# As-Quenched Martensite with Precipitation Hardening

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### Abstract

The hardness of martensite depends on the content of the interstitial element carbon and not on the substitutional elements such as Mn and Ni which do not raise the hardness of the martensite although these elements enhance the hardenability and promote the formation of martensite in quenching. This article reports the contribution of the heat treatment condition to hardness in quenching based on Fe-C-Ni-Mo steels. As a result of the research, there is a case in which Ni and Mo exert influence on the hardness of the microstructure by the combination of precipitation strengthening and as-quenched martensite.

#### 1. Introduction

In the transformation from austenite ( $\gamma$  phase) to ferrite ( $\alpha$  phase), the mechanisms of transformation, diffusional or displacive, have been clarified based on the transformation temperature and kinetics, while various phenomena in the transformation from  $\alpha$  to  $\gamma$  have also been clarified <sup>1-4</sup>). M. Lacoude et al.<sup>5</sup> and I. N. Kindin et al.<sup>6</sup> report that the transformation from  $\alpha$  to  $\gamma$  takes place by the displacive mechanism at the beginning of the transformation where the  $\gamma$  phase with a number of lattice defects is formed, then "recrystallized" immediately to the  $\gamma$  phase having less lattice defects. As a phenomenon that explains this  $\alpha$  phase to  $\gamma$  phase transformation mechanism, there is a report that in the case of maraging steel, the hardness of martensite austenitized at a lower temperature and then quenched becomes higher than that of the martensite austenitized at a higher temperature and then quenched<sup>7</sup>.

Although the effect of aging treatment after quenching is involved, the 18Ni maraging steel shows the highest hardness when the steel is austenitized around 800°C and then quenched. It is considered that martensite inherited the dislocation density of the  $\gamma$  phase formed by the displacive reverse transformation by being austenitized in the unrecrystallized region of the  $\gamma$  phase<sup>7)</sup>. According to researches on maraging steel, the addition of B or the like is reported to enhance the formation of such martensite<sup>8)</sup>. The compounds of Nb and B expand the unrecrystallized region of austenite with their pinning effect.

In low-carbon steels, although displacive transformation does not take place in the transformation from  $\alpha$  to  $\gamma$ , increasing the carbon content is an effective method of raising martensite hardness<sup>9</sup>. Regarding the hardness of martensite, in Mo-bearing steel, secondary hardening<sup>10</sup> is developed by separate precipitation<sup>11, 12</sup> from cementite. Such precipitates dissolve when the steel is heated up to the  $\gamma$  region. However, the diffusion velocity of elements becomes smaller when the  $\alpha$  to  $\gamma$  transformation temperature is lowered. Therefore, in low carbon steels with lower  $A_{c3}$  temperature, there is a possibility of the appearance of another hidden phenomenon superimposed on  $\alpha$  to  $\gamma$  transformation. In this report, the  $\alpha$  to  $\gamma$  transformation metallurgy of the steel bearing Ni and Mo that are effective for improving hardenability and precipitation strengthening is studied.

#### 2. Experiment Method

# 2.1 Chemical compositions of sample steels and condition of processing to sheet plate

In this research, lowering the  $A_{c3}$  temperature of the sample steels was considered. Ni that lowers the A<sub>c3</sub> temperature as well as Mn was used in the research. Ni of 6-10% was added to Fe-Mo-C to form the alloy system. Nb of 0.03% was added to some of the sample steels. All the sample steels were produced by the 50kg high-frequency vacuum furnace installed in our research laboratory. The chemical compositions of the sample steels are shown in Table 1. All of the 50 kg round-shaped cast ingots of sample steels were held at 1150°C for two hours and then hot-forged at a temperature above 1000°C to blocks with a thickness of 50 mm. The blocks underwent homogenizing treatment at 1200°C for 48 hours and then were cooled to room temperature. Thereafter, the blocks were reheated up to 1150°C within one hour and hot-rolled to steel plates of 15 mm in thickness and then air-cooled to room temperature. The air-cooling rate at the surface point was approximately 1°C/s. Small size specimens (diameter 8 mm × height 12 mm) were taken from the rolled plates for the Thermomechanical Simulator Formastor-F of

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С	Si	Mn	Р	S	Ni	Cr	Мо	Sol.Al	Ν
0.10	0.034	< 0.001	0.005	0.005	6.12	0.16	0.02	0.004	0.0006
0.10	0.031	< 0.001	0.004	0.005	6.09	0.15	0.51	0.016	0.0010
0.10	0.024	< 0.001	0.005	0.006	6.18	0.15	1.02	0.015	0.0006
0.10	0.036	< 0.001	0.005	0.005	7.97	0.14	0.02	0.012	0.0005
0.10	0.030	< 0.001	0.005	0.005	8.14	0.14	0.33	0.018	0.0007
0.10	0.025	< 0.001	0.004	0.005	8.12	0.18	0.75	0.015	0.0010
0.003	0.026	< 0.001	0.005	0.006	8.04	0.15	0.49	0.001	0.0008
0.04	0.027	< 0.001	0.005	0.005	8.07	0.15	0.48	0.002	0.0009
0.23	0.035	< 0.001	0.004	0.006	7.88	0.14	0.24	0.013	0.0007
0.10	0.032	< 0.001	0.006	0.005	9.92	0.16	0.02	0.018	0.0006
0.10	0.027	< 0.001	0.005	0.006	10.05	0.16	0.59	0.014	0.0005
0.10	0.024	< 0.001	0.004	0.004	10.05	0.17	0.87	0.011	0.0006
0.002	0.026	< 0.001	0.005	0.006	10.06	0.16	0.50	0.002	0.0008
0.05	0.027	< 0.001	0.004	0.004	10.01	0.15	0.40	0.001	0.0006
0.20	0.029	< 0.001	0.005	0.005	9.89	0.15	0.40	0.019	0.0010

Table 1 Chemical compositions of the Fe-Ni-Mo alloy (mass%)

#### Fujidempa Kogyo. Co., Ltd.

#### 2.2 Heat treatment condition in Formastor

By using the Formastor, the specimens were heated up to various temperatures ranging from 600 to  $1\,100^{\circ}$ C at the heating rates in the range 3–30°C/s from room temperature. After being held for 2–300 seconds, the test specimens were cooled to room temperature by helium gas at the cooling rate of  $1.3^{\circ}$ C/s.

#### 2.3 Method of observation of microstructure

Observation samples were taken from the test specimens that were heat-treated in the Formastor for observation by optical microscope, scanning electron microscope (SEM), transmission electron microscope (TEM), and the replica method for the observation of precipitates. The following processing was applied to the samples for the observation by optical microscope and SEM. The sheet samples of  $1 \text{ mm} \times 6 \text{ mm} \times 12 \text{ mm}$  were polished with emery paper to 1.0 mm and 0.5 mm thickness and the observation sample surface was mirror-finished by buffing after polishing with #2000 emery paper and then nital-etched. Samples for the observation by TEM were processed in the following manner. The observation samples were polished to a thickness below 0.1 mm by wet mechanical polishing, punched to a disc of 3 mm in diameter and then electrolytic-polished by twin jets of an electrolytic solution of perchloric acid and acetic acid. Vickers hardness was measured under 1 kgf load on the observation samples for optical microscope observation.

#### 3. Experiment Result

#### 3.1 Effects of heating rate and heating temperature on the hardness of martensite

In **Fig. 1**, the quenched microstructures of (a) 0.1C-6Ni-0.5Mo steel and (b) 0.1C-10Ni-0.5Mo steel were obtained when the steels were heated up to 850°C in the  $\gamma$  phase region at the heating rate of 3°C/s, held at 850°C for 300 seconds and then cooled to room temperature by helium gas. Both microstructures were lath martensite. In **Fig. 2**, the hardness of the respective quenched microstructures is shown. The heat treatment condition was: heating up to 850°C at the rate of 3°C/s, holding for 300 seconds and then cooling to room temperature by helium gas. The hardness of martensite depends on

the carbon content, and the value of Vickers hardness increases from about 210 to 500 when the carbon content is increased from 0.005% to 0.2%.

On the other hand, the hardness remains almost unchanged even if the Ni content is increased from 8% to 10%. Figure 2 shows the effect of the Mo content on the hardness when the steel was heated at the rate of 3°C/s. As Fig. 2 shows, the increase in Mo content exerts almost no effect on the hardness of martensite heated at the rate of 3°C)/s. **Figure 3** shows the hardness of 0.5Mo-0.1C steels obtained when they were heated up to 850°C at the rate of 3°C/s, and heated up to 850°C at the rate of 30°C/s. Figure 3 also shows the hardness of the respective steel obtained when it was heated up to (A<sub>c3</sub> temperature + about 25°C) at the heating rate of 30°C/s, where the (A<sub>c3</sub> temperature + about 25°C) was 725°C for 0.5Mo-0.1C



Fig. 1 Microstructures of as quenched specimen (a) 0.1C-6Ni-0.5Mo and (b) 0.1C-10Ni-0.5Mo



Carbon content (mass%)

Fig. 2 Hardness of quenched microstructure (heating rate: 3°C/s, holding: 300s at 850°C)



Fig. 3 Comparison of hardness of quenched microstructure (heating rate: 3°C/s, holding: 300s and heating rate: 30°C/s, holding: 2s)

10Ni steel, 750°C for 0.5Mo-0.1C-8Ni steel and 770°C for 0.5Mo-0.1C-6Ni steel. When compared with the hardness obtained with the steel at the heating rate of 3°C/s, the hardness increases when the steel is heated at the rate of 30°C/s, and that the lower the heating temperature is, the higher the hardness becomes.

In the case of heating up to 850°C at the rate of 3°C/s, increase in the hardness when the Ni content is increased from 6% to 10% is below  $\Delta$ HV10. However, in the case of heating up to 850°C or just above the A<sub>c3</sub> temperature at the heating rate of 30°C/s, hardness increases as the Ni content is increased. The effect of the Ni content on hardness is greater with the heating temperature of just above the A<sub>c3</sub> temperature than with the heating temperature of 850°C. In the case of 10Ni-0.5Mo steel, by heating the steel up to 725°C at the rate of 30°C/s, hardness increases by about  $\Delta$ HV40 from the hardness of the steel heated up to 850°C at the rate of 3°C/s.



Fig. 4 Comparison of hardness of quenched microstructure (heating rate: 3°C/s, holding: 300s and heating rate: 30°C/s, holding: 2s)

**Figure 4** shows the hardness obtained when the steel was heated up to 850°C at the rates of 3°C/s and 30°C/s. Similar to the case in Fig. 3, in the case of heating at the rate of 3°C/s, increase in hardness with respect to the Mo content is small or hardness decreases rather with the addition of 1% of Mo. This is probably due to the formation of the residual  $\gamma$  phase. However, in the case of heating at the rate of 30°C/s, hardness increases, and the higher the Mo content is, the larger the increase becomes. In the case of the addition of Mo by 1%, even though the heating temperature is the same, hardness increases by about  $\Delta$ HV35 from the hardness level in the case of heating at the rate of 3°C/s.

#### 3.2 Effect of heat treatment condition on martensite microstructure

In **Fig. 5**, results of the observation of 0.1C-10Ni-0.5Mo by scanning electron microscope (SEM) are shown. The microstructure is refined by heating at the rate of  $30^{\circ}$ C/s. It is considered that the refined prior  $\gamma$  grain contributes to the refining of martensite packets and blocks.

**Figure 6** shows the difference between the microstructures of the steel heated at the rate of 3°C/s and at the rate of 30°C/s. The microstructures were observed by transmission electron microscope (TEM). The microstructure of the steel heated at the rate of 3°C/s shows the martensite with the lath-width of about 1  $\mu$ m or less, which is the typical type lath martensite microstructure clarified in precedent researches. However, in the case of the steel heated up to just above the A<sub>c3</sub> temperature at the rate of 30°C/s, the microstructure is characterized by the disappearance of martensite packets. Nevertheless width of the martensite lath remains almost unchanged between the cases of the steel heated at the rate of 30°C/s and at the rate of 30°C/s. **Figure 7** shows the result of the measurement of the lath width. The lath width is distributed mainly in the range of 0.1–0.4  $\mu$ m and no remarkable difference is observed between the two cases of the heating rates of 3°C/s and 30°C/s.

In **Fig. 8**, the effect of the heating rate up to  $725^{\circ}$ C on hardness is shown. With 30°C/s, the hardness reached is HV420–440 while with 3°C/s, the hardness drops to HV380–400, wherein the holding time at 725°C is 2 seconds for either case. The change in hardness does not start to progress rapidly at a certain heating rate but the



Fig. 5 Microstructures of 0.1C-10Ni-0.5Mo, (a) (b) heating rate: 3°C/s, holding: 300s, (c) (d) heating rate: 30°C/s, holding: 2s

change takes place gradually. Next, in **Fig. 9**, the effect of the holding time at 725°C on hardness is shown. With the holding time of 2 seconds, hardness ranges in 420–440. However, the hardness drops to the 380–400 range with the holding time increased to 300 seconds. Similar to the case of the heating rate, hardness drops gradually as the holding time increases.

Next, the effect of heating temperature on hardness is shown (**Fig. 10**). The heating rates are  $3^{\circ}$ C/s and  $30^{\circ}$ C/s, and the holding time is 300 seconds for the former heating rate case and 2 seconds for the latter heating rate case (Fig. 10). In the case of the steel with the heating rate of  $3^{\circ}$ C/s, the hardness becomes almost constant at 380 above the A<sub>c3</sub> temperature (in the neighborhood of 700°C). However, in the case of heating at the rate of  $30^{\circ}$ C/s, the hardness remains almost constant at 420 in the range from the A<sub>c3</sub> temperature up to 900°C and maintains a constant hardness difference with respect to the case of heating at the rate of  $3^{\circ}$ C/s in the temperature range from the A<sub>c3</sub> temperature to 900°C. However, it starts to drop at 900°C or above and the hardness becomes almost equal to the



Fig. 6 Microstructures of 0.1C-10Ni-0.5Mo, (a) heating rate: 3°C/s, holding: 300s, (b) heating rate: 30°C/s, holding: 2s



Fig. 7 Comparison of lath width of microstructures ((a) (b) heating rate: 3°C/s, holding: 300s and (c) (d) heating rate: 30°C/s, holding: 2s)

hardness of the steel heated at the rate of 3°C/s at 1000°C or above.

In **Table 2**, the hardness of the steels to which additional heat treatment was applied, as well as heating up to 900°C at the heating rate of 3°C/s, holding for 300 seconds after hot-rolling and air cooling to room temperature are shown. The heat treatment conditions after additional heat treatment are: heating rate:  $3^{\circ}$ C/s,  $30^{\circ}$ C/s, heating temperature: 900°C,  $1000^{\circ}$ C,  $1100^{\circ}$ C, and holding time: 2 seconds, 10 seconds and 300 seconds followed by cooling by helium gas. In the heat treatment of heating up to 900°C after air cooling, increase in hardness is not observed after holding for either 2 seconds or 300 seconds even though cooling by helium gas was applied. No difference in hardness is observed between the steel heat-



Fig. 8 Effect of heating rate up to 725°C on the hardness of microstructure



Fig. 9 Effect of holding time at 725°C on the hardness of microstructure

ed at the heating rate of  $3^{\circ}$ C/s and the steel heated at the heating rate of  $30^{\circ}$ C/s under the heat treatment conditions of heating temperatures of 900°C-1100°C, holding times of 300 seconds and 2 seconds followed by cooling.

In **Fig. 11**, the hardness of Nb bearing 0.1C-0.5Mo steel applied with the same heat treatment condition as the one in Fig. 10 is shown. In this case, similar to the case in Fig. 10, in the range from  $A_{c3}$  temperature to the neighborhood of 900°C, the steel with the heating rate of 30°C/s maintains a constant hardness difference with respect to the steel with the heating rate of 3°C/s. The hardness of both steels becomes almost equal when the steel is heated up to 1050°C.

In Figs. 12–15, difference in the form of precipitates between the one in the martensite of the steel heated at the heating rate of  $3^{\circ}$ C/s and the one in the martensite of the steel heated at the heating rate of  $30^{\circ}$ C/s is shown.

As shown in Figs. 12 and 13, in the microstructures of the steel



Fig. 10 Effect of heating temperature on the hardness of microstructures (heating rate: 3°C/s or 30°C/s)

Table 2 Hardness of microstructure applied additional heat treatment

	20	10a	200a	
	28	105	3008	
3°C/s	402	395	397	
30°C/s	400	396	392	
	900°C	1 000°C	1100°C	
3°C/s	402	395	397	
30°C/s	400	396	392	



Fig. 11 Effect of heating temperature on the hardness of microstructures (heating rate: 3°C/s or 30°C/s)

heated at the rate of  $3^{\circ}C/s$ , precipitation of carbon nitride like Nb(C,N) is not observed. In contrast, as shown in Figs. 14 and 15, in the microstructure of the steel heated at the rate of  $30^{\circ}C/s$ , precipitate of Nb(C,N) is observed. This indicates that in the martensite of the steel heated at the rate of  $30^{\circ}C/s$  and held for 2 seconds followed by cooling by helium gas, the carbon nitride that had precipitated and had not dissolved to solid before the heating remained as it is



Fig. 12 Precipitate of the specimen heated at 3°C/s up to 850°C and holded for 300s



Fig. 13 Precipitate of the specimen heated at 3°C/s up to 850°C and holded for 300s

after quenching.

When the extent of solid-solution of metal carbon carbide is considered, the solid-solution of carbide of the MoC system to the  $\gamma$ phase is considered to take place at 900°C or above<sup>13)</sup>. This fact agrees with the following results in this report. They are: when the hardness of the steel heated at the rate of 30°C/s and the hardness of the steel heated at the heating rate of 3°C/s are compared, constant difference in the hardness between the two steels is observed in the heating temperature range up to 900°C. In contrast, the hardness of each of the two steels almost agrees with that of each other at 1000°C or above. Namely, since fine carbon nitrides such as those of Mo and Nb had already precipitated before heating and since they are rapidly cooled by helium gas while they exist in a nonequilibrium state in the heat treatment condition of heating at the rate of 30°C/s, held for 2 seconds and then cooled by helium gas, both effects of precipitation strengthening by such carbon nitrides and strengthening by as-quenched martensite are superimposed. These carbon nitrides dissolve to the  $\gamma$  phase by being heated up to 1000°C or above, eliminating the precipitation strengthening capability.

In low-carbon low-alloy steels, as the  $A_{c3}$  temperature is higher than that of steels studied in this research and the dissolution of carbon nitrides is promoted by heating up to the  $\gamma$  region, it is considered that although the condition of superimposition of the effects of precipitation strengthening in a nonequilibrium state and strengthening by as-quenched martensite is limited, superimposition of such strengthening emerges when the  $A_{c3}$  temperature becomes lower.

#### 4. Conclusion

In the quenched martensite obtained by heating up to the  $\gamma$  region at the heating rate of 3°C/s, holding for 300 seconds and then cooling by helium gas, hardness depends on the carbon content and does not depend on the contents of added Ni, Mo, etc. On the other hand, the hardness of the martensite obtained by heating up to the  $\gamma$  region at the heating rate of 30°C/s, holding for 2 seconds and then cooling by helium gas becomes higher by about  $\Delta$ HV30 than the hardness of the former microstructure. The hardness increases as the



Fig. 14 Precipitate of the specimen heated at 30°C/s up to 850°C and holded for 2s



Fig. 15 Precipitate of the specimen heated at 30°C/s up to 850°C and holded for 2s

Ni and Mo contents increase. The microstructure thus obtained is lath martensite and, as compared with that of the steel heated up to the  $A_{c3}$  temperature or above at the heating rate of 3°C/s, held for 300 seconds and then cooled by helium gas, packets of the martensite are refined owing to the previous fine  $\gamma$  grain size. However, no difference in lath width or dislocation density is observed. The hardness of the microstructure of the quenched steel becomes lower gradually as the heating rate becomes lower and the holding time is increased, and has come to agree with the martensite hardness that is already known. Therefore, since the  $A_{c3}$  temperatures of specimens used in this research are low, fine undissolved precipitates are considered to remain in the specimens even after the transformation from  $\alpha$  to  $\gamma$  and thus, superimposition of the effects of quenched martensite and precipitation strengthening is observed.

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