# Behavior of Hardness in Heat-treated Multi-alloyed White Cast Irons with Varying Mo Content

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**Abstract.** *In this work, the effect of molybdenum (Mo) content on behavior of hardness in heat-treated multi-alloyed white cast iron with varying Mo content from 0 to 7.60 wt% was investigated. The cast irons were prepared under the basic alloy composition of 5 wt% Cr, W and V each. After annealing at 1223K for 18 ks, the test specimens were austenitized at 1323K for 3.6 ks in a vacuum furnace and subsequently hardened by a jet-spray of liquid nitrogen. The tempering was carried out at temperatures from 673 to 873K at 50K intervals for 12 ks. It was found that the hardness in the as-hardened state was increased progressively with an increase in the Mo content. In the tempered state, the hardness curve showed clear secondary hardening due to the precipitation of fine secondary carbides and a reduction of the retained austenite. The maximum tempered hardness ($H_{Tmax}$) was obtained in the specimen tempered at 798K in all specimens. The $H_{Tmax}$ increased first, and then subsequently decreased with an increase in the Mo content. The highest $H_{Tmax}$ value, 910 HV30, was obtained in the specimen with 5wt% Mo.*

***Keywords:*** Multi-alloyed white cast iron, heat treatment, hardness, Mo effect

## 1. Introduction

Multi-alloyed white cast iron is a new type of alloyed white cast iron with multi-components that contains several kinds of strong carbide forming elements, such as chromium (Cr), molybdenum (Mo), vanadium (V) and tungsten (W).[1-4] This white cast iron has been preferably applied to work roll materials in hot strip mills in the steel-making industry as well as some parts and components of pulverizing mills in the cement industry.

The typical microstructure of the multi-alloyed white cast iron consists of complex eutectic carbides such as MC, $M_2C$, $M_6C$ and $M_7C_3$ and the matrix consists of austenite, bainite and/or martensite together with secondary carbides.[1,2] The type and amount of carbides and the matrix structure are determined by the chemical composition and its heat treatment.[5-7] Compared to conventionally rolled materials, such as Ni-hard cast iron and high Cr cast iron, the multi-alloyed white cast iron provides superior abrasive wear resistance, higher quality and longer service life.[5] For these reasons, the most of the hot strip mill rolls made by high Cr cast iron have been replaced with rolls made by multi-alloyed white cast irons [5,7].

In general, hardening and tempering are carried out to improve wear resistance and mechanical properties for the multi-alloyed white cast iron in the same way as tool steels [8]. During holding at austenitizing temperature, the supersaturated austenite in as-cast state is destabilized by the precipitation of secondary carbides. Consequently, the austenite transforms into martensite during cooling after post cooling. In the tempering, the precipitation of special carbides occurs by the carbide reaction from martensite and the retained austenite in the as-hardened state is also decomposed by precipitation of secondary carbides and subsequently transforms into martensite.

It is known that Mo is a strong carbide former and improves hardenability of the cast iron. It was reported that Mo in high Cr cast irons promotes the precipitation of secondary carbides during heat treatment [8]. Therefore, an addition of Mo to multi-alloyed white cast iron should be helpful to improve the hardness.

The research and development on the multi-alloyed white cast irons have been studied on solidification sequence and phase transformation using the cast iron with basic alloy composition with 5 wt% (henceforth wt% is expressed by %) each of Cr, Mo, W and V [1,4-7,9]. However, the systematic research on the behavior of hardness in heat-treated multi-alloyed white cast iron with Mo has not been found. In this research, therefore, the effects of Mo content on heat treatment behavior of multi-alloyed white cast irons varying Mo content from 0-7.6% was investigated.

# 2. Experimental Procedures

## 2.1 Preparation of Test Specimens

Charge materials such as steel scrap, pig iron, ferro-alloys and pure metals were prepared to get the target chemical compositions. The charge materials were melted in 10 kg-capacity high frequency induction furnace with alumina lining. The melt was heated to 1853K. After holding for a while, the melt was poured at 1773-1793K into preheated sand molds with cavity size of 25 mm in diameter and 65 mm in length with suitable size of riser. After pouring, the top of riser was soon covered by exothermic powder to prevent the riser from fast cooling. The ingots were sectioned by wire-cutting machine to obtain the disk-shape test piece with 7 mm in thickness. The chemical compositions of test specimens are summarized in Table 1.

**Table 1:** Chemical compositions of test specimens

| Specimen | Element ( wt% ) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | Cr | Mo | W | V | Co |
| No.1 | 2.05 | 0.51 | 0.48 | 5.13 | 0.12 | 4.95 | 5.09 | 1.99 |
| No.2 | 2.08 | 0.47 | 0.48 | 5.09 | 1.17 | 4.92 | 5.03 | 2.01 |
| No.3 | 2.09 | 0.52 | 0.50 | 5.11 | 3.02 | 5.06 | 5.10 | 2.01 |
| No.4 | 2.00 | 0.53 | 0.49 | 4.96 | 4.98 | 4.98 | 5.01 | 2.03 |
| No.5 | 2.06 | 0.50 | 0.47 | 5.00 | 7.66 | 4.98 | 5.01 | 1.98 |

## 2.2 Heat Treatment Process

The specimens were annealed at 1223K for 18 ks in an electric furnace and then cooled in the furnace to room temperature. The annealed test pieces were austenitized at 1323K for 3.6 ks in vacuum furnace and then quenched by liquid nitrogen spray. The hardened test pieces were tempered at the temperatures between 673-873K at 50K intervals for 12 ks in an electric furnace and cooled to room temperature in still air.

## 2.3 Microstructural Examination and Hardness Measurement

Microstructures of heat-treated specimens were observed by optical microscope (OM) and scanning electron microscope (SEM). The test piece was polished using emery papers and buffing with alumina powder. The microstructure was revealed by Villella's reagent (95 cc of ethyl alcohol, 5 cc of hydrochloric acid and 1 g of picric acid). Macro-hardness of specimen was measured using Vickers hardness tester with a load of 30 kgf and micro-hardness of matrix was performed using Micro-Vickers hardness tester with a load of 0.1kgf. The hardness was measured.

# 3. Results and Discussion

## 3.1 As-cast State

As-cast microstructures of specimens observed by OM are example shown in Fig.1 for Mo-free and 7.6%Mo specimens. All the specimens consist of primary austenite dendrite and eutectic structures. The eutectic carbides are mainly MC type but some of $M_7C_3$ eutectic carbides are observed in Mo-free. In the specimens with Mo content more than 3%, the $M_2C$ eutectic carbides crystallized and the amount of $M_2C$ eutectic increases with an increase in Mo content. The matrices of all specimens are mostly austenite but small amount of martensite should exist in the matrix of specimens containing some Mo content.

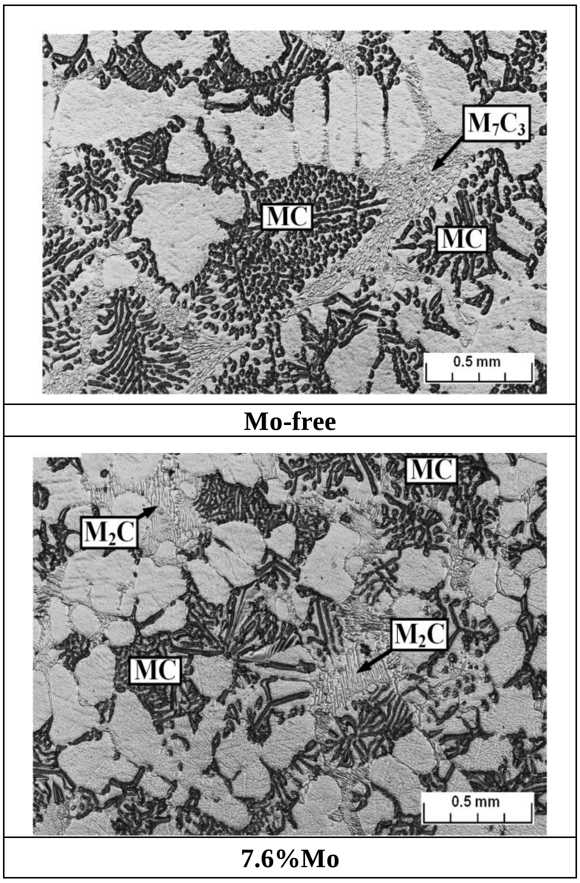


**Fig. 1:** As-cast microstructure of Mo-free and 7.6%Mo specimens

## 3.2 As-hardened State

Microstructures of as-hardened specimens are shown in Fig. 2 for 3% and 7.6% Mo specimens. The matrices are composed of fine secondary carbides (SC), martensite (M) and retained austenite ($\gamma$). The precipitation of secondary carbides (SC) occurs during austenitizing. The precipitated carbides rather increase in number with an increase in the Mo content. The martensite that transformed from the destabilized austenite can be found all over the matrix. However, the amount of martensite cannot be clarified from these microphotographs.

Relationship between macro- and micro-hardness and Mo content are shown in Fig. 3. The macro-hardness increases steadily with raising of the Mo content. The micro-hardness shows similar trend to the macro-hardness. The reason of an increase in hardness is caused by an increase in the amount of eutectic $M_2C$ carbides with high hardness. In addition, an increase in Mo content promotes the precipitation of $M_2C$ secondary carbides and as a result, more martensite should be transformed in the matrix due to a rise in Ms temperature.

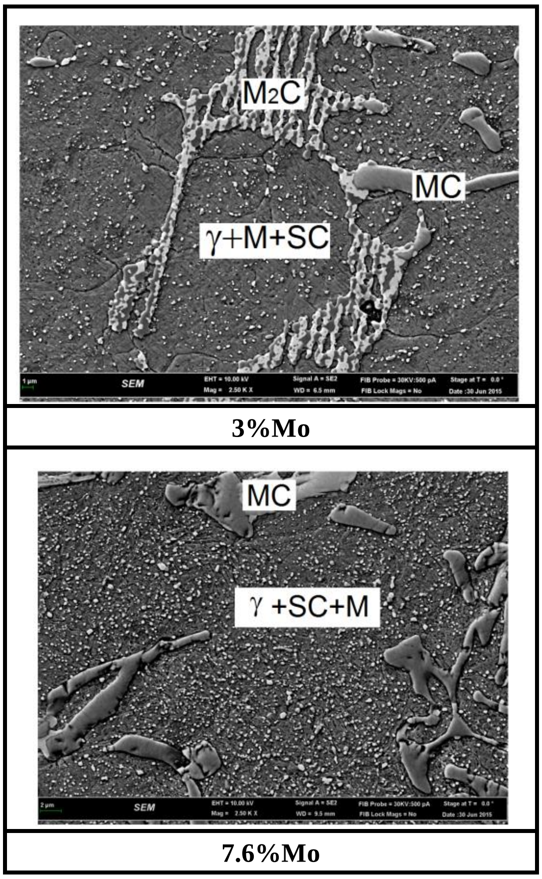


**Fig. 2:** As-hardened microstructure of 3 and 7.6% Mo specimens

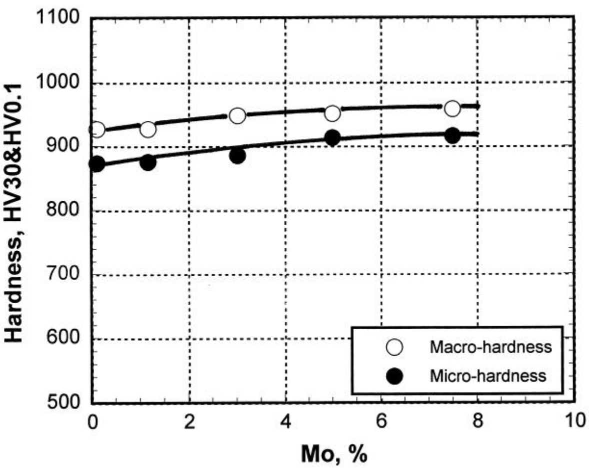


**Fig. 3:** Effect of Mo content on macro- and micro-hardness in as-hardened state

## 3.3 Tempered State

In the tempered state, martensite in as-hardened state dissolved or was tempered by precipitating carbides and additionally, strong carbide forming elements like Mo and V could form each pure carbide with much higher hardness according to the carbide reactions. As a result of tempering, the stability of austenite was reduced and allowed the transformation of austenite to martensite during the post-cooling. Therefore, tempered martensite, newly transformed martensite and mixed secondary carbides formed during hardening and tempering exist in the matrix of tempered specimens. It is expected that such phases strengthen matrix structure and improve mechanical properties such as tensile strength, compression strength and wear resistance.

After hardening at 1323K, the specimens were tempered at several temperatures from 673-873K. The relationships between macro-hardness, micro-hardness and tempering temperature for 3, 5 and 7.6%Mo specimens are respectively shown as an example in Fig. 4. The hardness in as-hardened state are plotted for the comparison.

When the as-hardened specimen is tempered at 673K, the hardness drops greatly from that in the as-hardened state. After that, the hardness begins to rise to the maximum value and then, lowers over a certain tempering temperature. In other words, the tempered hardness curve shows an evident secondary hardening. It is believed that this deviation of hardness is related to the phase transformation of matrix. The first increase of hardness is due to the precipitation of secondary carbides from austenite during tempering and the rest of austenite transforms to martensite during post cooling. Additionally, a decrease in austenite is one reason. The mutual relationship between an increase in martensite and a decrease in retained austenite as well as the precipitation of secondary carbides determine the hardness. From each tempered hardness curve, the maximum tempered hardness ($H_{Tmax}$) is obtained when the test piece was tempered at 798K. After the $H_{Tmax}$ was obtained, the hardness decreases remarkably due to the over-tempering.

The $H_{Tmax}$ values of all the specimens were related to the Mo content and they are shown in Fig. 5. The $H_{Tmax}$ of macro- and micro-hardness increases gradually as the Mo content increases. The maximum $H_{Tmax}$ value, 910 HV30, was obtained in the specimen with 5% Mo. The $H_{Tmax}$ values increase up to 4.98%Mo is due to an increase in eutectic Mo carbide as well as that of Mo content in austenite which promotes more precipitation of Mo carbides during tempering. In addition, the decomposition of austenite to martensite during tempering also improved hardness as well. A paper reported that the precipitated secondary carbides in the tempered state are mainly MC and $M_6C$ types [9]. The carbides formed by carbide reaction in tempering can be expressed as following example for Mo;[9]

$$Martensite(Fe,Mo,C) \rightarrow M(FeMo)_{2\text{-}3}C \rightarrow M(FeMo)_6C \rightarrow Mo_6C \text{ at around } 773K$$

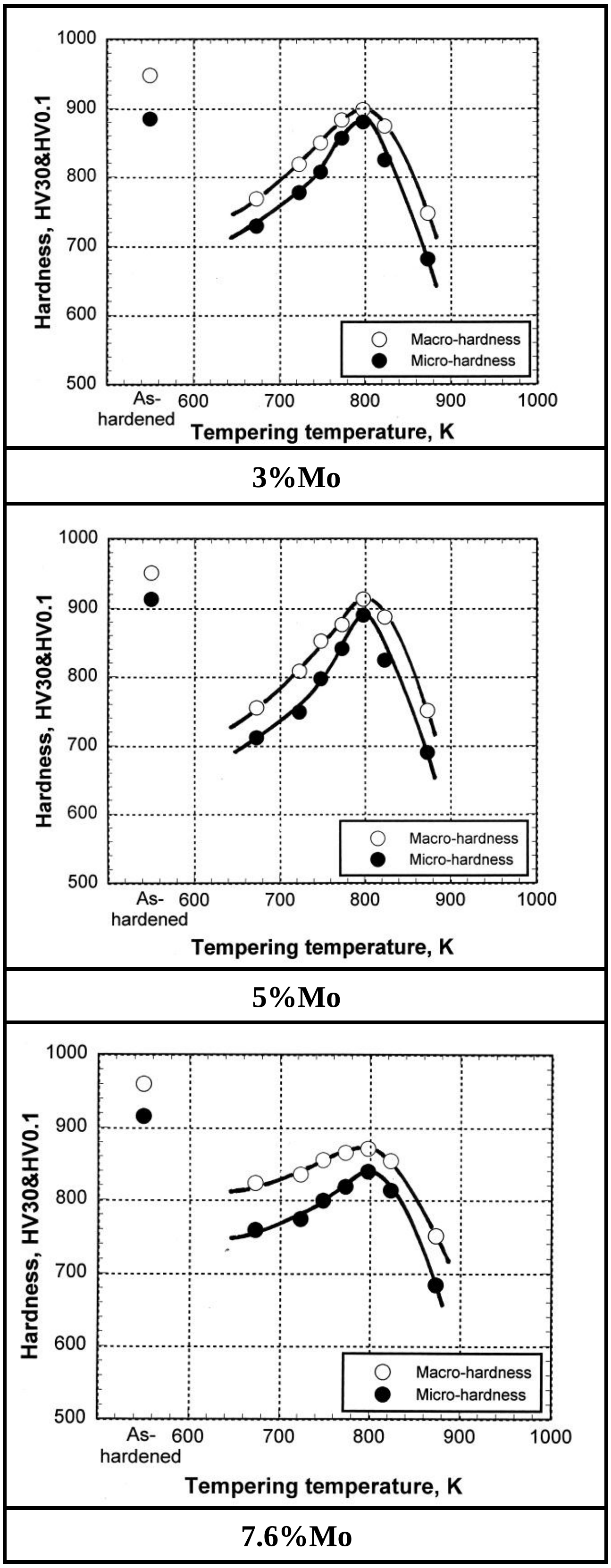


**Fig. 4:** Relationship between macro-hardness, micro-hardness and tempering temperature of 3, 5 and 7.5%Mo specimens

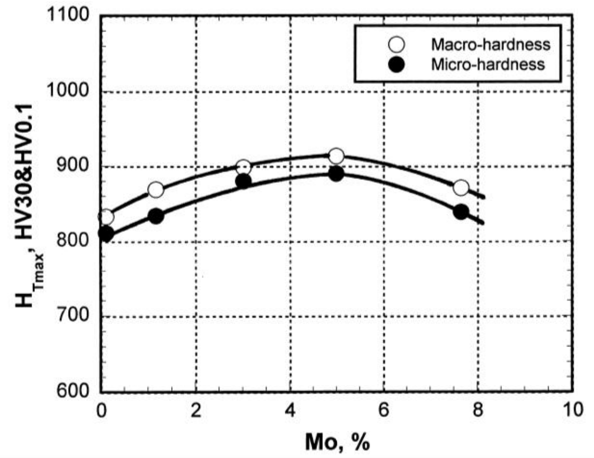


**Fig. 5:** Effect of Mo content on $H_{Tmax}$ of specimens

However, the $M_2C$ carbides could precipitate secondarily in the same manner in the specimen with high Mo content such as 7.66%. The pure carbides that are usually obtained by a carbide reaction at a high tempering temperature have extremely high hardness, such as carbides, which promoted the secondary hardening greatly. In the case of the 7.66% Mo specimen, the large mass of carbides produced by the cohering of the fine carbides could lower the matrix hardness. A decrease in the hardness of the martensite was also caused by a reduction in the C in the austenite. From Fig. 5, it can be said that the addition of 3-6% Mo is necessary to obtain the hardness over 900 HV30 by tempering.

## 4. Conclusions

The effect of Mo content on hardness of heat-treated multi-alloyed white cast iron with varying Mo content from 0 to 7.5% was investigated. After annealing, the specimens were austenitized at 1373K and then tempered at 673 - 873K. The correlations among hardness, tempering temperature and Mo content were clarified. The results are summarized as follows:

1. The macro- and micro-hardness in as-hardened state increased progressively as Mo content increased.

2. In tempered state, hardness curves showed an evident secondary hardening due to the precipitation of secondary carbides and the transformation of retained austenite to martensite.

3. The maximum tempered hardness ($H_{Tmax}$) was achieved in the specimens tempered at 798K. The $H_{Tmax}$ increased gradually as Mo content rose.

4. The highest value of $H_{Tmax}$, 910 HV30, was obtained in the specimen with 5%Mo.

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