

Original Paper

Estimation for Hardness of Tempered Steels

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Hardness of tempered steels was investigated for five types of low alloy steels, including high strength steels and ferritic heat resisting steels. Tempering was carried out by two different ways; the quenched specimen was held at a constant temperature, and it was subjected to a rising temperature with a given heating rate. Hardness of tempered steel is a function of the tempering parameter including temperature and time. In this paper, three parameters were employed for three tempering processes of 1) decomposing martensite, 2) delaying softening by the alloy elements and 3) secondary hardening by precipitating fine carbides, such as Mo_2C and V_4C_3 . Although these parameters have the similar form of the conventional tempering parameter, λ , three different values of activation energies were employed for three processes. The changes of hardness brought by three processes were expressed by the functions of a linear, logistiquè and Gaussian distribution, respectively. The measured hardness could be approximated by the total of three functions.

Key words: Tempering, Hardness, low alloy steel, tempering parameter, delay of softening, secondary hardening

1. Introduction

It is one of the most important problems to clarify the effect of temperature and time on the progress in the tempering of quenched and hardened steels, not only in the heat treatment of steel but also in the "tempering in a wide sense", such as PWHT (post weld heat treatment) and the welded structures used at elevated temperature.

Several conditions are involved in the tempering of latter case, and many experimental works will be required for confirming the relationship between those conditions and the properties of tempered materials. Experiment,

however, will be almost impossible when it simulates, for example, the condition of a boiler, which is operated more than several years.

Tempering parameter has been proposed in order to evaluate the effect of time and temperature. This parameter is appropriate to estimate the hardness of tempered plain carbon steels, because the hardness of steels is controlled mainly by the diffusion rate of carbon. For alloy steels, special carbides (carbide of alloying element) will influence the hardness, influence of which will be independent of the influences of other reactions, such as the decomposition of martensite, the precipitation and coalescence of cementite (iron carbide). Alloying elements will also influence the diffusion rate of carbon.

In this paper, the authors investigate the hardness of tempered low alloy steels, and proposed the modified method to evaluate the hardness by the tempering parameters.

2. Experimental procedures

Chemical compositions of steels are listed in Table 1. S25C and S55C are plain carbon steels without any alloying elements. HT60 is 60 kgf/mm² class high strength steel, containing vanadium of 0.03%, and HT80 is 80 kgf/mm² class high strength steel, containing chromium, molybdenum and vanadium, as the carbide forming elements. Ferritic heat resisting steels, 1/2Mo, 1Cr-1/2Mo and 2 1/4Cr-1Mo contain only chromium and molybdenum as the alloying element.

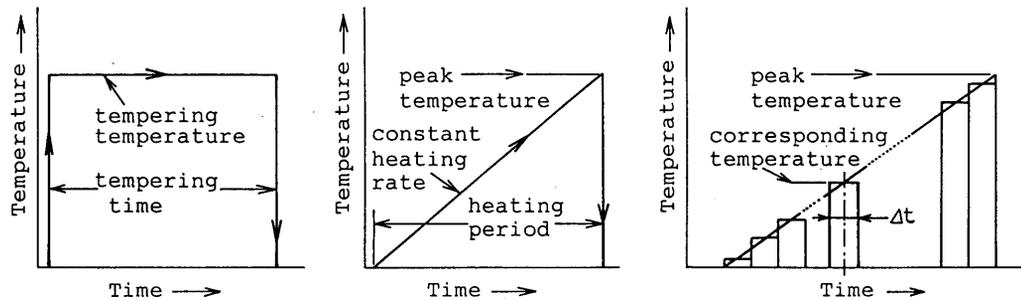
Blanks of 11 mm in diameter and 200 mm in length were machined from steel plates. They were austenized at 1225 K for 1.8 ks, and then quenched into water. The quenched specimens was judged to have fully martensitic microstructure, because their hardness agreed with that of martensite estimated from each carbon content.

Quenched specimen were tempered by two ways shown in Fig.1(a) and (b). Figure (a) shows the tempering at constant temperature. The specimen was inserted into an electric furnace, whose temperature was adjusted for tempering temperature, and held at that temperature. After passing the prescribed tempering time, the specimen was cooled rapidly by water to prevent further tempering during cooling. The ranges of the temperature and time in this experiment were 675 to 975 K and 35 to 3.5 Ms (about 40 days).

Figure (b) shows the tempering by way of raising the temperature. The specimen was heated by an electric furnace from room temperature to the peak temperature with the constant heating rate. When its temperature reached to the prescribed peak temperature, it was cooled by water. The ranges of the peak temperature and the heating rate were 725 to 975 K and 10 to 400 K/hr. The Vickers hardness (Hv) of each specimen was measured under the loading of

Table 1 Chemical compositions of steels used (wt%)

steel	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	V	B	Sol.Al
S25C	0.26	0.20	0.46	0.024	0.019	0.01	0.02	0.02	-	-	-	-
S55C	0.53	0.21	0.67	0.021	0.018	0.05	0.05	0.12	-	-	-	-
HT60	0.15	0.30	1.27	0.018	0.005	-	-	-	-	0.03	-	-
HT80	0.13	0.28	0.83	0.015	0.006	0.23	0.85	0.49	0.43	0.04	0.0012	-
1/2Mo	0.21	0.21	0.82	0.014	0.005	-	-	0.01	0.47	-	-	0.012
1Cr-1/2Mo	0.15	0.28	0.57	0.011	0.008	-	-	1.09	0.55	-	-	0.024
2 1/4Cr-1Mo	0.12	0.16	0.47	0.010	0.004	-	-	2.43	1.02	-	-	-



(a) Tempering at the constant temperature (b) Tempering at rising temperature by the constant heating rate (c) Approximation of tempering at rising temperature

Fig.1 Illustrations of heating ways for tempering

294 N for 15 second. The measurement was repeated for each specimen in five times giving an average.

3. Regression of hardness of tempered steel by the tempering parameters

Two parameters, P and λ have been proposed by J.H.Hollomon, L.D.Jaffe[1] and T.Inoue[2] to evaluate the amount of progressing tempering process at different temperature, and for different time. That is,

$$P = T(\log(t) + C) \tag{1}$$

$$\lambda = \log(t) - Q/2.3R (1/T) + 50 \tag{2}$$

Where, T and t are tempering temperature (K) and time (s). C is constant which depends on the carbon content of steel. Q is the activation energy (cal/mole K), and R is gas constant. Both parameters are derived from the Arrhenius' assumption. Although they differ in form, they have almost similar meaning in each other. For the tempering conditions in the practical heat treatment, both parameters can be employed, because there is the relationship of a straight line between them.

Q is the observed value for many fundamental processes, such as the decomposition of martensite, the precipitation and coalescence of cementite and other alloying carbides. The parameter, λ has a physical meaning as the logarithm of the amount of such reactions. For the sequence of some tempering treatments of different temperature and time, the total parameter, g can be evaluated by the additional rule as followings.

$$\lambda(\text{total}) = \log[10^{\lambda_2} + 10^{\lambda_3} + \dots] \tag{3}$$

This advantage of λ is very useful for treating the results of tempering in which the temperature is changed. Therefore, the parameter, λ is introduced in this research.

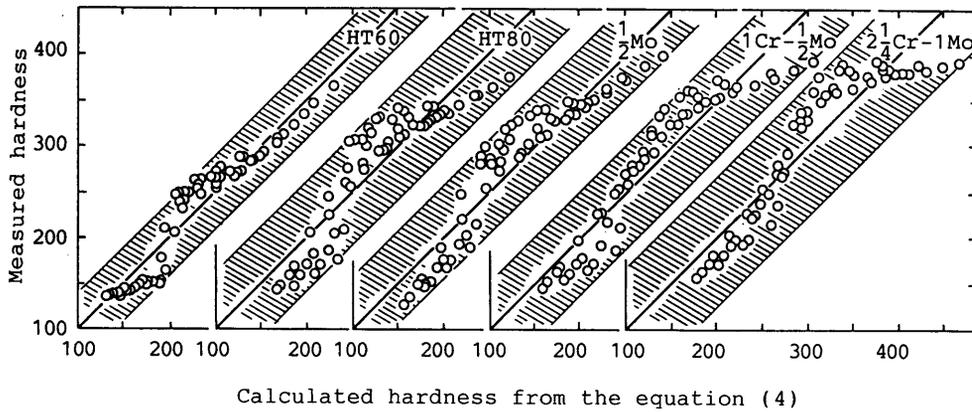


Fig.2 The measured values of tempered hardness of low alloy steels, comparing with the calculated hardness

3.1. Regression of hardness by parameter, λ

Assumed that the measured values of Hv would be approximated by the following linear equation, the value of Q in the parameter, λ was determined.

$$Hv = A \cdot TP + C = A (\log(t) + B/T) + C \quad (4)$$

where, TP is the tempering parameter. Constants, A, B and C were determined by the least squares method. In this calculation, all the authors' data of tempering at constant temperature were used. Each measured value is plotted

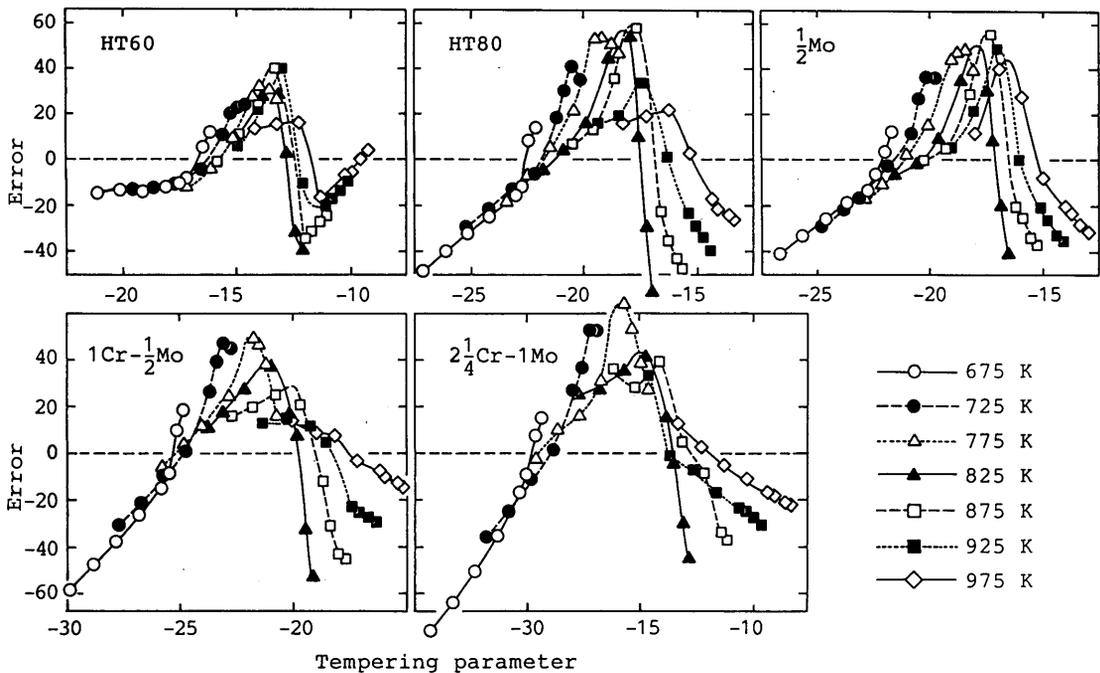


Fig.3 Errors between the measured hardness and approximated hardness obtained by the equation (4)

against each calculated one as shown in Fig.2. The width of scatter band shown by shaded zone is too large as more than one hundred for each steel. Therefore, it is judged that equation (4) does not satisfactorily approximate the hardness of tempered low alloy steels.

Fig.3 shows the error between the measured and approximated values in Fig.2. The errors in plus side become maximum at certain λ values, -23 to -13 depending on steel type. This error around the peak will be due to the secondary hardening which occurs usually in alloy steels.

The λ value which gives the peak shifts to right side (side of longer tempering time) with tempering temperature. This improper result suggests that the constant B in eq.(4) will not be appropriate for expressing the phenomenon of secondary hardening.

3.2.Three processes in tempering

Fig.4 shows the measured hardness of tempered HT80 steel against the logarithm of tempering time. The plots of circular mark lie on a straight line for each temperature. These lines were obtained by the tempering of lower temperature and shorter time, and have the same inclinations as the case of plain carbon steels. The plots of triangular mark indicate the hardness brought by the secondary hardening. The time at which the peak hardness is attained increases with a falling temperature. The secondary hardening appears only in the specified range of tempering, and disappears by the further tempering. The plots of solid circular mark indicate the sudden softening. This phenomenon will be due to the fact that alloying elements lose their effect of preventing the softening.

As mentioned above, there are three processes in the tempering. Therefore, the authors propose the following equation to express the hardness of tempered steel.

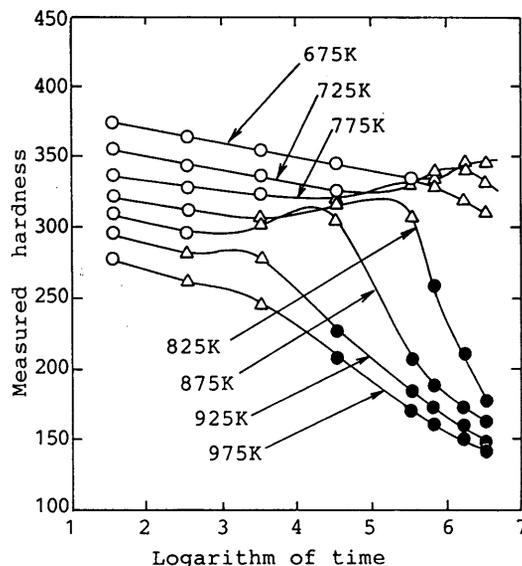


Fig.4 Measured hardness of tempered HT80 steel plotted against the logarithm of tempering time

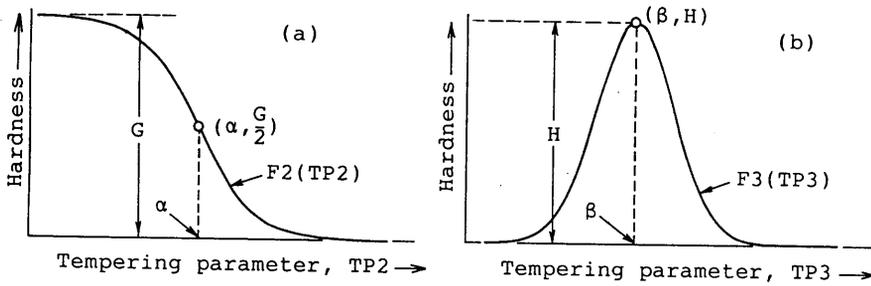


Fig.5 Illustrations of the logistic function, F2 and Gauss distribution, F3

$$H_v = F_1(TP_1) + F_2(TP_2) + F_3(TP_3) \quad (5)$$

where, the functions of F_1 , F_2 and F_3 concern to the three independent processes of the ordinary softening, the delay of softening by alloying elements and the secondary hardening by precipitation of alloy carbides. TP_1 , TP_2 and TP_3 are the tempering parameters corresponding to three processes, respectively. The tempering parameters have the same form as eq.(2), but the constant, B is not identical for three processes.

$$TP_1 = \log(t) + B_1/T, \quad TP_2 = \log(t) + B_2/T, \quad TP_3 = \log(t) + B_3/T \quad (6)$$

The authors assumed that the functions, F_1 , F_2 and F_3 will be approximated by the following mathematical forms, respectively.

$$F_1 = A \cdot TP_1 + C \quad (7)$$

$$F_2 = \frac{G}{1 + \exp(TP_2 - \alpha)} \quad (8)$$

$$F_3 = H \cdot \exp\left(-\frac{1}{2} \cdot \frac{(TP_3 - \beta)^2}{\sigma^2}\right) \quad (9)$$

F_1 , F_2 and F_3 are the linear, logistic and Gauss distribution functions of the tempering parameters, respectively. The shapes of F_2 and F_3 are illustrated in Fig.5. The value of F_2 approaches G when TP_2 is decreased. In vicinity to α , F_2 is decreased suddenly, and is equal to $G/2$ when TP_2 is equal to α . The value of F_2 approaches zero when TP_2 increases exceeding α . The function, F_3 gives a bell shape, and the maximum height is equal to H .

Fig.6 shows the results for HT80 steel comparing with the calculated value from equation (5). Circular marks indicate the measured hardness, and dotted lines indicate the calculated values of F_1 , F_2 and F_3 . The solid line is the total of three functions. Calculated value agrees with the measured one in general. But, for the data at 975 K, the misfits were recognized in the range of secondary hardening. At such temperatures, it is expected that the secondary hardening occurs at short time as 100 to 1000 seconds, and the value of F_2 will be decreased suddenly at the same time period. The authors thought that the large error of estimation at this temperatures would be brought by the local difference in the progress of tempering. The constants used in Fig.6 for HT80 steel are listed in Table 2, comparing with those of other steels.

Fig.7 shows the measured hardness comparing with the calculated hardness

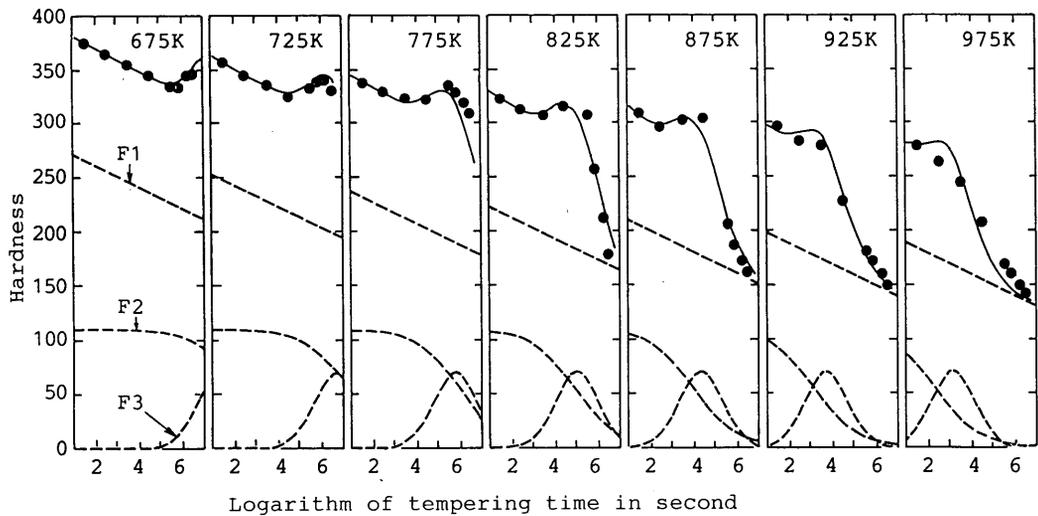


Fig.6 The measured hardness for HT80 steel comparing with the equation (5)

Table 2 List of the obtained constants in equations (6), (7), (8) and (9)

steel	A	B1	C	B2	G	α	B3	H	β	σ^2
S25C	-19.5	-14800	-50	-	-	-	-	-	-	-
S55C	-34.1	-11800	-54	-	-	-	-	-	-	-
HT60	-18.4	-16000	-70	-16000	20	-15	-13000	60	-11.3	1
HT80	-9.7	-18400	15	-14000	110	-12	-10000	70	-7.1	1
1/2Mo	-14.2	-18800	-60	-14800	90	-13	-10000	60	-7.1	1
1Cr-1/2Mo	-9.7	-17200	30	-17200	130	-16	-10000	60	-7.1	1
2 1/4Cr-1Mo	-4.5	-12900	120	-20900	190	-20	-10000	40	-6.8	2

by the equation (5) employing constants in Table 2.

4. Additional rule of tempering parameter

For the tempering carried out by raising the temperature, the tempering parameters were calculated as follows. The tempering parameters, TP1, TP2 and TP3, respectively, are defined as the logarithm of the amounts of reactions

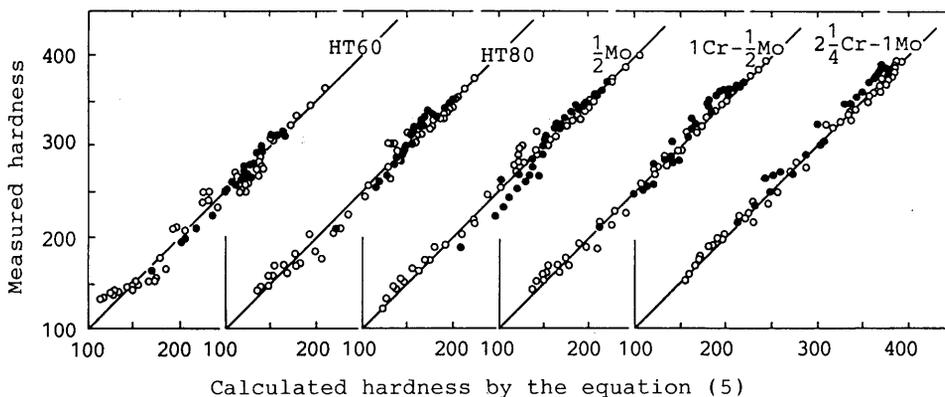


Fig.7 The measured hardness of tempered steels comparing with the calculated values from the equation (5) using constants shown in Table 2

mark; ○ tempering at constant temperature

● tempering at rising temperature

progressed. Assuming that one reaction is independent to the others, each parameter can be treated by an additional rule, such as equation (3). Heating period were divided into one hundred segments. Each trapezoid was regarded as the narrow rectangle, as shown in Fig.1(c). Tempering at rising temperature was approximated by the total of one hundred tempering processes at the corresponding constant temperature for time of Δt .

The solid circular marks in Fig.7 indicate the values of tempered hardness at rising temperature, comparing with the calculated value by equation (3). In calculation, the constants in Table 2 were used. The measured values agree well with the calculated values, therefore, this fact is suggestive of the validity of the additional rule by equation (3).

5. Discussions for the roles of alloying elements

The constants, listed in Table 2 were determined individually for each steels using the experimental results. These constants depend on the type of steel. It is desired that these constants can be estimated from the chemical compositions of steel. At present, its estimation is impossible, because the data are insufficient to perform the calculation. In this section, the authors will give only the qualitative discussions on the influences of alloying elements, chromium, molybdenum and vanadium.

5.1. The first process

The first process is the decrease in hardness from quenched hardness, and determined as a linear function of the parameter, TP1 (eq.(6)). B1 in TP1 will be related to carbon content of steel, because this process is controlled by the diffusion rate of carbon. The values of B1 are plotted against carbon content in Fig.8(a). B1 is increased with carbon content from the plot of S25C to that of S55C steel. The B1 for alloy steels are smaller than that expected from the carbon content, except for 2 1/4Cr-1Mo steel. The authors think that these difference is due to the influence of alloying elements on the diffusion rate of carbon.

The authors defined $\Delta B1$ as the difference in B1 between the actual value and the value expected from carbon content. $\Delta B1$ indicates the effects of alloying elements. $\Delta B1$ for 1/2Mo steel is -3.5×10^3 . If the effect of molybdenum on B1 is proportional to its content and its effect is not affected by other elements, the change of B1 by chromium ($\Delta B1(\text{Cr})$) can be estimated for HT80, 1Cr-1/2Mo and 2 1/4Cr-1Mo steels as follows.

$$\Delta B1(\text{Cr}) = \Delta B1 - (-3.5 \times 10^3 / 0.47) \times (\% \text{Mo})$$

$\Delta B1(\text{Cr})$ increases with chromium content as shown in Fig.8(b). That is, molybdenum and chromium affect B1 in reverse manner as the former decreases B1 and the latter increases it. However, the effects of both elements are not additional in linear manner. Vanadium of 0.03% does not influence B1 judging from the B1 value for HT60 steel.

Fig.8(c) shows the values of constant, A (eq.(7)) against carbon content.

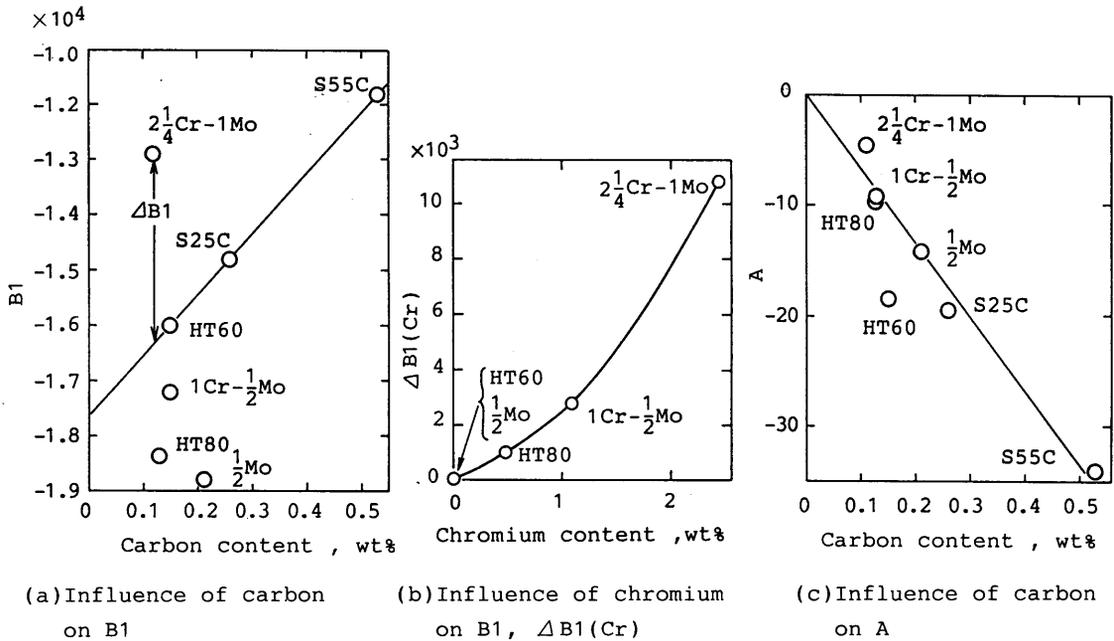


Fig.8 The influence of carbon and other alloying elements on the values of constants concerning the first process of tempering

The value of A indicates the contribution of tempering on softening, and therefore, the absolute value of A becomes naturally larger for the steel of higher carbon content whose hardness is larger in as-quenched condition.

5.2 The second process

Fig.9 shows the tempering conditions, in which the F2 is equal to 2/G, that is, TP2 is equal to a. The inclination of line increases with the value of B2 (eq.(6)). Chromium shifts the line to longer time and higher temperature side, as seen from the lines of 1Cr-1/2Mo and 2 1/4Cr-1Mo steels. Chromium prevents the diffusion of carbon, and delays the time period softening of the quenched steel.

The value of G indicates the magnitude of effect on preventing the softening. The following table shows the contents of alloying elements and the values of G.

steel	%Cr	%Mo	%V	[%Cr]+[%Mo]+[%V]	G	H
HT60			0.03	0.03	20	60
1/2Mo	0.01	0.47		0.48	90	60
HT80	0.49	0.43	0.04	0.96	110	70
1Cr-1/2Mo	1.09	0.55		1.64	130	60
2 1/4Cr-1Mo	2.43	1.02		3.45	190	40

The value of G increases with the total amount of alloying elements, but their influences are not linear.

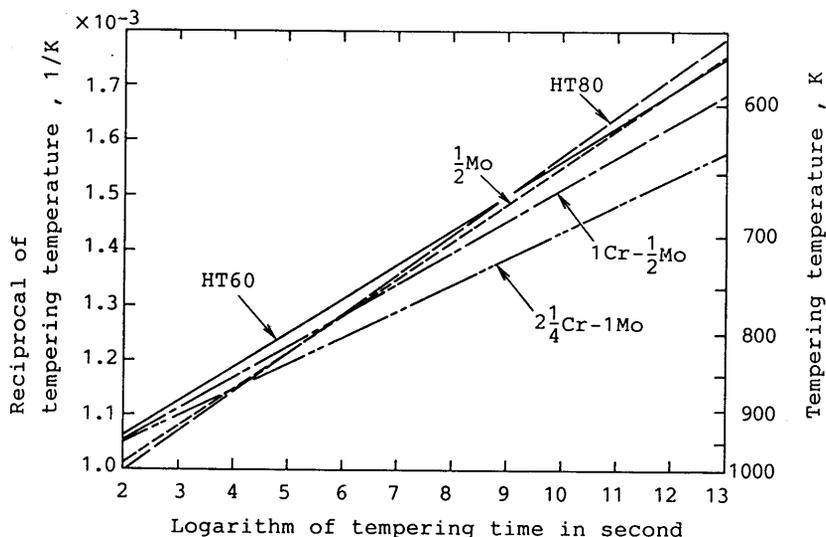


Fig.9 The tempering conditions in which the F2 is equal to G/2

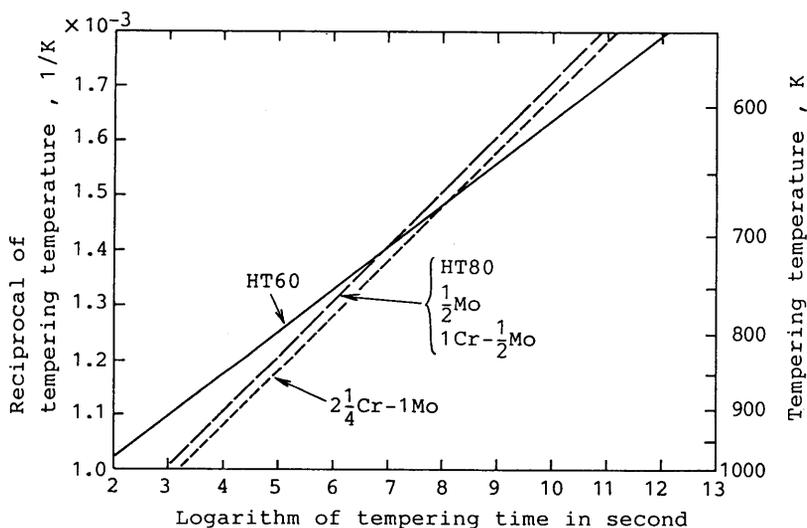


Fig.10 The tempering conditions in which the F3 is equal to H

5.3 The third process

Fig.10 shows the tempering conditions, in which the F3 value reaches the maximum, that is, TP3 is equal to β . The line of HT60 steel has the inclination different from that of other steels. The authors think this fact as the condition, where the secondary hardening reaches maximum, depends on the type of carbide; HT60 steel is hardened by vanadium carbide, V₄C₃, and other steels are hardened by molybdenum carbide, Mo₂C.

The magnitude of secondary hardening, H is shown in the last table. The simple relationship is not clearly recognized between the H value and the contents of alloying elements. Vanadium of as small as 0.03% has a large effect of causing the secondary hardening, as seen from the H for HT60 steel. The H for 2 1/4Cr-1Mo steel is small in spite of a large amounts of molybdenum

by the reason that chromium interferes in precipitation of molybdenum carbide, Mo₂C.

6. Conclusions

The hardness of tempered steel was investigated for a wide range of tempering condition using some low alloy steels. And a new method was proposed to estimate the hardness from the tempering condition. The results are summarized as followings.

- 1) The tempering parameter, g which employs a single activation energy is not appropriate for evaluating the effect of tempering on the hardness of tempered low alloy steels.
- 2) The hardness of tempered steel is controlled by three processes, the decomposition of martensite, the delay of softening and the secondary hardening. Three parameters should be employed for the corresponding processes.
- 3) The hardness of low alloy steels can be approximated by following equation.

$$H_v = A \cdot TP1 + C + \frac{G}{1 + \exp(TP2 - \alpha)} + H \cdot \exp\left(-\frac{1}{2} \cdot \frac{(TP3 - \beta)^2}{\sigma^2}\right)$$

- 3) The tempering parameters are evaluated by the additional rule (eq.(3)) for the tempering with changing temperature.

References

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