Effect of Carbon Content on Heat Treatment Behavior of Multi-Alloyed White Cast Iron for Abrasive Wear Resistance

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Effect of carbon (C) content on heat treatment behavior of multi-alloyed white cast irons with basic alloy composition was investigated. The multi-alloyed white cast irons with varying C content of 1.73–2.34% were prepared. After annealing, the test specimens were austenitized at 1323 and 1373 K, and then hardened by fan air cooling. The hardened specimens were tempered between 673 and 873 K. It was found that the hardness in as-hardened state increased first and then decreased as C content increased. The volume fraction of retained austenite (fV) increased with increasing C content. In tempered state, each hardness curve showed secondary hardening due to the precipitation of secondary carbides as well as the transformation of decomposed austenite to martensite during post cooling. The fV began to decrease greatly when the tempering temperature was elevated over 723 K. The maximum tempered hardness (HTmax) was obtained in the specimens tempered between 798 K and 823 K where the fV ranged from 8 to 12%. The highest value of HTmax was obtained in the 2.00% C specimen hardened from 1373 K austenitizing and in the 2.34% C specimen hardened from 1323 K austenitizing. [doi:10.2320/matertrans.M2015001]

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1. Introduction

Alloyed white cast irons have been developed for materials with abrasive wear resistance for more than a half century. The main purpose of the research and development for this kind of alloy is to improve abrasive wear resistance and toughness.1–5) Currently, alloyed white cast irons are widely used in steelmaking, mining, cement industries and thermal power plants, where various kinds of machines are working to crush and pulverize stones and minerals.5) The surface of parts or components in the machines is heavily damaged by abrasive wear. This failure directly affects the initial cost. Therefore, technical innovation to increase the wear performance of materials within an acceptable cost becomes necessary.

The transition of alloyed white cast irons for steel rolling and mineral pulverizing mill rolls changed from low-alloyed white cast iron via Ni-hard to high Cr cast iron. High Cr cast iron has been used for a long time because of its high abrasive wear resistance. However, a large volume fraction of eutectic chromium carbide precipitated in high Cr cast iron reduced the toughness and caused failure under an impact load. Until now, therefore, a new alloy which had greater toughness and higher performance has been researched and developed. To achieve this purpose, cast iron containing multiple types of carbides with higher hardness than chromium carbides and low volume fraction of carbides had to be designed.

A multi-alloyed white cast iron was developed in Japan around 30 years ago that contains several carbide forming elements such as, chromium (Cr), molybdenum (Mo), tungsten (W) and vanadium (V).1,2) The carbides existing in multi-alloyed white cast iron are MC, M2C, M6C, M7C3 and M23C6 types.1–4) It is well known that MC, M2C, M6C are the main carbides precipitated secondarily in high speed tool steel and chromium carbides of M7C3 and M23C6 types are in high Cr cast iron. These complex carbides have extremely high hardness, and they improve the abrasive wear resistance. In the alloyed cast irons, the carbide forming elements not only form their own special or complex carbides but also distribute into the matrix. The alloys dissolved in the matrix should affected phase transformation of matrix.

Multi-alloyed white cast iron with basic alloy composition is expressed as Fe-5 mass% Cr-5 mass% Mo-5 mass% W-5 mass% V-5 mass% Co-C system (hereafter mass% is shown by %).1,2) Cobalt (Co) is added in order to improve the high temperature properties, especially hardness. In this alloy system, hypoeutectic composition is preferred because of its higher toughness.5–9) The carbide structure depends on the kind and amount of alloying elements and the solidification rate.8) The heat treatment is very important even if the expected alloying elements are added. This is because the matrix structure and the mechanical or wear properties can be controlled or modified by heat treatment.

Nowadays, multi-alloyed white cast irons are widely applied to hot strip mill rolls and show higher quality and better performance than conventional rolls made by Ni-hard and high Cr cast iron.1,10) Undoubtedly, this type of cast iron will be applied increasingly in many industrial fields.

Looking back, the researches on heat treatment of multi-alloyed white cast iron are not many.11) In this study, the effect of C content on the variation of hardness and volume fraction of retained austenite (fV) during heat treatment was clarified in multi-alloyed white cast irons with basic chemical composition.

2. Experimental Procedure

2.1 Preparation of test specimens

The charge calculation was carried out for the target...
was poured from 1793 to 1773 K into preheated CO2 molds. After holding at the temperature of 1853 K, the melt lining. Charge materials were melted and superheated to capacity high frequency induction furnace with alumina materials. The test specimens were produced using a 30 kg pig iron, ferro-alloys and pure metals were used as charge chemical composition. Raw materials such as mild steel, pig iron, ferro-alloys and pure metals were used as charge materials. The test specimens were produced using a 30 kg capacity high frequency induction furnace with alumina lining. Charge materials were melted and superheated to 1853 K. After holding at the temperature of 1853 K, the melt was poured from 1793 to 1773 K into preheated CO2 molds with cavity size of 25 mm in diameter and 65 mm in length as shown in Fig. 1. The surface of the top riser was immediately covered with preheated dry exothermic powder to prevent rapid cooling of the riser. The size of test piece is in disk-shape with 7 mm in thickness. The chemical compositions of the ingot are shown in Table 1.

Table 1 Chemical composition of test specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>V</th>
<th>Co</th>
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<tr>
<td>No.1</td>
<td>1.73</td>
<td>0.50</td>
<td>0.49</td>
<td>5.09</td>
<td>5.05</td>
<td>4.98</td>
<td>5.05</td>
<td>2.03</td>
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<tr>
<td>No.2</td>
<td>2.00</td>
<td>0.53</td>
<td>0.49</td>
<td>4.96</td>
<td>4.98</td>
<td>4.98</td>
<td>5.01</td>
<td>2.03</td>
</tr>
<tr>
<td>No.3</td>
<td>2.34</td>
<td>0.54</td>
<td>0.49</td>
<td>4.98</td>
<td>5.02</td>
<td>4.98</td>
<td>5.04</td>
<td>1.98</td>
</tr>
</tbody>
</table>

2.2 Heat treatment procedures

The specimens were coated with an anti-oxidation paste to reduce oxidation and decarburization during heat treatment. Annealing of specimens was carried out in an electric furnace at 1223 K for 18 ks. Annealed specimens were austenitized at 1273 K and 1373 K for 3.6 ks, and hardened by fan air cooling (FAC). The hardened specimens were tempered between 623–873 K for 12 ks and cooled in still air.

2.3 Measurement of hardness and volume fraction of retained austenite

Macro- and micro-hardness of test pieces were measured using a Vickers hardness tester with the loads of 294.2 N (30 kgf) and 0.98 N (0.1 kgf) respectively. The measurement was done at more than five locations in random, and the average value was adopted.

The volume fraction of retained austenite ($V_\gamma$) was obtained by X-ray diffraction using a special goniometer with an automatic rotating and swinging sample stage. The diffraction peaks used for ferrite ($\alpha$) or martensite ($M$) calculations were $(200)_\alpha$ and $(220)_\alpha$ planes and those for austenite ($\gamma$) were $(220)_\gamma$ and $(311)_\gamma$ planes. Vilella’s reagent was used to reveal the microstructure. Observation of the microstructure using OM and SEM was introduced to stimulate discussion of the experimental results.

3. Results and Discussions

3.1 As-cast state

The typical as-cast microstructures of test specimens with three C contents are respectively shown in Fig. 2. All specimens show hypoeutectic structure consisting of austenite dendrite and eutectic. The eutectic carbides are mainly granular or string-like MC and plate-like or lamellar M$_2$C that appears at the boundary region of austenite dendrite. The amount of eutectic carbide increases with increasing C content. Matrix of all specimens is mostly austenite with small amount of martensite.

3.2 As-hardened state

The as-hardened microstructures of test specimens with three C contents are respectively shown in Fig. 3. The matrix of all specimens is composed of secondary carbides (Sc), martensite (M) and retained austenite ($\gamma_R$). The austenite existed in as-cast state was now greatly reduced, and instead, more carbide can be observed. This proves that the destabilization of austenite occurred during austenitizing. There are more secondary carbides in the specimen with high C content. The martensite can be seen in the high C specimens of No.2 and No.3 coexisting with clear retained austenite.

The effect of C content on the hardness and $V_\gamma$ in an as-hardened state is shown in Fig. 4. In the specimen hardened from 1323 K austenitzing, the hardness increased to the maximum value as C content rose, and then it decreased. In case of 1373 K austenitizing, the relation of hardness vs. C content was found to be similar. At the same C content, the hardness was high in the specimen hardened from 1323 K except for 1.73% C specimen. On the other hand, the $V_\gamma$ increased continuously as C content rose regardless of austenitizing temperature. At the same C content, the higher austenitizing temperature provided higher $V_\gamma$ value. It can be explained that the solubility of C and alloying elements in austenite increased by elevating the temperature, and subsequently these alloys lowered Ms temperature. With respect to the relation of hardness and $V_\gamma$, it is evident from Fig. 5 that the hardness increases with increasing $V_\gamma$ up to around 28% because the increase in precipitated carbides affected much more the increase in hardness. At high $V_\gamma$ value over 28%, however, the hardness decreases because an excess of soft retained austenite causes the matrix hardness drastically low together with reduction of martensite.

3.3 Tempered state

After the specimens were hardened from two austenitizing...
temperatures, they were tempered at several temperatures of 673–873 K. The relationships between macro-hardness, $H_T$ and tempering temperature for all specimens with three C contents are shown in Fig. 6, respectively. The hardness and $V_T$ in as-hardened state are plotted for comparison. It is found that the tempered hardness curve of each specimen shows a peak at $T_{max}$ value and then decreases as the tempering temperature increases. The reason why there is a wide range of hardness at the $T_{max}$ value is due to the fact that the hardness was not influenced mainly by the $V_T$ value but more by the change of other phase, say, over-tempering of martensite.

After the tempering temperature rises over the temperature at which the $H_{T_{max}}$ was obtained, the hardness decreases remarkably. This is because fine secondary carbides precipitated during tempering begin to agglomerate. The degree of secondary hardening, which is defined as the difference of the lowest and highest hardness, is larger in the specimen hardened from higher temperature than from lower temperature. The degree increases with increasing C content. The highest value of $H_{T_{max}}$ 940 HV30, was obtained in the 2.00% C specimen hardened from 1373 K. As shown in Fig. 6, the $V_T$ in tempered state decreases gradually as the tempering temperature increases to 723–773 K and after that it decreases abruptly but a certain amount of austenite still remains in this experiment. The $V_T$ values at $H_{T_{max}}$ are 3% in the 1.73%C specimen, 4% in the 2.00%C specimen and 10% in the 2.34%C specimen of 1323 K austenitizing, while they are 4% in the 1.73%C specimen, 6% in the 2.00%C specimen and 14% in the 2.34%C specimen of 1373 K austenitizing.

As mentioned previously, the hardness of cast iron depends on the eutectic carbides and the matrix structure. In general, the eutectic carbide changes little during tempering, and therefore, the hardness is mainly influenced by the constituent phases in matrix. The relationship between macro-hardness and $V_T$ of all tempered specimens is shown in Fig. 7. It is found that the hardness increases to the maximum value and then decreases as the $V_T$ increases. The maximum hardness more than 900 HV30 was obtained at about 5 to 15% $V_T$, irrespective of austenitizing temperature. In the range of very low $V_T$, the hardness is low because the specimen was over-tempered, while the hardness over maximum hardness decreases gradually with increasing $V_T$. The hardness varies with a range against the $V_T$ value. Over 20% of $V_T$, the hardness decreases proportionally as the $V_T$ rises. The reason why there is a wide range of hardness at the $V_T$ less than 5% is due to the fact that the hardness was not influenced mainly by the $V_T$ value but more by the change of other phase, say, over-tempering of martensite.

Effects of C content on the $H_{T_{max}}$ and $V_T$ are demonstrated in Fig. 8. At each austenitizing temperature, the $H_{T_{max}}$ increases to the maximum value as C content increases to 2.00% because the solubility of C in austenite increases with increasing C content of specimen and as a result, large amount of secondary carbides precipitate during tempering. Of course, it is true that alloying elements dissolved more in matrix promoting the precipitation of carbides. Over the highest value, the hardness decreases because much more $V_T$ already remained from the beginning in as-hardened state. The $V_T$ values of the specimens hardened from 1323 K are higher than those from 1373 K. Even in the specimen with $H_{T_{max}}$ considerable amount of retained austenite exists in the matrix. This reason could be due to the decomposition of secondary carbides from retained austenite during tempering and the residual austenite transforms to martensite during post cooling. It can be said that the change of matrix by phase transformations made hardness increase while the martensite formed by hardening was tempered to lower the hardness. It was reported that the secondary carbides were MC, $M_6$C and $M_7$C$_3$ or $M_5$C$_6$ types. The maximum tempered hardness ($H_{T_{max}}$) is obtained by tempering at 798–823 K in each austenitizing temperature. However, the specimen hardened from higher temperature gives higher $H_{T_{max}}$ value than that hardened from lower temperature except for 2.34% C specimen.

Fig. 2 Microstructures of as-cast specimens with different C content.

![Microstructures of as-cast specimens with different C content.](image-url)
of austenite or the precipitation of secondary carbides was not sufficient in this tempering condition. If the complete decomposition of retained austenite is tried by increasing the temperature and holding time, the hardness decreases due to the coarsening of precipitated carbides. In order to increase the hardness more with some $V\gamma$, an extension of the holding time will be preferred.

It is also found in Fig. 8 that the highest value of $H_{T\text{max}}$ for 1373 K austenitizing is obtained in the 2.00% C specimen and that for 1323 K is in the 2.34% C specimen. This indicates that the low C specimen needs higher austenitizing temperature, and that the high C specimen needs lower austenitizing temperature to obtain the highest hardness by tempering. When this is discussed concerning alloying elements, the highest $H_{T\text{max}}$ is obtained when their solubility in austenite reach the critical value. If alloying elements dissolve over the critical value, the $V\gamma$ is increased and then $H_{T\text{max}}$ is lowered.

The relationship between $H_{T\text{max}}$ and $V\gamma$ value at $H_{T\text{max}}$ is shown in Fig. 9. The maximum value of $H_{T\text{max}}$ seems to appear at about 6% $V\gamma$. Here, the $V\gamma$ in as-hardened state is

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Austenitizing</th>
<th>1323K x 3.6ks-FAC</th>
<th>1373K x 3.6ks-FAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>Sc + M + $\gamma_R$</td>
<td>Sc + M + $\gamma_R$</td>
<td></td>
</tr>
<tr>
<td>(1.73% C)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>No.2</td>
<td>Sc + M + $\gamma_R$</td>
<td>Sc + M + $\gamma_R$</td>
<td></td>
</tr>
<tr>
<td>(2.00% C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No.3</td>
<td>Sc + M + $\gamma_R$</td>
<td>Sc + M + $\gamma_R$</td>
<td></td>
</tr>
<tr>
<td>(2.34% C)</td>
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</table>

Fig. 3 Typical microstructures of as-hardened specimens.
connected to $H_{\text{tmax}}$ and the relation is shown in Fig. 10. From this result, the $V_{\gamma}$ more than 15% in as-hardened state is necessary to get the $H_{\text{tmax}}$ value over 900 HV30 in tempered state. This proves that the retained austenite in as-hardened state contributes more to heat treatment, particularly the precipitation of secondary carbides and the transformation of martensite.

4. Conclusions

The effect of carbon content on heat treatment behavior of multi-alloyed white cast iron with basic alloy composition was investigated using specimens with varying C content from 1.73 to 2.34 mass%. Various heat-treatments were given to the specimens and correlations among hardness, volume fraction of retained austenite ($V_{\gamma}$), tempering temperature and C content were clarified. The results are summarized as follows:

1. The hardness in as-hardened state increased first and then decreased as C content increased, but the $V_{\gamma}$ increased gradually with increasing C content.
2. In tempered state, hardness curves showed obvious secondary hardening due to the precipitation of secondary carbides and the transformation of residual retained austenite into martensite during post cooling. On the other side, the $V_{\gamma}$ began to reduce markedly when the tempering temperature got over around 723 to 773 K. The maximum tempered hardness ($H_{\text{tmax}}$) was obtained in the specimens tempered between 798 and 823 K where the $V_{\gamma}$ was near 10%.
3. The $H_{\text{tmax}}$ increased first and then decreased as C content rose. The highest value of $H_{\text{tmax}}$ was 930 HV30 in the No.2 specimen with 2.00% C hardened from 1373 K austenitizing and 920 HV30 in the No.3 specimen with 2.34% C hardened from 1323 K.
(4) The $V_\gamma$ more than around 15% in as-hardened state is needed to obtain high $H_{T_{max}}$ over 900 HV30.

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REFERENCES