentration in the retained austenite and therefore, the M_s temperature is elevated. Finally, the residual unstable austenite transforms to martensite (Laird et al., 2000).

The heat treatment behaviors of multi-alloyed white cast iron with several alloying elements are representatively shown in Figure 2.17 (a) to (f). It is found in each cast iron that the tempered hardness curve shows remarkable secondary hardening depending on the kind and the amount of alloying elements and heat treatment conditions. The volume fraction of retained austenite (V_γ) begins to reduce rapidly when the tempering temperature rises over the certain temperature. The evident secondary hardening is caused by the precipitation of secondary carbides and the decomposition of austenite to martensite. The secondary carbides are MC, M_6C and

M_7C_3 types (Hashimoto et al., 2004a). The maximum tempered hardness is obtained at 798K (525°C) tempering. After that, the hardness decreased due to the coarsening of secondary carbide together with the transformation of retained austenite to ferrite or pearlite.

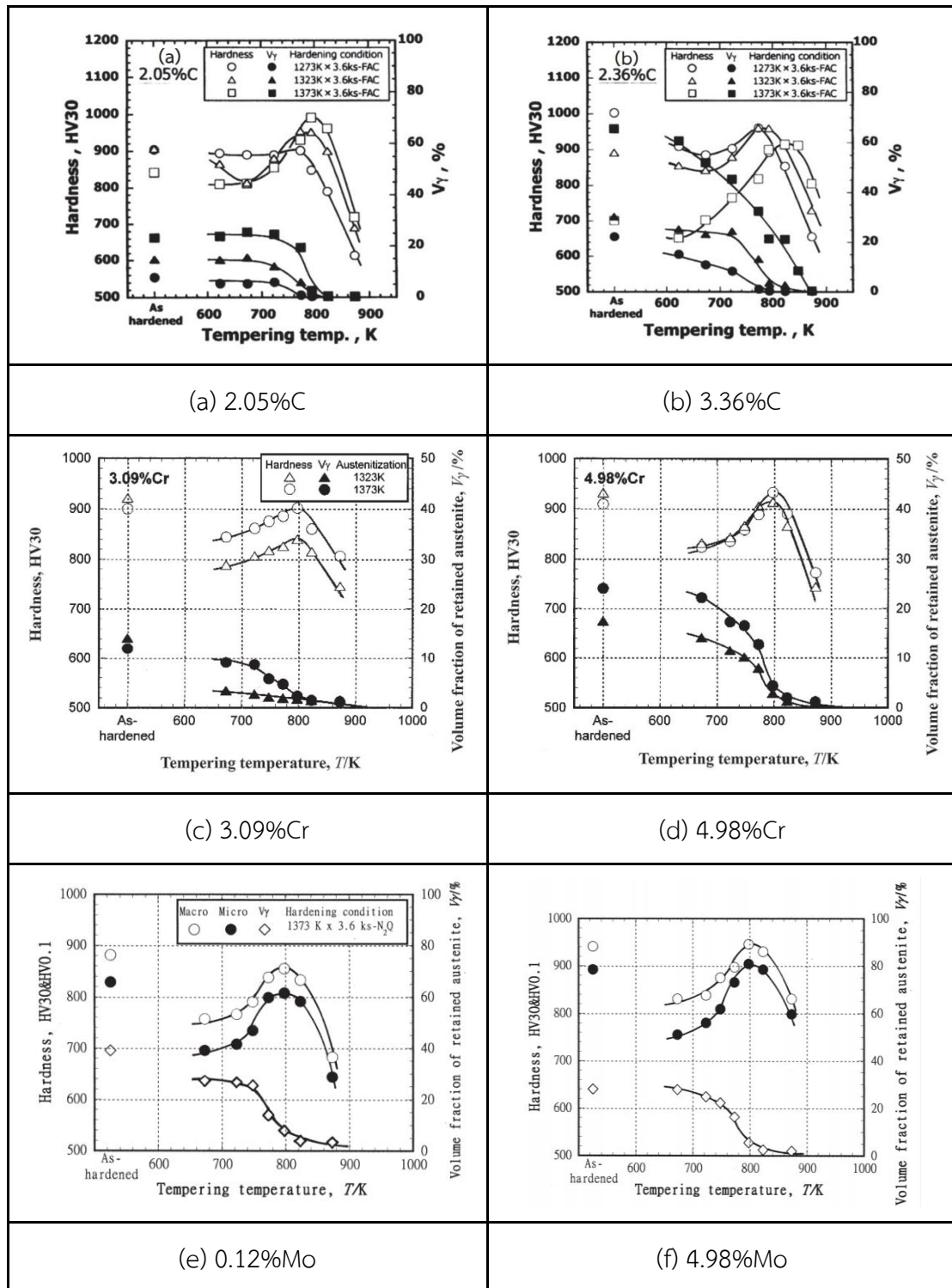


Figure 2.17 Relationship between the tempering temperature, volume fraction of retained austenite (V_γ) and hardness of multi-alloyed white cast iron with different alloying elements. (C effect: (a) and (b), Cr effect: (c) and (d), Mo effect: (e) and (f)) (Matsubara et al., 2000; Meebupha et al., 2017; Opapaiboon et al., 2019a).

2.4 Abrasive wear resistance

2.4.1 Mechanism of abrasive wear

A simplified model of abrasive wear is introduced to understand the underlying wear mechanism. This model, which illustrates material being worn by a single abrasive particle or grit, is shown in Figure 2.18. The relationship between the material's hardness and the load applied to the grit is expressed by equation 2.10.

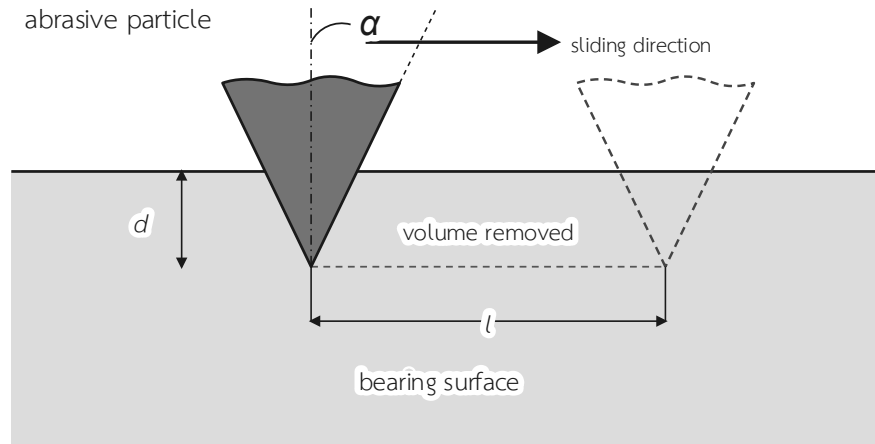


Figure 2.18 Schematic drawing of model showing abrasive wear by single grit with cone shape (Booser, 1997).

$$F = A \times H_v \quad (2.10)$$

Here, F represents the force applied to the grit, A is the surface area of the resulting indentation, and H_v denotes the Vickers hardness of the materials. Consequently, the individual load on a single grit (L_g) can be calculated using the following equation.

$$L_g = 0.5\pi (d \cdot \cot \alpha)^2 H_v \quad (2.11)$$

Where d represents the depth of indentation (m) and α is the slope angle (degrees) of the cone. Given that the approximate volume of the material removed by the cone is the product of the indentation's cross-sectional and the traversed distance, the relation is expressed by following equation.

$$V_g = l d^2 \cot \alpha \quad (2.12)$$

Here, V_g is the volume of material removed by the cone (m^3) and l denotes the distance travelled by the cone (m). By eliminating 'd' from equation (2.11) and equation (2.12), Equation (2.13) is obtained, which expresses the relationship between V_g , the shape of the grit, the sliding distance (l) and L_g .

$$V_g = \frac{2l \tan \alpha}{\pi H} \times L_g \quad (2.13)$$

The total wear is the sum of the volumes of material removed by each grit. Therefore, the total volume of wear loss (V_{tot}) can be expressed by the following equation,

$$V_{tot} (m^3) = \frac{2l \tan \alpha}{\pi H} \times W_{tot} \quad (2.14)$$

Where, W_{tot} represents the total load (N). From equation 2.14, it is evident that wear loss is closely related to both the applied load and the material's hardness. Since the load is often determined by the operating environment, hardness serves as a critical indicator of wear resistance.

2.4.2 Classification of abrasive wear

Abrasive wear occurs due to hard particles or hard protuberances that are forced against and move along a solid surface. Wear is defined as a solid surface that generally involves progressive loss of material and is due to relative motion between that surface and a contacting substance or substances. When two surfaces contact, wear occurs on both surfaces. Individuals and industry tend to focus on the wearing surface that has the greatest potential for their own economic loss and consider the other surface to be the abrasive. Abrasive wear is typically categorized according to types of contact as well as the environment. Types of contact include two-body and three-body wears as schematic drawing in Figure 2.19. The former occurs when an abrasive slides along a surface, and the latter, when an abrasive is caught between one surface and another. Two-body systems typically experience much higher severity than three-body systems (ASTM G40, 2018; Glaeser, 1986; Laird et al., 2000; Lighvan, 2021; Kovarikova et al., 2009).

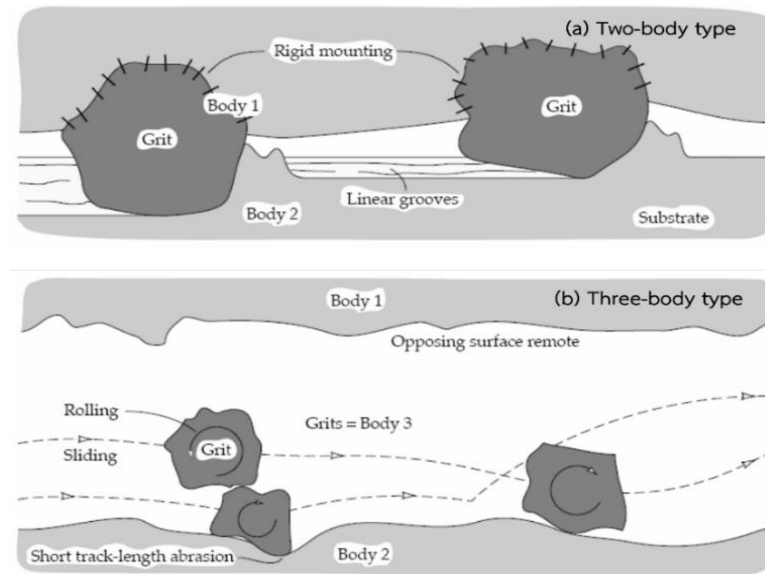


Figure 2.19 Schematic drawing of abrasive wear type. (a) Two-body type and (b) Three-body type (Kovarikova et al., 2009).

The abrasive wear resistance is expressed by wear loss which is measured from digital balance or by term of volume loss in the next equation.

$$\text{Volume loss (mm}^3\text{)} = \frac{\text{mass loss (g)}}{\text{density (g/cm}^3\text{)}} \times 1000 \quad (2.15)$$

Abrasive wear is commonly divided into three modes of gouging abrasion, grinding abrasion and scratching (Gates & Gore, 1995; Laird et al., 2000). Generally, the combination wear of two or three types occurs on the surface of the part during service.

(1) Gouging abrasion occurs in high-stress situation and is followed by plastic deformation. The groove from gouging abrasion can be macroscopically visible in the worn material.

(2) Grinding abrasion occurs when the abrasive particles are caught between two surfaces with moderately high stress. The worn surface can be distinguished with the naked eye and a low magnification microscope.

(3) Scratching or low-stress abrasion occurs in situations in which small particles are freely moving through the contacting surfaces with low-stress.

The difference between high-stress and low-stress abrasion is that in the case of low-stress abrasion, abrasive particles are smaller than in high-stress abrasion, and

abrasive particles do not fracture. Wear mechanism is the process by which wear loss occurs. Zum Gahr (1987) suggested that there are three possible wear mechanisms, namely micro-ploughing, micro-cutting, and micro-cracking. Gates & Gore (1995) summarized the most common mechanisms in pure abrasion mode as shown in Table 2.4.

Table 2.4 Wear mechanism in abrasion (Gates & Gore, 1995).

Gouging abrasion	Grinding abrasion (High-stress abrasion)	Scratching abrasion (Low-stress abrasion)
- Micro-ploughing	- Micro-ploughing	- Micro-ploughing
- Micro-cutting	- Micro-cutting	- Micro-cutting
- Micro-fracture	- Micro-fracture	- Micro-fracture
		- Accelerated oxidation

2.4.3 Abrasive wear resistance of alloyed white cast iron

Alloyed white cast irons are the most abrasion-resistant materials. Their resistance to the abrasion is due to the crystallization of very hard carbides during solidification. Unfortunately, they have limited impact resistance compared to steels, they are very difficult to machine and are not weldable. The common group of alloyed white irons include pearlitic, Ni-hard and high Cr cast irons. The composition of typical white cast irons is given at Table 2.5. The high Cr cast irons are currently favored over the Ni-hard or pearlitic white cast irons because of their improved resistance to impact in the heat-treated condition.

Table 2.5 Alloy composition of abrasion-resistant white cast irons (Laird et al., 2000).

Common name	Class	Type	ASTM designation	Composition, wt%						
				C	Mn	Si	Ni	Cr	Mo	Cu
NiHard I	I	A	Ni-Cr-Hc	2.8-3.6	2.0 max	0.8 max	3.3-5.0	1.4-4.0	1.0 max	...
NiHard I	I	B	Ni-Cr-Lc	2.4-3.0	2.0 max	0.8 max	3.3-5.0	1.4-4.0	1.0 max	...
NiHard IV	I	C	Ni-Cr-GB	2.5-3.7	2.0 max	0.8 max	4.0 max	1.0-2.5	1.0 max	...
	I	D	Ni-HiCr	2.5-3.6	2.0 max	2.0 max	4.5-7.0	7.0-11	1.5 max	...
	II	A	12%Cr	2.0-3.3	2.0 max	1.5 max	2.5 max	11.0-14.0	3.0 max	1.2 max
Cr-Mo	II	B	15% Cr-Mo	2.0-3.3	2.0 max	1.5 max	2.5 max	14.0-18.0	3.0 max	1.2 max
Cr-Mo	II	D	20% Cr-Mo	2.0-3.3	2.0 max	1.0-2.2	2.5 max	18.0-23.0	3.0 max	1.2 max

As well known, wear resistance of alloyed cast iron is closely related to the microstructure which determines the mechanical properties mainly hardness, toughness, and strength. All these factors influence the abrasive wear resistance. Since the eutectic carbide changes little in both the quantity and morphology after solidification, the matrix structure becomes a very important factor to improve the wear property. The effect of distribution of carbide to abrasive wear is schematic drawing shown in Figure 2.20. To achieve favorable abrasive wear resistance, carbides must have extremely high hardness, large enough in size and discontinuous morphology. Tiny carbides may be chipped out when the wear proceeds. The matrix structure shows great influence on the wear resistance as well. The matrix should be high hardness and strength to support carbide under the wear condition. It has been reported that martensite matrix is preferred for abrasive wear resistance (Albertin & Sinatora, 2001; Matsubara et al., 2001; Sare, 1979).

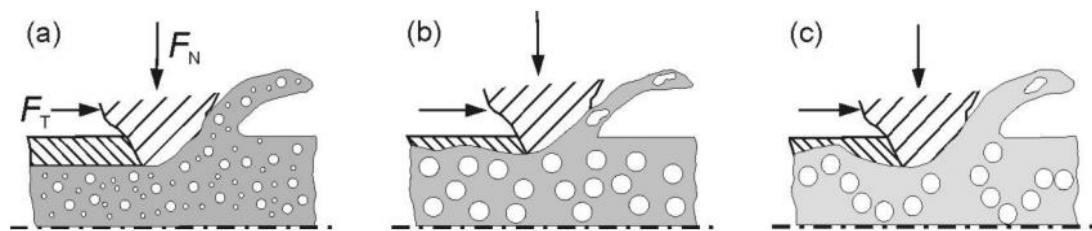


Figure 2.20 Schematic drawing of wear due to different distribution and size of carbides. (a) too small size carbides, (b) effective size carbides and (c) continuous or net-like carbides (Theisen, 2008).

There are several researchers who have investigated the abrasive wear resistance of alloyed white cast irons. The results show that an increase in the amount and hardness of carbide could improve the abrasive wear resistance. Zum Gahr and Doane (1980) carried out a rubber wheel abrasion test of high Cr cast irons with an austenitic and martensitic matrix in order to assess the effect of carbide volume fraction (CVF). They found that although the hardness of the cast iron increase with CVF increases, the lowest volume loss or the highest wear resistance was obtained around 30%CVF in both austenitic and martensitic matrices. They stated that the observed increasing weight loss of samples beyond 30%Cr-CVF is due to grooving and then spalling of massive carbide particles. Too many carbide particles suffer from low support from matrices.

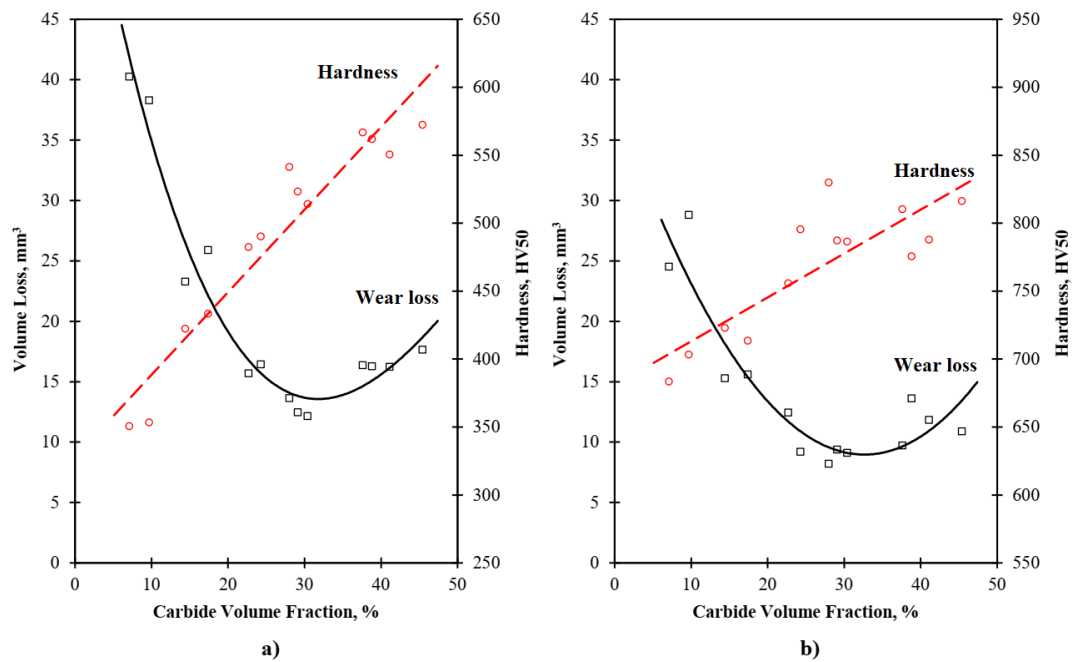


Figure 2.21 Effect carbide volume fraction (CVF) on hardness and wear loss of high Cr cast irons with a) austenitic matrix and b) martensitic matrix (Zum Gahr & Doane, 1980).

Doğan et al. (1997) used 15% and 26%Cr cast irons in as-cast state to investigate the wear resistance and connected to CVF value. The relationship between CVF and wear rate is shown in Figure 2.22. The wear rate decreases as the CVF value increases and the decreasing rate is greater in 15%Cr cast iron, but the quantity of wear at the same CVF value is three times higher than in 15%Cr cast iron than in 26%Cr cast iron. As shown in Figure 2.23, the wear rate decreases roughly in proportion to the hardness. From the finding, they concluded that the abrasive wear resistance of 26%Cr cast iron, which has more austenite in matrix and high volume fraction of carbide, is better than that of 15%Cr cast iron with bainitic and pearlitic matrix and lower volume fraction of carbide.

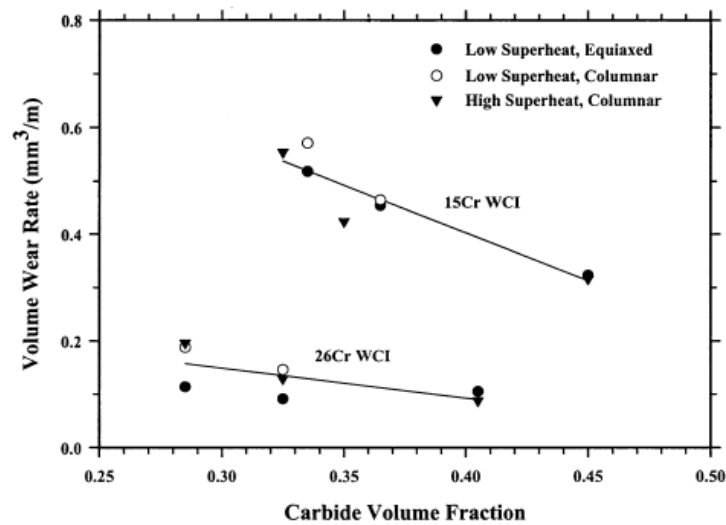


Figure 2.22 Effect of carbide volume fraction (CVF) on volume wear rate of high Cr cast irons with different matrix structure (Doğan et al., 1997).

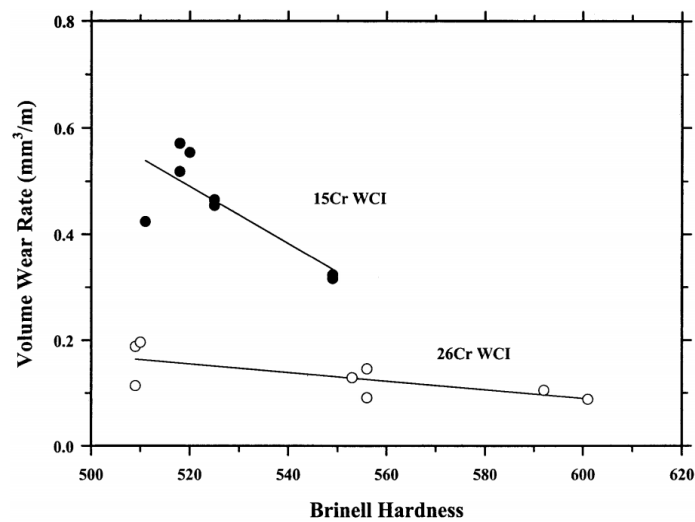


Figure 2.23 Effect of hardness on wear rate of high Cr cast irons (Doğan et al., 1997).

The abrasive wear behavior of multi-alloyed white cast irons with 20% carbide forming elements was reported by Matsubara et al. (2001) and the results are illustrated in Figure 2.24. The results indicated that the highest abrasive wear resistance is obtained in cast iron with high vanadium content (No.2). This is because the crystallization of MC carbide with very high hardness improves the wear resistance effectively. By contrast, the lowest abrasive wear resistance is found in the cast iron with high chromium content (No.1). The reason is that the crystallization of M_7C_3 carbide with low hardness reduces the wear resistance.

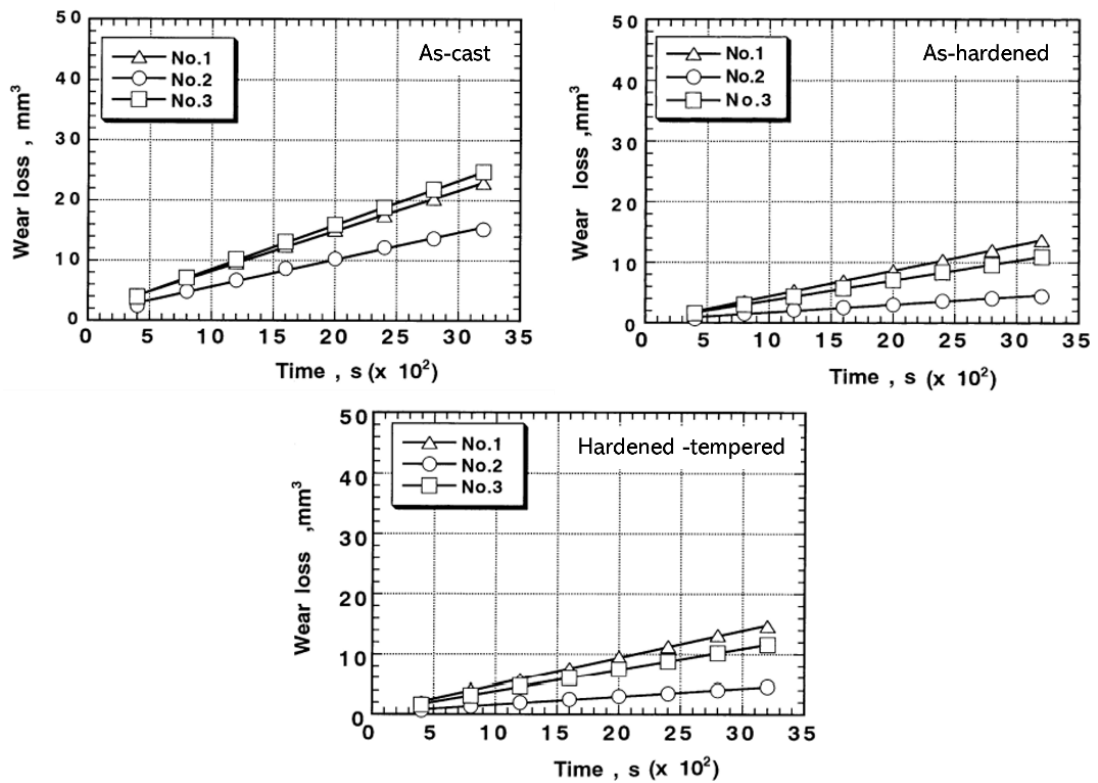


Figure 2.24 Relationship between wear loss and testing time of white cast irons alloyed with 20% carbide forming elements. (No.1: Fe-3%C-10%Cr-5%Mo-5%W, No. 2 : Fe-3%C-10%V-5%Mo-5%W, No. 3 : Fe-3.5%C-17%Cr-3%V) (Matsubara et al., 2001).

The effect of cobalt on wear behavior of heat-treated multi-alloyed white cast iron was clarified by Sasaguri et al. (2010) as shown in Figure 2.25. They stated that the wear resistance in the as-hardened state is higher than those in the as-cast and annealed states. The reason is due to the difference in the matrix structure. They also reported that cobalt reduces the wear resistance in the as-cast and annealed states because it promotes the pearlite transformation.

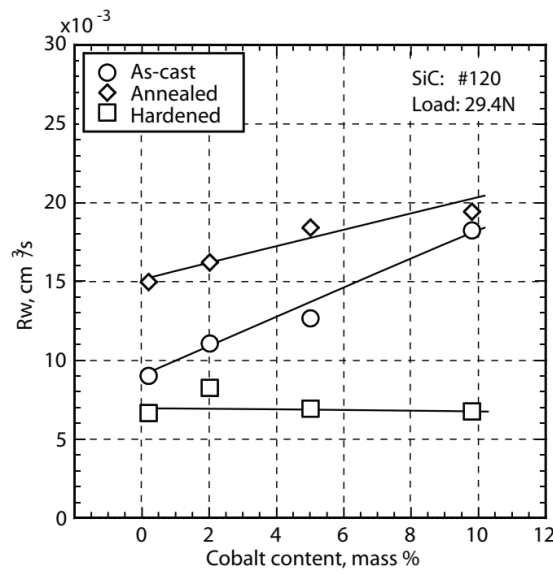


Figure 2.25 Effect of cobalt content on wear rate (R_w) of multi-alloyed white cast irons heat treated with different conditions (Sasaguri et al., 2010).

Effect of carbon content on three-body type abrasive wear behaviors of multi-alloyed white cast irons was reported by Inthidech et al. (2021a). The specimens were hardened from 1100°C austenitizing. It is found that the wear rate (R_w) value decreases with an increase in the carbon content up to 2.3%. This is because an increase of carbon content produces more eutectic carbide and causes increased secondary hardening in the tempering. The lowest R_w value or highest wear resistance is almost obtained in the as-hardened state (As-H). In the tempered state, the highest wear resistance is obtained in the specimen with maximum tempered hardness (T_{HTmax}).

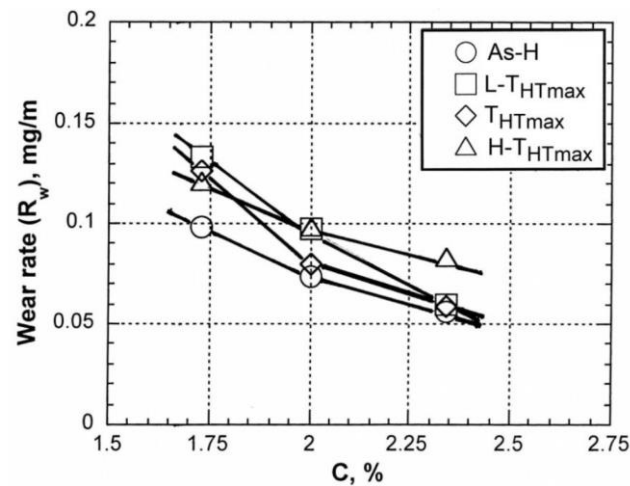


Figure 2.26 Effect of carbon (C) on wear rate (R_w) of multi-alloyed white cast iron with basic alloy composition with different heat treatment conditions. (Austenitizing: 1100°C). (As-H: as-hardened, T_{HTmax} : maximum tempered hardness, $L-T_{HTmax}$: lower than maximum tempered hardness and $H-T_{HTmax}$: higher than maximum tempered hardness) (Inthidech et al., 2021a).

Opapaiboon et al. (2019b) studied the effect of chromium on three-body type abrasive wear resistance of heat-treated multi-alloyed white cast irons. As shown in Figure 2.27, the lowest R_w or highest wear resistance is obtained in the as-hardened specimen and followed by the $H-T_{max}$ specimen. The wear resistance of the $L-H-T_{max}$ specimen is the smallest. The highest wear resistance is obtained at 6%Cr. The wear resistance reduces over 6%Cr is considered due to a reduction of hardness. An increase in chromium content promotes the precipitation of eutectic M_7C_3 and secondary $M_{23}C_6$ carbides with lower hardness than that of MC , M_2C , and M_6C carbides as well as lowers the secondary hardening.

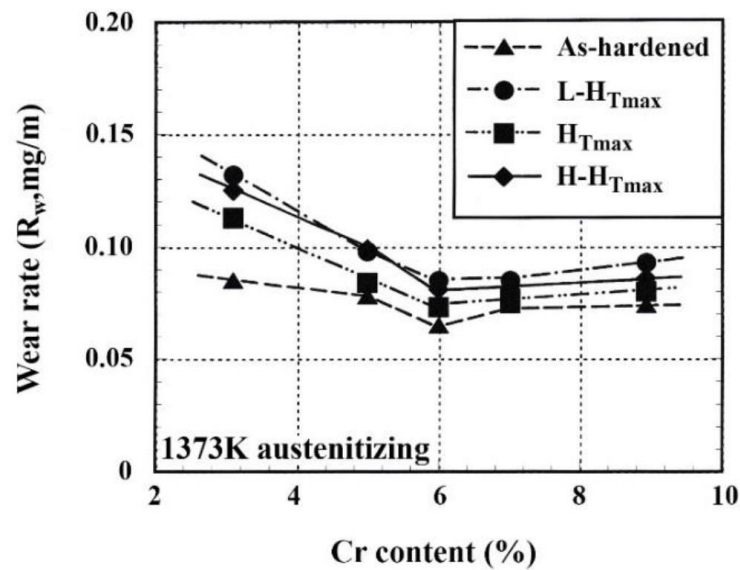


Figure 2.27 Effect of chromium (Cr) on wear rate (R_w) of multi-alloyed white cast iron with basic alloy composition with different heat treatment conditions. (Austenitizing: 1373K (1100°C)). (H_{Tmax} : maximum tempered hardness, $L-H_{Tmax}$: lower than maximum tempered hardness, $H-H_{Tmax}$: higher than maximum tempered hardness) (Opapaiboon et al., 2019b).

2.5 Niobium in alloyed white cast iron

It is well known that niobium is a transition metal that has excellent carbide formability and forms NbC with a face-centered cubic lattice. NbC mostly appears in its pure form in the cast iron with less partitioning into austenite or other carbides (Melo et al., 2020; Shabalin, 2019; Silva et al., 2021). The hardness of NbC is around 2400 – 3000HV (Mohrbacher & Delagostini Jarreta, 2015; Wu, 2000). NbC appears promising to reinforce white cast irons due to their very high hardness values. It was reported that some niobium can dissolve in MC eutectic carbide to increase its density near that of molten metal and decrease the segregation of eutectic carbide that occurs in the centrifugal casting process (Ichino et al., 1997).

There are several attempts to add niobium into alloyed white cast irons. Guesser (1985) added 1 and 3%Nb into 3%C-18%Cr cast irons. The results showed that an increase in niobium content improves wear life more than the same level of molybdenum. However, addition of niobium more than 1% does not show any further improvements. This work suggested that combined niobium and molybdenum should be considered in the viewpoint of improving the wear resistance.

He-Xing et al. (1993) reported that the addition of 3.47%Nb increases the hardness of 15%Cr cast iron. It is considered due to finer microstructure of matrix. In addition, the blocky NbC particles observed coexisting with M_7C_3 carbides. The authors related the observed matrix refinement to the role of NbC particles as heterogeneous nucleation sites during solidification, proposing that this reduces the effective dendrite size of the surrounding austenite and raise matrix hardness independently of any change in the wear-resisting carbide fraction itself.

Filipovic et al. (2013) also investigated microstructure and wear resistance of 2.9%C-19%Cr cast irons containing 0.54 and 2.06%Nb. Their finding is that an increase in niobium improves hardness, three-body type wear resistance and fracture toughness of the cast irons. Again, 2.06%Nb cast iron showed the best compromise between wear resistance and fracture toughness. They also studied the addition of niobium and vanadium with 0.5 and 2.0% each into 2.9%C-19%Cr cast irons in the as-cast condition. The results indicated that the primary petal-like NbC carbide is observed in cast iron with 0.5%Nb. The primary NbC carbide crystallizes in cast iron with 2.0%Nb with nodular or hexagonal morphology. An increase in niobium content promotes the crystallization of NbC carbide but reduces the M_7C_3 carbide. Moreover, dendrite arm spacing is decreased. Consequently, the cast iron has higher hardness, abrasive wear resistance and fracture toughness.

Bedolla-Jacuinde et al. (2015) studied the abrasive wear resistance of 3%C-17%Cr cast irons with 2% of vanadium, niobium and titanium each. They reported that the MC carbide crystallized as the primary phase in all three variants and improved the wear resistance relative to a Nb/V/Ti-free 17%Cr base iron. A dry-sand rubber wheel abrasion test was used to measure volume loss for each variant and the niobium alloyed iron showed particularly favorable wear performance, attributed to the coarseness and discreteness of the primary NbC particles, which resist carbide pull-out during abrasion better than finer eutectic MC formed with vanadium.

Lighvan (2021) studied the effect of niobium in the solidification structure of 17%Cr cast iron with varying niobium content from 0.0-10.7%. As shown in Figure 2.28, the primary NbC appears in the cast irons with over 2.69%Nb. The morphology of NbC changes from flower/petal-like to blocky morphology as the niobium content increases.

Maja et al. (2016) added 0.1 – 0.6%Nb to high Cr cast iron. They stated that the addition of niobium from 0.1 to 0.4% promotes the crystallization of NbC with high hardness before that of M_7C_3 carbides and then, finer and isotropic carbides are obtained. When the niobium content is in the range of 0.4 – 0.6%, however, the hardness decreases due to excessive NbC carbides consuming carbon to form carbide greatly. This leads to a lower volume fraction of M_7C_3 carbide. Furthermore, an increase in niobium content improves the fracture strength due to a change in morphology from rod-like and needle-like M_7C_3 carbide to a finer and isotropic shape. Bouhamla et al. (2008) studied the effects of niobium in 2.31%C-15.01%Cr cast iron by varying niobium from 0.0 to 3.0%Nb. In Nb-free cast iron, the solidification sequence starts with crystallization of primary austenite and followed by eutectic of (γ + M_7C_3). In 3.0%Nb cast iron, the crystallization of primary NbC carbide occurred before the eutectic of (γ + M_7C_3). The crystallization of NbC carbide reduces the abrasive wear loss and friction during wear tests.

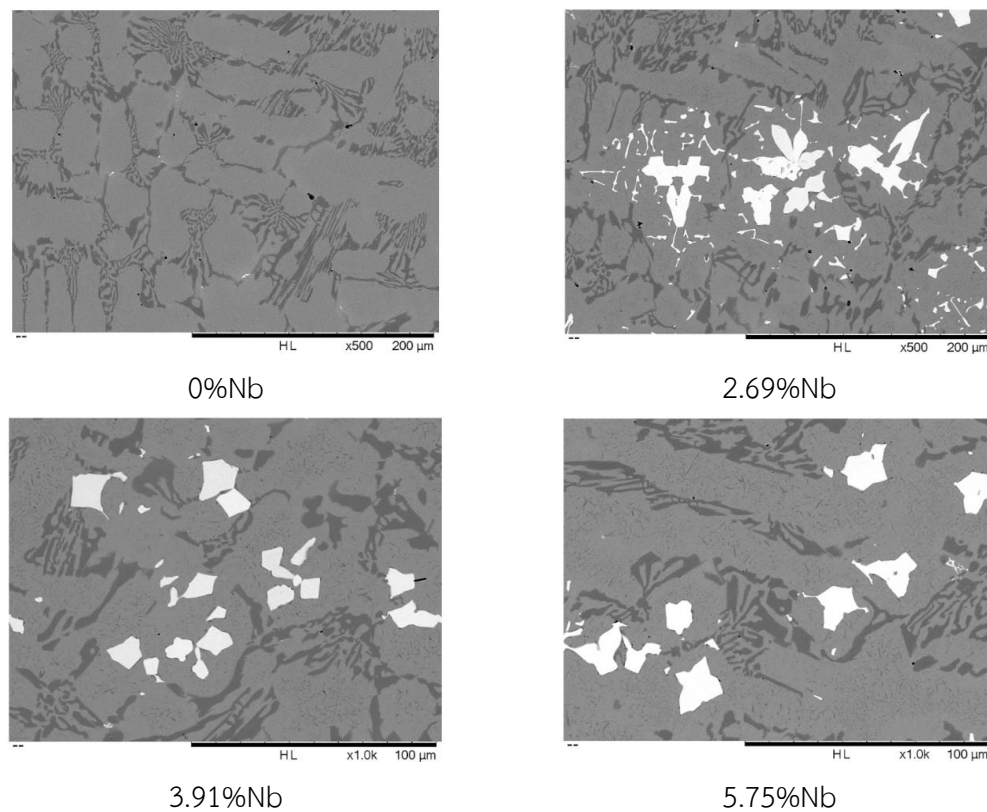


Figure 2.28 SEM images of NbC morphologies in high Cr cast iron with varying Nb contents (Lighvan, 2021).

Ma et al. (2013) studied the microstructure and properties of 3%C-25%Cr cast iron with niobium and other carbide formers. They reported that the as-cast microstructure changes from hypereutectic to eutectic and hypo-eutectic compositions when niobium content increases. The addition of niobium refined austenite dendrite and eutectic structure. The highest hardness and impact toughness are obtained in the cast iron with 0.6%Nb.

Boccalini et al. (2008) studied the effect of niobium on the solidification structure of multi-alloyed white cast iron with 0.5 – 2.0%Nb. The quasi-solidification sequence diagram of multi-alloyed white cast iron with different niobium contents is shown in Figure 2.29. With increasing niobium content up to around 0.7%, the alloys are hypo-eutectic composition. The solidification path consists of primary crystallization of austenite followed by two eutectics of (γ +MC) and (γ +M₂C). When niobium is over 0.7%, by contrast, the chemical composition changes to hyper-eutectic composition. The primary Nb-rich carbides or NbC solidify first from the melt, while the subsequent eutectic reactions are the same described previously. The as-cast microstructure of cast iron with 1.9%Nb is illustrated in Figure 2.30. The microstructure shows short dendrites, large primary NbC carbides and two eutectics of (γ + MC) and (γ + M₂C).

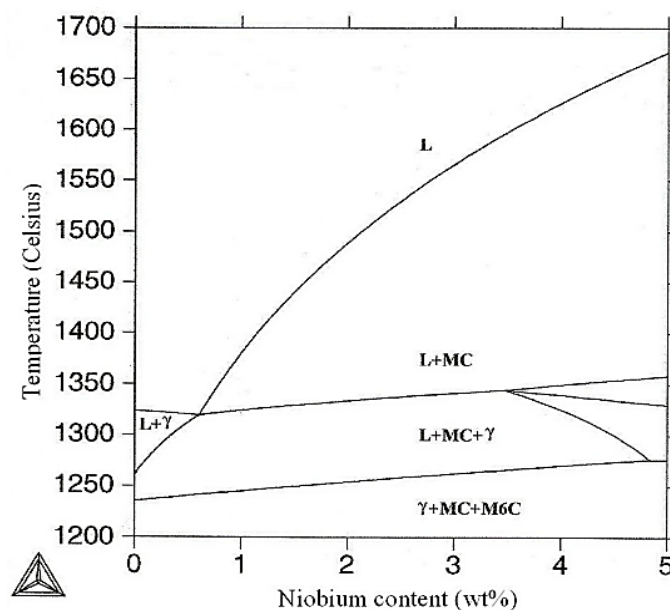


Figure 2.29 Calculated isopleth Fe-2.1%C-4.5%V-4.3%Mo-4.6%Cr-4.8%W-Nb by ThermoCalc program (Boccalini et al., 2008).

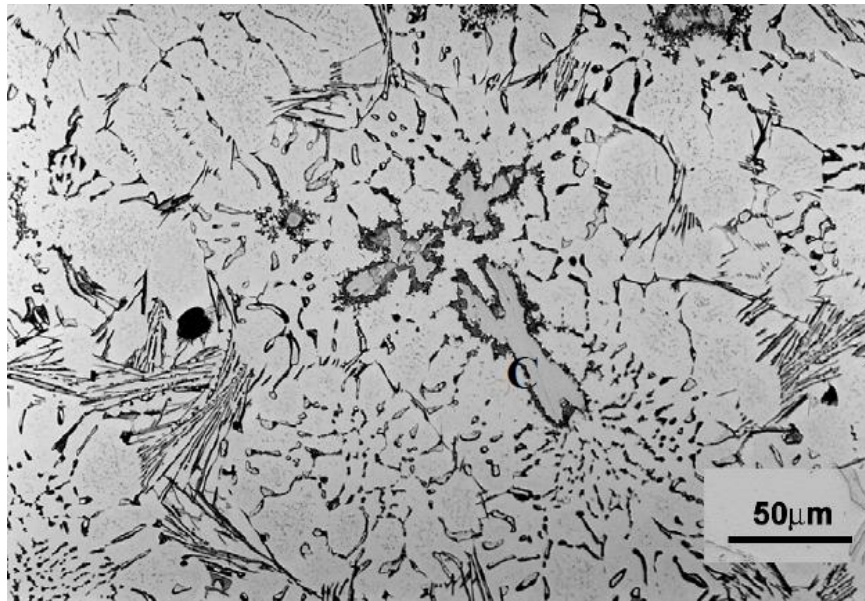


Figure 2.30 As-cast microstructure of multi-alloyed white cast iron with 1.9%Nb (Boccalini et al., 2008).

Kusumoto et al. (2017) studied the abrasive wear behavior of multi-alloyed white cast iron with 5%Nb. They reported that the cast iron with 5%Nb shows better abrasive wear resistance compared to multi-alloyed white cast iron without niobium. It is considered that a large size of primary NbC carbides is more effective to suppress the scrape of abrasive particles as schematically shown in Figure 2.31.

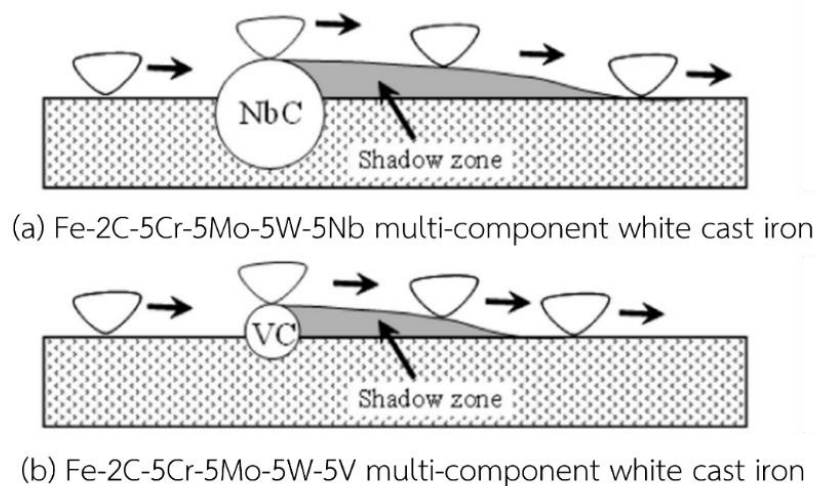


Figure 2.31 Schematic view of abrasive wear mechanism (Kusumoto et al., 2017).

Melo et al. (2020) studied the effect of niobium addition on an 18-19%Cr white cast iron in both the as-cast and heat treated (destabilized) conditions. The results showed that niobium addition changes the microstructure from one dominated solely by M_7C_3 eutectic carbide to one containing discrete NbC particles together with M_7C_3 . This is explained by the niobium addition shift the eutectic line to the right, changing the crystallization path and the resulting carbide balance.

De Mello and Polycarpou (2010) studied the effect of eutectic carbides and matrix hardness on the micro-abrasive wear of multi-component ferrous alloy based on the M2 high-speed steel composition, using two alloy series with variable vanadium or molybdenum content. The results showed that the wear coefficient was not influenced by the nature or amount of eutectic carbides, nor by matrix hardness; however, the carbide-free matrix alloy showed a considerably higher micro-abrasive wear rate, up to five times, than the carbide-rich alloy. The dominant wear mechanism was directional grooving, similar to a two-body mechanism, examined by SEM and by focused ion beam (FIB) taper sectioning combined with high-resolution SEM. Sectioning showed that removal of matrix material by the fine silica particles reduced the mechanical support for the carbides, which caused their gradual fracture and pull-out, particularly for larger MC carbides, while MC carbides caused stoppage and deviation of the abrasive grooves and the smaller M_2C carbides were instead cut and scratched rather than pulled out.

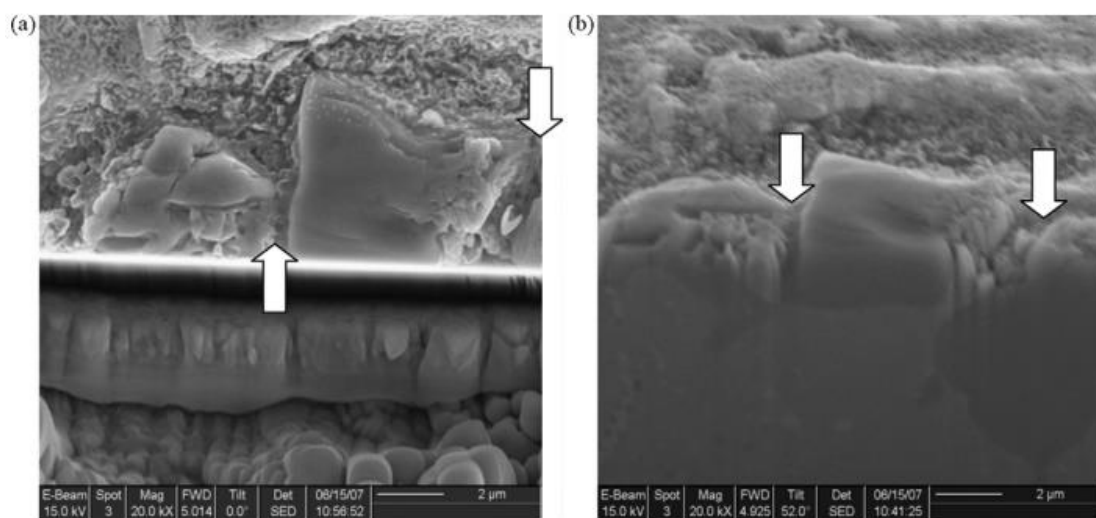


Figure 2.32 Typical aspect of taper section produced by FIB; (a) upper view and (b) side view (de Mello & Polycarpou, 2010).