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----(2.1)

## Chapter 2 Literature Survey

## Multi-component white cast iron

Basic chemical composition of multi-component white cast iron proposed by Y. Matsubara<sup>1)</sup> is 5 mass% of each alloying element, chromium (Cr), vanadium (V), molybdenum (Mo), tungsten (W) and cobalt (Co), and the carbon content is 2 mass%. This reason is to design the carbon balance (C<sub>bal</sub>) almost 0%. This carbon content is much higher than that of high speed tool steels with similar alloying elements so that eutectic carbides can precipitate in the iron for wear resistance. The roll made of multi-component white cast iron is called "high speed steel (HSS) roll" in the trade in spite of its cast iron composition<sup>2)</sup>. Typical microstructure of multi-component white cast iron consists of two or three kinds of precipitated carbides such as MC, M<sub>2</sub>C and M<sub>7</sub>C<sub>3</sub> in the matrices of bainite, martensite and austenite. The type, morphology and volume fraction of carbide remarkably depend on the combination of chemical composition<sup>4-6)</sup>. The type and three-dimensional morphology of carbides are classified as shown in Table 2-1<sup>1), 2), 4)</sup>. The morphology of MC and M<sub>2</sub>C carbides are shown in Fig. 2-1 and Fig. 2-2, respectively.

In the study on carbides in multi-component white cast iron, it is found that carbon balance  $(C_{bal})^{(1), (2)}$  is one of the important factors, and it is shown by the equation (2.1).

 $C_{bal} = \%C$  in iron  $-C_{stoich}$ 

Here,  $C_{\text{stoich}}$  is the amount of carbon which combines stoichiometricly with all carbide forming elements.  $C_{\text{stoich}}$  can be theoretically calculated from the next equation (2.2),

 $C_{\text{stoich}} = 0.060\%\text{Cr} + 0.063\%\text{Mo} + 0.033\%\text{W} + 0.235\%\text{V}$  -----(2.2)

In case that eutectic  $M_7C_3$  precipitates, the equation (2.2) should be modified to be the equation (2.3).

 $C_{\text{stoich}} = 0.099\%\text{Cr} + 0.063\%\text{Mo} + 0.033\%\text{W} + 0.235\%\text{V}$  -----(2.3)

| Type of                       | Three-dimensional Morphology of |
|-------------------------------|---------------------------------|
| Carbide                       | Carbide                         |
| MC                            | 1. flaky or petal-like          |
|                               | 2. nodular or granular          |
|                               | 3. rod-like or coral-like       |
| M <sub>2</sub> C              | 1. lamellar                     |
|                               | 2. plate-like                   |
| M <sub>7</sub> C <sub>3</sub> | 1. rod-like                     |
|                               | 2. ledeburitic                  |

Table 2-1Type and three-dimensional morphology<br/>of precipitated carbides

As for the materials of hot work rolls, the MC and  $M_2C$  carbides are desirable. From this point of view,  $C_{\text{stoich}}$  should be calculated from equation (2.2) to keep the  $C_{\text{bal}}$  of the iron near 0%. The  $C_{\text{bal}}$  connecting to the carbon content in the iron has some allowance and it is changeable in a certain range of minus or plus from zero. Cobalt (Co) is also added to improve corrosion and oxidation resistance and high temperature strength<sup>1),2)</sup>. Since Co does not take part in the formation of carbide, however, it is put off in these equations.

Among the carbides precipitated in the solidification structure, MC carbide has the highest hardness of  $2300-2700 \text{ HV}^{7}$ . Therefore, MC carbide plays a very important role as a wear resistant component in the hot work rolls. Simultaneously, the morphology and distribution of MC carbide is considered to affect the mechanical properties like strength and toughness.







Fig. 2-2 Morphology of M<sub>2</sub>C carbide. (SEM microphotograph)

H.Q. Wu and et al.<sup>4)</sup> reported the influence of alloying elements and solidification rate on the type and three-dimensional morphology of carbides which precipitated during the solidification. The influence of V and C contents on carbide structure is shown in Fig. 2-3. MC carbide precipitates in the specimens throughout the whole chemical composition but exhibits different morphology as shown in Table 2-1. At high V content, the coral-like MC carbide precipitates and more carbon is necessary to obtain  $M_7C_3$  carbide.



Fig. 2-3 Relationship between V, C contents and type and morphology of precipitated carbide. (Fe-5%Cr-2%Mo-2%W-5%Co-V-C alloy)

The influence of tungsten equivalent  $(W_{eq})$  and C content on carbide structure is shown in Fig. 2-4.  $W_{eq}$  is expressed by (%W+2x%Mo). Nodular MC carbide precipitates exactly in a region of  $W_{eq}$  value less than 11 % and C content more than 2 %. Out of this region, petal-like or flaky MC carbide exists. The precipitation of chunky MC carbide is restricted to the area of  $W_{eq}$  value and C content beyond 12 % and 2 %, respectively.

Lamellar  $M_2C$  carbide appears with  $W_{eq}$  value lower than 15 % and low carbon content, while plate-like  $M_2C$  carbide appears with  $W_{eq}$  value higher than 15 % in spite of the difference in C content.



Fig. 2-4 Relationship between tungsten equivalent (W<sub>eq</sub>), C content and type and morphology of precipitated carbide. (Fe-5%Cr-5%V-5%Co-Mo-W-C alloy)

The influence of Co and C contents on carbide structure is shown in Fig. 2-5. Both of the type and morphology are not changed by Co content if the carbon content is constant.

As described above, it is clear that the carbide structure can be changed remarkably by the variation of alloying elements. Fig. 2-6 tells that solidification rate hardly influences the type of precipitated carbide but the carbide tends to become fine with an increase in solidification rate. In lower C content less than 2.5 %C, MC and M<sub>2</sub>C carbides are found. In the region of higher C content,  $M_7C_3$  carbide exists in addition to them, and M<sub>3</sub>C carbide may also appear at very low solidification rate.



Fig. 2-5 Relationship between Co, C contents and type and morphology of precipitated carbide. (Fe-5%Cr-2%Mo-2%W-5%V-Co-C alloy)



Fig. 2-6 Schematic illustration of carbide type corresponding to solidification rate and carbon content. (Fe-5%Cr-5%Mo-5%W-5%V-5%Co -C alloy)

Y. Matsubara and et al.<sup>1)</sup> have reported the influence of solidification rate on the number and size of MC carbide. Fig. 2-7 shows that the average number of MC carbide ( $N_{MC}$ ) increases and the diameter of MC carbide ( $D_{MC}$ ) decreases when solidification rate (R) is increased. At a large solidification rate,  $N_{MC}$  and  $D_{MC}$  increase as C content rises. The volume fraction of MC carbide ( $V_{MC}$ ) increases with an increase in C content as shown in Fig. 2-8.



Wear resistance and mechanical properties are closely related to the amount and morphology of carbide. The relationship between volume fraction of carbides (V<sub>c</sub>) and C content is shown in Fig. 2-9<sup>2</sup>). The amount of both MC and M<sub>2</sub>C carbides increases with an increase in C content except for the great decrease of M<sub>2</sub>C carbide at high carbon content due to the precipitation of eutectic M<sub>7</sub>C<sub>3</sub> carbide. This can be understood from the work by N. Sasaguri and et al.<sup>5</sup> on solidification sequence of multi-component white cast iron with chemical composition of



Fig. 2-8 Influence of C content on volume fraction of MC carbide ( $V_{MC}$ ). (Fe-5%Cr-5%Mo-5%W -5%V-5%Co-C alloy)



Fig. 2-9 Influence of C content on volume fraction (V<sub>c</sub>) of carbides. (Fe-5%Cr-5%Mo -5%W-5%V-5%Co-C alloy)

Fe-5%Cr-5%Mo-5%W-5%V-5%Co-2.89%C. The following solidification processes are proposed,

$$\begin{array}{cccc} L & \rightarrow & \gamma \text{ or MC (primary)} + L_1 \\ L_1 & \rightarrow & \gamma + \text{MC (eutectic)} + L_2 & & -----(2.4) \\ L_2 & \rightarrow & \gamma + M_7 C_3 (eutectic) + L_3 \\ L_3 & \rightarrow & \gamma + M_2 C (eutectic) \end{array}$$

S.K. Yu and et al.<sup>6)</sup> studied the effects of C content on the amount of retained austenite in as-cast and heat-treated multi-component white cast iron containing carbon up to 3 %. Interesting fact is that fine secondary carbides precipitate in all the heat-treated iron and remarkable precipitation hardening occurs by the post martensite transformation from retained austenite, even if their carbon balance ( $C_{bal}$ ) are negative. These results suggest that some amount of residual carbon due to the unequilibrium solidification, contributes to form retained austenite after tempering. Influence of C content on the amount of retained austenite in as-cast iron is shown in Fig. 2-10. The amount of retained austenite increases as the C content increases up to 2.5% and decreases at 3% C.



Fig. 2-10 Relationship between C content and volume fraction of retained austenite (Vγ) in as-cast state. (Fe-5%Cr-5%Mo-5%W -5%V-C alloy)

Relationship between C content and V $\gamma$  value in the air-hardened state from three different austenitizing temperatures is shown in Fig. 2-11. The V $\gamma$  value increases continuously with increasing the C content. When compared at the same carbon levels, the higher austenitizing temperature, the more austenite is retained.

Relationship between C content and V $\gamma$  value in the tempered state is shown in Fig. 2-12. The V $\gamma$  value is lower than that of air-hardened state. When compared at the same carbon levels, the amount of retained austenite exists more in the tempered state at lower temperature.



Fig. 2-11 Relationship between C content and volume fraction of retained austenite  $(V\gamma)$  in the air-hardened state. (Fe-5%Cr-5%Mo-5%W -5%V-C alloy)

Also, S.K. Yu and et al.<sup>8)</sup> reported the effects of retained austenite on abrasion wear resistance and hardness of hypoeutectic high chromium white cast iron. The amount of retained austenite  $(V\gamma)$  is changed depending upon the heat treatment condition. The V $\gamma$  value is mainly related to the hardness and the relationship between V $\gamma$  and wear rate (R<sub>w</sub>) is clarified in Fig. 2-13. The R<sub>w</sub> decreases with an increase in the V $\gamma$  value that is to say, the wear resistance is improved. This suggests that work-hardening arises during wear test.



Fig. 2-12 Relationship between C content and volume fraction of retained austenite (V $\gamma$ ) in the air-hardened and tempered state. (Fe-5%Cr -5%Mo-5%W-5%V-C alloy)



Fig. 2-13 Relationship between wear rate  $(R_w)$  and volume fraction of retained austenite  $(V\gamma)$ . (Fe-2.3%C-26%Cr-1%Ni-0.5%Mo)