1. Introduction

Lath martensite is the most important structure in high-strength structural steels. The strength of lath martensite is contributed by several strengthening mechanisms, i.e., fine-grain strengthening, dislocation strengthening, solid solution strengthening, and particle dispersion strengthening. When lath martensite is tempered below A1 temperature to improve ductility and toughness, supersaturated carbon precipitates as carbides (cementite) which contribute to dispersion strengthening whereas solid solution strengthening diminishes. In the tempering at higher temperatures, martensite structure recovers to reduce its dislocation density and cementite coarsens rapidly, resulting in remarkable softening. It is necessary to obtain uniform distribution of fine cementite for establishment of high strength and toughness by tempering. Kawasaki et al. reported that the application of induction heating with a rapid heating rate (100 K/s or 1 000 K/s) is effective for the improvement of strengthening and cementite dispersion. TEM observation has revealed that finer cementite is dispersed more uniformly in the rapidly heated specimen than in the slowly heated specimen. It is considered that the temperature where cementite precipitation starts is raised by increasing the heating rate to tempering temperature, resulting in a higher nucleation rate and a finer dispersion of cementite.

KEY WORDS: steel; martensite; precipitation; recovery; tempering; rapid heating; cementite; dislocation; strength; ductility.

2. Experimental Procedure

An alloy steel for machine structural use (SCM435: Fe–0.35C–0.24Si–0.77Mn–1.05Cr–0.17Mo (mass%)) was used in the present study. After austenitized at 1 123 K for 1.8 ks and quenched into oil, the specimens with full lath martensite structure were tempered at various temperatures in a range of 723–923 K for periods up to 3.6 ks using an infrared furnace. Heating rate to the tempering temperature was set to be 100 K/s or 1 000 K/s (hereafter rapid heating) or 2 K/s (hereafter slow heating). It should be mentioned that, for the specimen rapidly heated and held at a tempering temperature for some periods, there was some overshooting (about 20 K) of the specimen temperature during heating although it decreases to the tempering temperature originally set within 10–20 s. Also, induction-heating was performed to establish a rapid heating rate of 1 000 K/s.

Microstructure observation was performed by means of SEM (scanning electron microscopy) and TEM (transmission electron microscopy). Cementite size was measured from transmission electron micrographs. Dislocation density was measured by a line-intersection analysis. The number of dislocations was counted along a line intersecting a cementite particle.
ber of dislocations, \( N \), intersecting a given straight line of the length \( L \) was counted on the TEM micrograph taken in the two-beam diffracting condition for \( g = 002 \) or \( 004 \) in which all the \( a(111)_a \) dislocations in lath martensite should be visible. The average dislocation density \( \rho \) was calculated by the following Eq. (1).

\[
\rho = \frac{2 \sum N_i}{\sum L_i t} \quad \text{(1)}
\]

Local thickness of the thin foil, \( t \), is necessary for the measurement of dislocation density. It was determined using a convergent beam electron diffraction technique. The two-beam diffracting condition necessary for the measurement was the same as the imaging condition for observation of dislocations. Those procedures are already described in the previous study on the dislocation density of lath martensite in Fe–C alloys.

Vickers hardness measurement with a load of 9.8 N was conducted on the tempered specimens. Tensile properties were measured for the tempered specimens, of which gauge size is 2.5 mm × 8.5 mm × 0.5 mm, at an initial strain rate of \( 2.0 \times 10^{-3} \text{s}^{-1} \).

3. Results

3.1. Effect of Heating Rate on the Microstructure of Tempered Martensite

Figure 1 schematically shows various nucleation sites of cementite in a lath martensite structure during tempering. Lath martensite structure contains various kinds of grain boundaries, such as prior austenite grain boundaries, packet boundaries, block boundaries (all high-angle boundaries) and lath boundaries (low-angle boundaries). Those boundaries, as well as dislocations within laths, act as nucleation sites of cementite during tempering. Figure 2 shows the SEM microstructures of the specimens tempered for 0 s at 923 K. Cementite precipitates at various nucleation sites described in Fig. 1. The comparison between the specimens heated at 2 K/s (Fig. 2(a)) and at 100 K/s (Fig. 2(b)) shows that cementite dispersion is finer for a larger heating rate. In order to examine quantitatively the variation of cementite size with the heating rate in relation with the precipitation site in lath martensite, TEM observation was performed.

Figure 3 shows transmission electron micrographs of the specimens tempered at 823 K for 0 s at heating rates of (a) 2 K/s, (b) 100 K/s, and (c) 1000 K/s. Cementite precipitates in needle-shape within lath and at lath boundary. The dispersion of cementite is finer when the specimen is heated to the tempering temperature at a more rapid heating rate. The transmission electron micrographs in Fig. 4 show that cementite also precipitates at high-angle boundaries in the lath martensite structure. Those cementite precipitates are roughly in disc-shape and grow preferentially along the boundary plane. It is clear that cementite precipitates on the high-angle boundaries are refined by rapid heating and tempering.

Figures 5 and 6 show the size distribution of cementite in the specimens tempered for 0 s at 923 K and 823 K, respectively. The diameter of needle-shaped cementite within lath and at lath boundaries (low-angle boundaries) and the thickness of cementite discs at high-angle boundaries were measured in order to compare the cementite sizes quantitatively. In each of Figs. 5 and 6, cementite size is finer within laths and at lath boundaries than at high-angle boundaries. Comparison between Figs. 5 and 6 reveals that cementite precipitates are finer at 823 K than 923 K. Cementite size within lath in the rapidly heated specimen is distributed in finer sizes as heating rate is increased (see Figs. 5(a) to 5(c) or Figs. 6(a) to 6(c)). At high-angle boundaries, the number of coarse cementite particles is much less in the rapidly heated specimen (Figs. 5(e) and 5(f), or Figs. 6(e) and 6(f)) than in the slowly heated specimen (Fig. 5(d) or Fig. 6(d)). In the rapidly heated specimen, the size distribution of cementite is relatively similar for two distinctive precipitation sites, i.e., high-angle boundary and lath boundary/within lath. The results described above indicate that cementite dispersion becomes finer and more
uniform by employing rapid heating and tempering.

The refinement of cementite becomes less obvious as tempering proceeds. Figure 7 shows the size distribution of cementite in the specimens heated at different heating rates and tempered for 3.6 ks at 923 K. Cementite precipitates are clearly larger in comparison with the early stage of tempering shown in Fig. 5. However, the comparison between the specimens heated at 2 K/s (Fig. 7(a)) and at 100 K/s (Fig. 7(b)) shows that the difference in cementite size is small.

During high-temperature tempering, the dislocation structure within lath undergo recovery, resulting in the decrease of dislocation density. TEM micrographs in Fig. 8 show the dislocation substructure within martensite lath in the as-quenched specimen and the tempered specimens heated at different heating rates. In the as-quenched specimen, dislocations are distributed, more or less, uniformly. By tempering, dislocations tend to form networks by recovery although recovery seems to be more extensive in the slowly heated specimens. Figure 9 shows the variation of dislocation densities of lath martensite in the specimens as-quenched and tempered. In the as-quenched specimen, dislocation density is as high as $10^{15}$ m$^{-2}$. During tempering, dislocation density in lath martensite decreases and higher densities of dislocations are observed in the rapidly heated specimens than in the slowly heated specimens in the same tempering condition.

3.2. Effect of Heating Rate on the Mechanical Property of Tempered Specimens

Figure 10(a) shows the Vickers hardness of specimens tempered at 823 K and 923 K for various periods up to 3.6 ks with different heating rates. Hardness of the as-quenched specimen is HV570. The hardness of specimens is decreased with an increase in tempering temperature or tempering time. When a specimen is tempered at the same temperature for a shorter time, hardness of the rapidly heated specimen is larger than that of the slowly heated specimen. However, when a specimen is held at a higher tempering temperature for a longer time, the effect of heating rate becomes smaller. Figure 10(b) shows the strength–ductility balance of the specimens tempered at 723–923 K for 0 s with different heating rates. At 923 K, elongation remains nearly constant although strength increases with heating rate. For the tempering at 823 K and 723 K, both of strength and elongation are higher in the rapidly heated specimens. When comparison is made for the same strength level, better ductility seems to be established by rapid heating and tempering.
tempering.

4. Discussion

4.1. Effect of Rapid Heating and Tempering on the Precipitation Kinetics of Cementite

The presence of cementite precipitate in the specimens heated and immediately quenched without holding at the tempering temperature indicates that nucleation and growth of cementite occurs during heating. When there is some incubation time for cementite precipitation to start, the temperature at which cementite nucleates should be different during heating depending upon heating rate. In the following, the nucleation kinetics of cementite on defects in lath martensite structure was examined.

For the nucleation of cementite at a high-angle boundary, the formation of a classical double spherical cap nucleus on the planar boundary was assumed. In such a case, the activation energy for nucleation is described as follows;

\[
\Delta G_{\text{GB}} = \Delta G_{\text{hom}} \cdot f(\phi) \tag{2}
\]

\[
\Delta G_{\text{hom}} (= 16\pi \sigma_{\text{c}}^2/3 \Delta G_s^2) \] is the activation energy for the homogeneous nucleation of spherical cementite and the shape factor \( f(\phi) \) is a function of the wetting angle \( \phi \) as follows;

\[
f(\phi) = (2 + \cos \phi)(1 - \cos \phi)^2/4 \tag{3}
\]

where \( \Delta G_s \) is a driving force for nucleation of cementite, \( \cos \phi = 2\sigma_{\text{c}}\sigma_{\text{c}}/\sigma_{\text{c-f}} \) and \( \sigma_{\text{f-c}}, \sigma_{\text{gb}} \) are the ferrite (i.e. martensite) grain boundary and ferrite/cementite interphase boundary energies, respectively. The steady state nucleation rate can be given by the following equation:

\[
J_{\text{GB}}^* = N_{\text{GB}}^* \beta_{\text{GB}}^* \cdot \exp \left( - \frac{\Delta G_{\text{GB}}^*}{kT} \right) \tag{4}
\]
Where \( Z \) is a non-equilibrium Zeldovich factor, \( \beta^* \) is a rate of atomic attachment at the ferrite/cementite interphase boundary when cementite nucleates on dislocations in martensite, the stress field around the dislocation interacts with a nucleus of cementite. For simplicity, it is assumed that the strain energy around the dislocation in ferrite decreases in the volume transformed by following Cahn.\(^{10}\) For the formation of a cylindrical embryo of radius \( r \) around a straight screw dislocation, the free energy change per unit length of the embryo is given as follows:

\[
\Delta G_{\text{dis}} = 2\pi r \sigma_{\text{coh}} + \pi r^2 \Delta G_v - A \left\{ \ln \left( \frac{r}{r_0} \right) - 1 \right\} \quad \ldots (5)
\]

where \( r \) is the distance from the dislocation line, \( r_0 \) is the radius of dislocation core. The constant \( A \) is equal to \( \mu b^2 / 4\pi \) where \( \mu \), \( b \) and \( \nu \) are the shear modulus, the magnitude of the Burgers vector and the Poisson’s ratio of ferrite, respectively. When the parameter \( a = (2\Delta G_v / \sigma_{\text{coh}}^2) < 1 \), the activation barrier for nucleation; \( \Delta G_{\text{dis}}^* \) exists as the minimum free energy change for local bulging of a metastable cylindrical embryo. The detail is described in the previous study.\(^{11}\) Then, the steady state nucleation rate on the dislocation was calculated by the following equation.\(^{12}\)

\[
J^*_{\text{dis}} = N_v^{1/3} \cdot \rho \cdot \beta^* \cdot \exp \left( - \frac{\Delta G_{\text{dis}}^*}{kT} \right) \quad \ldots (6)
\]

For both calculations, the driving force for cementite nucleation in an Fe-0.35 mass%\%C binary alloy was used. The dislocation density \( \rho \) was taken as \( 10^{15} \text{m}^{-2} \). It was assumed that nucleation kinetics is controlled by volume diffusion.

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**Fig. 8.** TEM micrographs showing the dislocation structures in the specimens tempered for 0 s at 923 K; (a) as-quenched, (b) heated by 2 K/s and (c) 100 K/s, respectively.

**Fig. 9.** Dislocation density in lath martensite in the specimens tempered for 0 s.

**Fig. 10.** (a) Vickers hardness and (b) tensile properties of the tempered specimens.
Rapid heating affects the dislocation density in connection to cementite dispersion in the following manners: (1) Density of dislocations as nucleation site is higher because annealing is shorter for rapid heating, resulting in finer cementite dispersion: (2) Fine and dense cementite precipitation on dislocations for rapid heating retards the annihilation of dislocations by recovery. Thus, the effect of rapid heating and tempering on dislocation density should be complex.

4.2. Examination of Tempering Parameter for Rapid Heating and Tempering Process

It is widely known that tempering parameter ($P$) proposed by Hollomon and Jaffe\(^{15}\) is closely related to the mechanical properties of the tempered specimens, such as hardness. This parameter $P$ for the conventional tempering is given as follows;

$$P = T \cdot (\log(t/3 600) + C)$$

where $T$ is tempering temperature (K), $t$ is tempering time (s) and $C$ is constant ($=21.3–5.8\times$(mass\%C)). This kind of parameters cannot be used in cases of different heating rates even for the same combination of tempering temperature and time. There are some attempts to deduce a tempering parameter applicable for temperature cycles.\(^16,17\) In the following, we examine if those parameters are applicable to the microstructure and property changes obtained during the rapid heating and tempering.

Inoue\(^16\) (as well as Tsuchiyama\(^17\)) described that the tempering parameter $P$ physically means the activation energy of the reaction taking place during tempering. The form of the Eq. (7) shows that this activation energy is also dependant in the tempering temperature and thus, does not have a physical meaning. He proposed a new tempering parameter using a constant activation energy applicable to the continuous heating process given as follows:

$$I = \int \left( \log t - \frac{Q}{2.3RT} + 50 \right) dt$$

He made a recursion analysis to determine the value of $Q$ for a series of structural steels which describes strength and hardness experimentally measured well.

On the other hand, Tsuchiyama\(^17\) proposed the additive rules for time during the tempering cycle to reach an arbitrary value of the tempering parameter by Hollomon and Jaffe. According to him, when the heating cycle was fine steps of isothermal holding for short periods, the tempering parameter after $n$-th steps can be given by as follows;

$$P_n = T_n(\log t_n + 20)$$

where $t_n=10^{5T_n/T_1} (\log t_n + 20) + \Delta T$, $t_1=\Delta t$, $T_n = T_{n-1} + \alpha \Delta t$, $T_1$ is starting temperature of the heating cycle and $\alpha$ is the heating or cooling rate at the temperature $T_{n-1}$.

Here we simply take the derivative of the tempering parameter $P$ with respect to time and try to analyze the tempering behavior in the rapid heating and tempering. When a specimen is heated at a constant heating rate $dT/dt$ (K/s), temperature $T$ (K) changes linearly with time $t$ (s) as $T=273+(dT/dt) \cdot t$. Thus, by integrating the derivative of the parameter $P$ with respect to time ($i.e. dP/dt$), the para-
meter during heating $P_1$ can be expressed as follows.

$$\frac{dP_1}{dt} = \frac{dT}{dt} (\log t + C) + \frac{1}{\ln 10} \left( \frac{dT}{dt} + \frac{273}{t} \right) \quad \ldots \ldots \ldots (10)$$

Integration with respect to time was performed between $t_0$ (the time when temperature reaches to room temperature (293 K) from 273 K) and $t_1$ (the time when temperature reaches to the tempering temperature). Then, by adding the contribution for isothermal tempering, the modified parameter $P'$ is given as follows:

$$P' = T \cdot \log (t_h/t_i) \quad \ldots \ldots \ldots \ldots (12)$$

where $t_i$ is the holding time and $t_h$ is the tempering time which is required to achieve the parameter $P_1$ at the final tempering temperature.

Figure 13 shows the relationships between the Vickers hardness of the specimens tempered at 923 K and 823 K and the three different parameters described above. Each of the parameters has a reasonably good linear correlation with the hardness when there are some isothermal holding at the final tempering temperature. However, when there is no isothermal holding (i.e., $t_i = 0$ in the Eq. (12)), significant deviation from the straight line can be seen. Thus, any of these tempering parameters is not so useful to predict the mechanical property in rapid heating and tempering.

This deviation might be caused by the following reason. The experimental data used for deduction of the parameters is not suitable for application to tempering during heating. In early stage of tempering, the actual rate controlling process in tempering behavior changes in complex manners. Inoue$^{16}$ mentioned that the activation energy deduced from the tempering experiment at tempering temperatures between 723 K and 973 K for tempering periods between 0.01 and 1 000 h was close to that of self diffusion of iron in ferrite. Since it is expected that the rate controlling process of cementite precipitation during heating would be carbon diffusion in ferrite, it is considered that a large deviation in Fig. 13(a) is naturally obtained for 0 s tempering. Also, the empirical Eq. (7) was deduced from the properties of the isothermally tempered specimens for various periods at various tempering temperature for a wide variety of carbon steels with different carbon contents. It should be mentioned that the correlation between hardness and tempering parameter is not so good for a smaller value of the tempering parameter, i.e., a shorter tempering period or a lower tempering temperature, especially for medium and high carbon steels in the original paper by Hollomon and Jaffe. Thus, application of the Eq. (7) would not be so successful even if it was used in some derivative forms like $P_n$ and $P'/H_{11032}$. Thus, it is concluded that new tempering parameters should be proposed by deducing appropriate parameters in order to describe the rapid heating and tempering behavior.

Tables 1 and 2 show the microstructures and the properties of the tempered specimens, respectively, with the tempering parameter $P_n$ proposed by Tsuchiyama$^{17}$ which shows somewhat better correlation with the hardness in Fig. 13. Strength and hardness seem to have better correlation with the tempering parameter whereas correlation is poor for ductility. For microstructure, rapid heating and tempering corresponds to a smaller value of the tempering parameter, a smaller cementite size, and a higher dislocation
density at the same tempering temperature. However, there seems no unique tendency when the tempering temperature is different. It is concluded that cementite precipitates at high-angle boundaries in lath martensite structure are refined by rapid heating and tempering even for the same strength level. Since voids or cracks are preferentially formed at high-angle boundaries, the refinement of cementite at such sites should result in the improvement of ductility/toughness. It should be emphasized that the rapid heating and tempering achieves favorable microstructure and property which are not predicted in the ordinary (slow heating) tempering.

5. Conclusions

The effect of heating rate to the tempering temperature on the microstructure and property of lath martensite tempered at a temperature range between 723 and 923 K for periods up to 3.6 ks was studied. Cementite forms at both high-angle grain boundaries and dislocations. Cementite dispersion is finer and more uniform in the rapidly heated and tempered specimen (the heating rates are 100 K/s and 1000 K/s) than in the slowly heated and tempered specimen (the heating rate is 2 K/s). It is considered that increase of the heating rate to the tempering temperature leads to a higher nucleation rate and a finer dispersion of cementite. The application of rapid heating and tempering contributes to the improvement of strength–ductility balance.

Acknowledgements

The financial support of the Iron and Steel Institute of Japan through the Program for Strategic Research Projects (1999–2001) is gratefully acknowledged. The authors gratefully appreciate to Dr. Kazuhiro Kawasaki (Neturen Co. Ltd.) for allowing us to conduct induction-heating tempering experiments and to Prof. Toshihiro Tsuchiyama (Kyushu University) and Mr. Goro Miyamoto (Graduate student, Kyoto University) for stimulating discussions and valuable comments.

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