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Original Paper

Time-Temperature-Hardness Diagrams of Tempered Steels

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Tempered hardness were investigated for carbon steels and low alloy steels containing chromium, molybdenum and vanadium. The ranges of temperature and time were 675 to 975 K and 35 to 3.5 x10^6 s, respectively. The following results were obtained. 1) The tempered hardness of carbon steels can be approximated with a linear function of the tempereing parameter, λ proposed recently by T.Inoue, and is roughly a reciprocal proportion to the conventional tempering parameter, P. 2) The tempered hardness of low alloy steels, however, can not be expressed by the function of tempering parameter, because the secondary hardening or the delay of softening occur due to the precipitation of carbide, and therfore, the activation energy changes with the advance of tempering. 3) Time-temperature-hardness diagrams are proposed for showing the tempered hardness of low alloy steels.

Key words: Tempered hardness, Tempering parameter, Low alloy steel, Secondary hardening, Precipitation of carbide

1. Introduction

Hardness of quenched steel is changed by tempering, due to the decomposition of martensite, precipitation and coalescence of carbide and rearrangement and disappearance of dislocation. The mechanical properties, such as hardness, strength and toughness, are changed with advancing these metallurgical reactions during tempering.

The effect of tempering is very difficult to be defined, because it depends not only on the tempering-temperature but also on tempering-time. Arrhenius' assumption gives a qualitative estimation for the effect of tempering. According to his assumption, the rate of reaction, r can be written in the following form.

$$r = A \cdot \exp(-Q/RT)$$

where, Q is activation energy, T is temperature in kelvin, R is gas constance and A is a constant for an interested reaction. Then, the amount of the reaction can be considered as the product of r and the reaction period [1][2]. On the basis of these assumptions, some tempering parameters were proposed and further several attempts were made that the mechanical properties would be expressed as a function of those parameteres [1]-[5].

During tempering, many reactions will occur simultaneously and a mechanical property will be influenced by the combination of some reactions with different activation energies. In such case, it may be difficult to express the mechanical property only by one tempering parameter. In this paper, the hardness of some steels tempered various conditions were experimented. The steels included carbon steels and low alloy steels, in which the precipitation of carbide has a remarkable effect on hardness. The availability of tempering parameter is discussed for tempered hardness of these two types of steels.

2.Experimental procedures

Chemical compositions of steels are listed in Table 1. S10C, S25C and S55C are plain carbon steels without any carbide forming elements. HT60 and HT80 are high strength steels, and 1/2Mo, 1Cr-1/2Mo and 2 1/4Cr-1Mo are heat resisting steels. These steels contain carbide forming elements, such as chromium, molybdenum and vanadium.

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 quenched into water. As-quenched hardness was measured by Vickers hardness test machine under the loading of 294 N for 15 sec. For each specimen, the measurement was repeated in five times giving an average.

The hardness numbers of as-quenched specimens are shown in Fig.1 plotted against the carbon content. As the hardness of martensite depends only on carbon content, the plots lie on a straight line. The straight line in the figure is the regression line showing the relationship between the hardness of martensite and the carbon content, proposed by M.Okumura et al.[6]. An exception of the plot for S10C steel informs that this steel was not fully quench-hardened. Therefore, S10C steel was not employed for succeeding experiments.

Table 1 Chemical compositions of steels used (wt%)

steel	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	V	B	Sol.Al	Sn	Sb	As
S10C	0.09	0.19	0.38	0.013	0.013	0.07	0.04	0.07	-	-	-	-	-	-	-
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	tr	tr	tr
1Cr-1/2Mo	0.15	0.28	0.57	0.011	0.008	-	-	1.09	0.55	-	-	0.024	tr	tr	tr
2 1/4Cr-1Mo	0.12	0.16	0.47	0.010	0.004	-	-	2.43	1.02	-	-	-	tr	tr	0.002

tr;trace (trace limit; Sn $\leqq$ 0.005 Sb,As $\leqq$ 0.001)

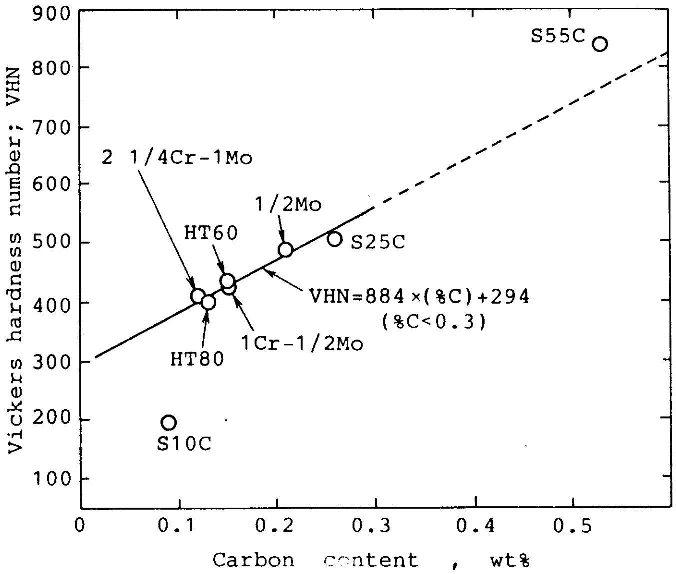

Fig.1 As-quenched hardness of steels against the carbon content

Quenched blanks were heated upto the tempering temperature. After the prescribed tempering-time, the specimens were rapidly cooled by water. The ranges of the temperature and time were 675 to 975 K and 35 to 3.5 $\times 10^6$ s (40 days).

The hardness numbers of tempered specimens were measured by the same way as for quenched blanks.

3.Hardness of tempered carbon steels

Fig.2(a) and (b) show the influences of tempering temperature and -time, respectively, on the hardness of tempered S25C steel. In the figure (b), the logarithmic scale was adopted for tempering time. The hardness (VHN) is decreased uniformly with increasing the tempering temperature and time. The relation between the hardness and the logarithm of time is essentially in one straight line for each temperature, and the inclination of each line is almost same. While, the relation between the hardness and the temperature lies on one convex curve. Then, the latter plots were rearranged by taking the reciprocal of temperature (1/T) as abscissa, as shown in Fig.3. Thus, the hardness increased linerly with the 1/T, and the inclination of each line also becomes the same for every tempering time. Fig.2(b) and Fig.3 inform that the hardness of tempered S25C steel can be expressed by the following equation.

$$\text{Vickers hardness number (VHN)} = A \cdot \log(t) + B/T + C \qquad (1)$$

where t is tempering time in second, T is tempering temperature in Kelvin and A, B and C are constants. The following equation is obtained by substituting into eq.(1) the constants, A, B and C which are determined by using the least squares method.

$$VHN = -19.5\log(t) + 290000/T - 49.8 \quad \text{(for S25C steel)} \qquad (2)$$

The results for S55C steel are shown in Fig.4. The VHNs are plotted against the reciprocal of temperature in the figure (a). The same tendency as the case of S25C steel is recognized for this steel. Thus, constants for S55C steel were determined by the same manner as S25C steel, as,

$$VHN = -26.8\log(t) + 346000/T - 52.0 \quad \text{(for S55C steel)} \qquad (3)$$

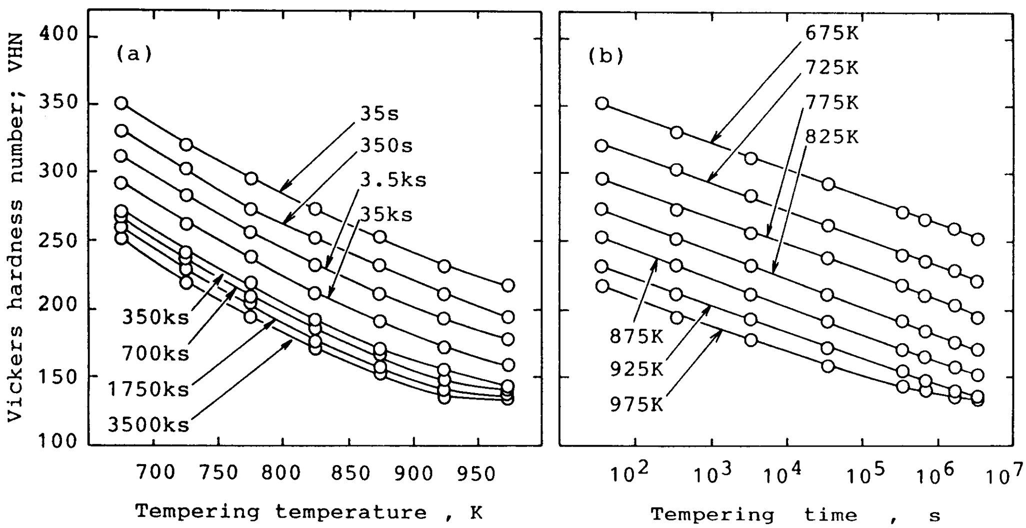

Fig.2 Influences of temperature (a) and time (b) on the tempered hardness of S25C steel

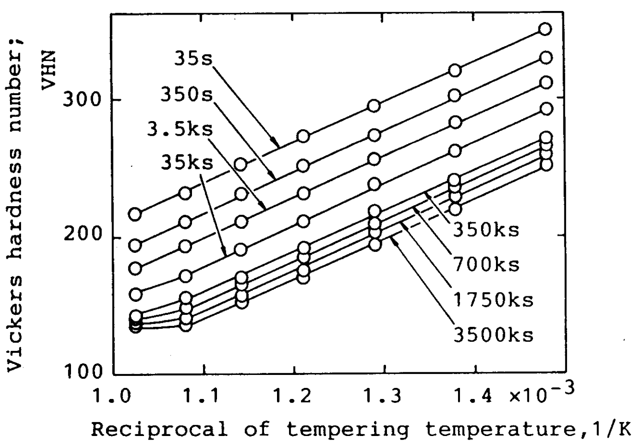

Fig.3 The tempered hardness of S25C steel against the reciprocal of tempering temperature, 1/T

The coefficients of regression equations for both the eq.(2) and (3) are beyond 0.99, and so the eq.(1) is proved to be a fairly good approximation for the steels of S25C and S55C. Eq.(1) has the same meaning as the parameter "λ" proposed by T.Inoue [2].

$$\lambda = \log(t) - Q/2.3R\ (1/T) + 50 \qquad (4)$$

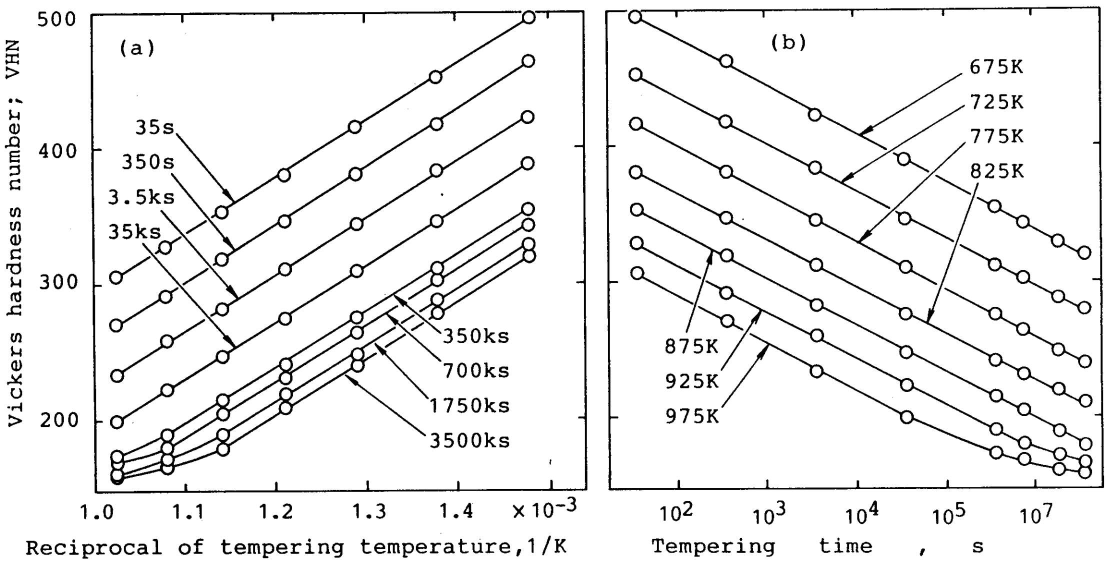

Fig.4 Influences of temperature (a) and time (b) on the tempered hardness of S55C steel

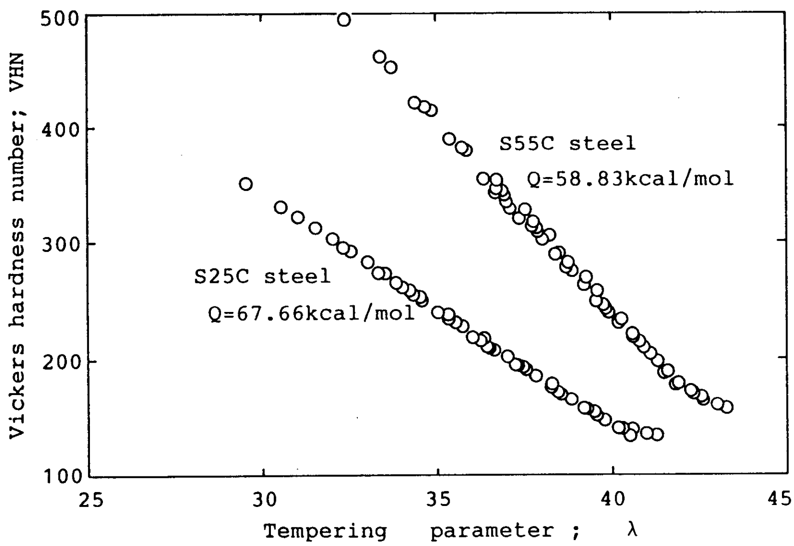

Fig.5 The tempered hardness of S25C and S55C steels against the parameter, λ

The λ indicates the effect of tempering, that is, the degree of advancing metallurgical reactions in a tempered steel. Assuming that the tempered hardness will be linear to the λ, he proposed the following equation.

$$\begin{aligned} VHN &= m\ (\lambda\text{-value}) + n \\ &= m\ (\log(t) - Q/2.3RT + 50) + n \\ &= m \log(t) - m\ Q/2.3R\ (1/T) + 50\ m + n \qquad (5) \end{aligned}$$

Eq.(5) has the same form as eq.(1). In Fig.5, the measured values are plotted against the λ, in which 67.66 kcal/mol (S25C) and 58.83 kcal/mol (S55C) are adopted as the activation energies. Each of these values was calculated as the ratio of constants in eq.(2) or (3). The plots in Fig.5 lie on a straight line except for the range of largest λ (high temperature and long time range). That is, for the plain carbon steels such as S25C and S55C, the λ-value is a suitable parameter to estimate the degree of tempering, and has an advantage of approximating with its linear function.

J.H.Hollomon and L.D.Jaffe proposed the following tempering parameter, "P" [1].

$$P = T\ (\log(t) + C) \qquad (6)$$

where, C is constant, which depends on the carbon content of steel, as,

$$C = 17.7 - 5.8\ (\%C) \qquad \text{(time in second)} \qquad (7)$$

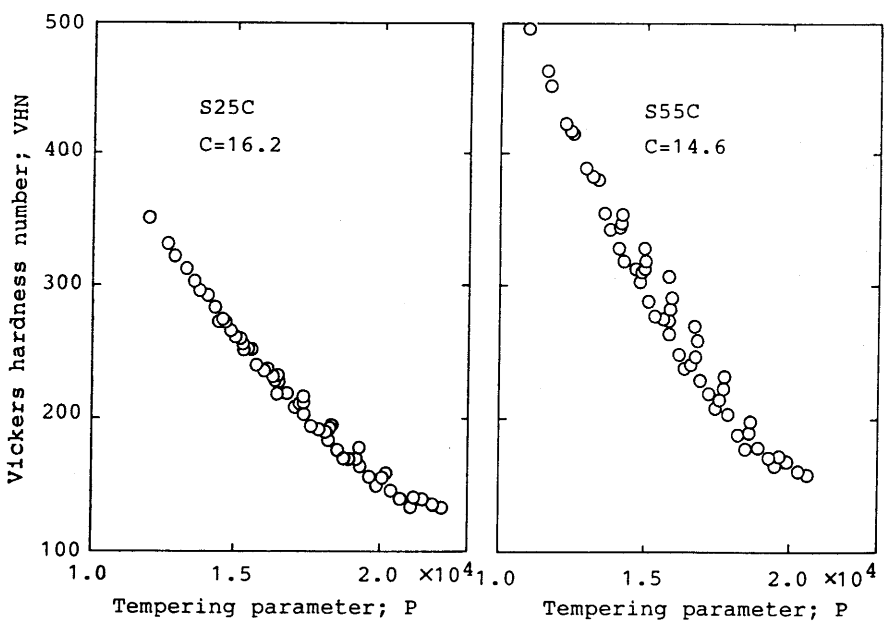

Fig.6 The tempered hardness of S25C and S55C steels against the parameter, P

This parameter is widely applied to express the contributions of temperature and time on the effect of tempering. The measured hardness are plotted against the parameter, P, as shown in Fig.6. The constants, C obtained from eq.(7) are 16.2 and 14.6 for S25C and S55C steels, respectively. The plots have large scatter for both steels, and the hardness seems to be inversely proportional to the P. Thus, the hardness is assumed to be expressed by the following equation.

$$VHN = A/(P\text{-value}) + B = A/T\ (\log(t) + C) + B \qquad (8)$$

The constants obtained determined by a least squares method are listed below.

Steel	A	B	C
S25C	5650000	-139	15.1
S55C	6350000	-212	11.4

Using these values, the measured hardness is plotted against the estimated hardness as in Fig.7. The width of scatter band of this figure is smaller than that of Fig.6.

Although both the parameters of λ and P are derived on the basis of Arrhenius'assumption, there is a difference in the physical significance; the λ indicates clearly the effect of tempering as the logarithm of a product of the rate and time of reaction. But the P has little physical meaning. From those view points, the parameter, λ was adopted in the succeeding discussions.

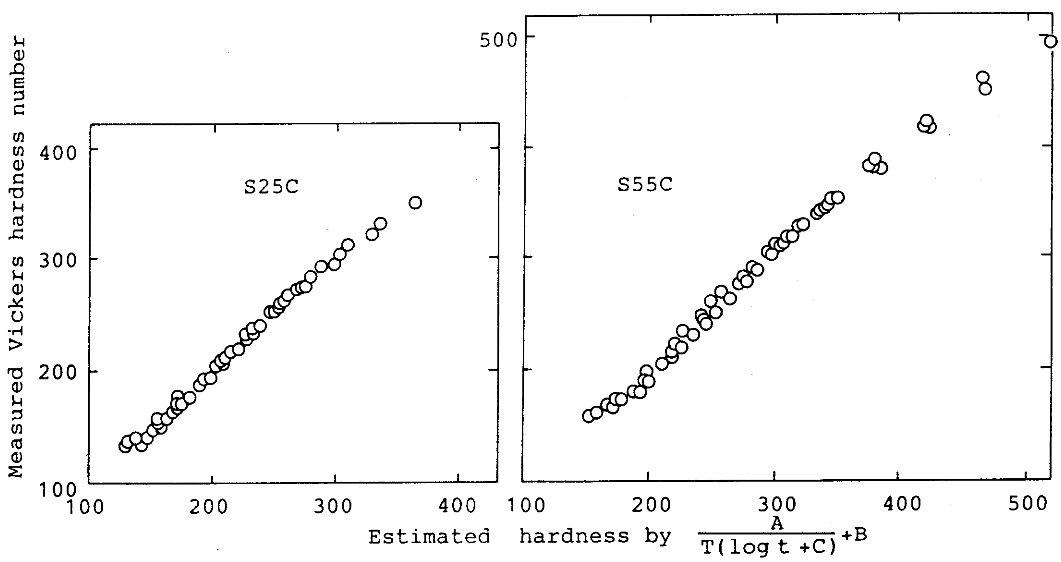

Fig.7 The tempered hardness of S25C and S55C steels comparing with the estimated value by eq.(8)

4.Hardness of low alloy steels

Fig.8 shows the influences of tempering-temperature and -time on the hardness of tempered HT60 steel. The hardness is decreased generally with the temperature and the time. As HT60 steel contains 0.03%V, the secondary hardening or the delay of softening occurs due to the precipitation of vanadium carbide during tempering. Therfore, the plots of hardness against log(t) and 1/T deviate abruptly from the linear relations in the temperature ranges where the secondary hardening occurs. However, there is a common tendency that the temperature of hardening falls with increasing tempering time, and the time of hardening is shortened with elevating tempering-temperature. Thus, the eq.(1) is applied again in order to arrange the results of HT60 steel and other four steels, HT80, 1/2Mo, 1Cr-1/2Mo and 2 1/4Cr-1Mo in Fig.9. The constants and the activation energy are listed below.

Steel	A	B	C	Q (kcal/mol)
HT60	-24.8	336000	-54.0	61.9
HT80	-23.2	342000	-59.9	67.1
1/2Mo	-22.7	353000	-70.5	70.7
1Cr-1/2Mo	-22.3	365000	-83.0	74.6
2 1/4Cr-1Mo	-21.7	375000	-92.9	78.9

Each group of plots in Fig.9 is in one curved line regardless of the different temperature and time. However, the plots scatter widely, especially, in the range of secondary hardening. The difference in hardness number is more than fifty at one tempering parameter. Therefore, the parameter λ can not be applied for expressing the tempered hardness in the whole range of tempering including

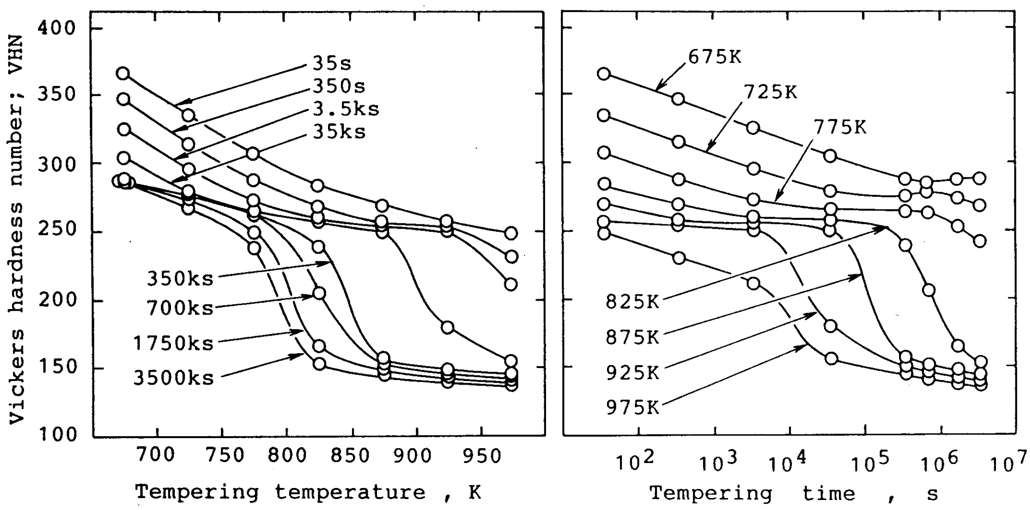

Fig.8 Influences of temperature and time on the tempered hardness of HT60 steel

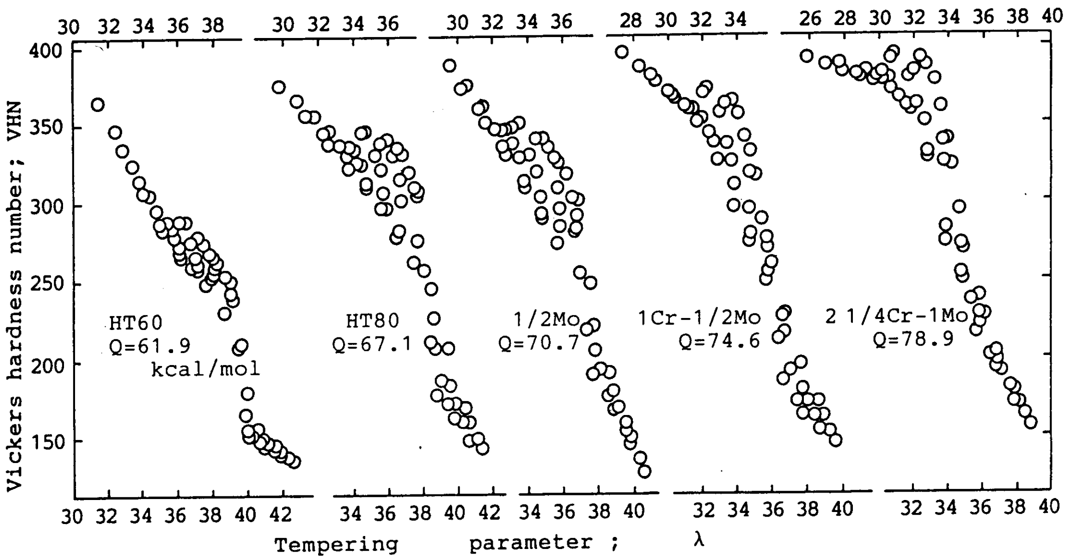

Fig.9 The tempered hardness of HT60, HT80, 1/2Mo, 1Cr-1/2Mo and 2 1/4Cr-1Mo steels against the parameter, λ

the secondary hardening or the delay of softening. Nevertheless, the λ is useful in the ranges other than this. In these limited ranges, the hardness can be expressed by eq.(1), and the actvation energy can be obtained by the same manner as the carbon steels as listed below.

Steel	before hardening	after hardening
HT60	70 kcal/mol	40 kcal/mol
HT80	90	30
1/2Mo	90	50
1Cr-1/2Mo	80	30
2 1/4Cr-1Mo	50	60

For the range of secondary hardening, the activation energy could not be calculated, because the measured hardness changes remarkably with each combination of temperature and time. Therefore, it will be very difficult or impossible to express the hardess number including secondary hardening by the tempering parameter, even if more complex equation excepting eq.(1) will be applied.

5.Time-temperature-hardness diagrams of low alloy steels

The diagram composed of the reciprocal of temperature and the logarithm of time is employed in order to show the tempered hardness number of each steel, in which the secondary hardening or delay of softening occurs. The level lines of hardness are drawn in the diagram. As shown in Fig.10, the diagram can be divided into three regions;

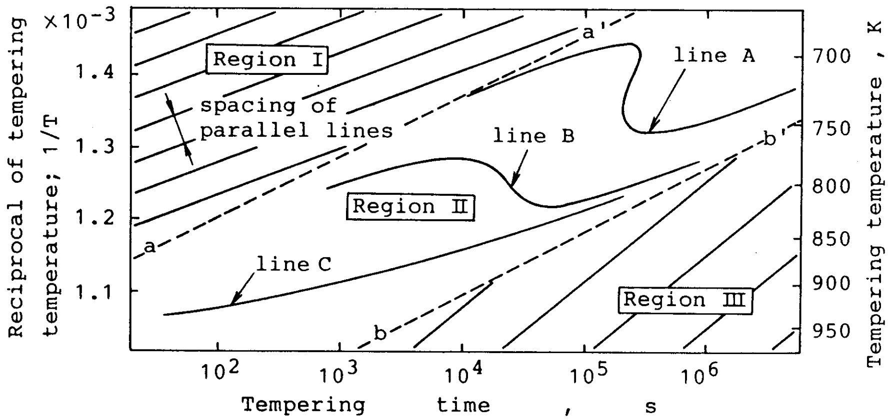

Fig.10 Schematic illustration of the time-temperature-hardness diagram

Region I : before hardening (left-upper side of line aa')
Region II : secondary hardening or remarkable delay of softening (between lines of aa' and bb')
Region III: after hardening (right-lower side of line bb')

As eq.(1) is adopted in the regions of I and III, the level lines are parallel straight lines and their spacing is constant for each range. There is a difference in the inclination between the ranges of I and III because of the different activation energy. In the region II, curved lines are drawn by free-hand according to measured hardness numbers.

The time-temperature-hardness diagrams of HT60, HT80, 1/2Mo, 1Cr-1/2Mo and 2 1/4Cr-1Mo steels are shown in figures 11 to 15, respectively. The hardness at any tempering conditions can be read from these diagrams.

The inclinations of parallel lines in the ranges of I and III are dependent only on the activation energy. The inclination of straight line is increased with the activation energy. While, the spacing of parallel lines does not depend on the activation energy, but depends on the absolute value of constants, A and B in eq.(1). The spacings in region I are smaller for HT60 and 1/2Mo steels, while larger for HT80 and 2 1/4Cr-1Mo steels.

In the region II, the level lines curve, and the spacing of them are generally wide, because the delay of softening occurs in this region. The lines in this region are classified into three types according to the manner of deflexion from a straight line.

Type I : line deflecting toward both sides of decresing 1/T and log(t) (line A)
Type II : line deflecting toward the side of decreasing 1/T only (line B)
Type III: curved line without any turning point (line C)

In the cases of HT60 and 1/2Mo steels, which contain no chromium, the level lines are Type II over the whole range of region II. In thses steels, the

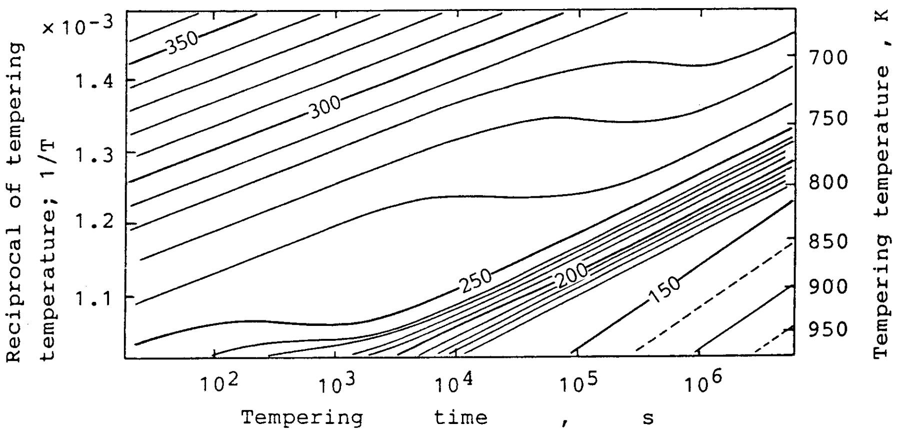

Fig.11 The time-temperature-hardness diagram of HT60 steel

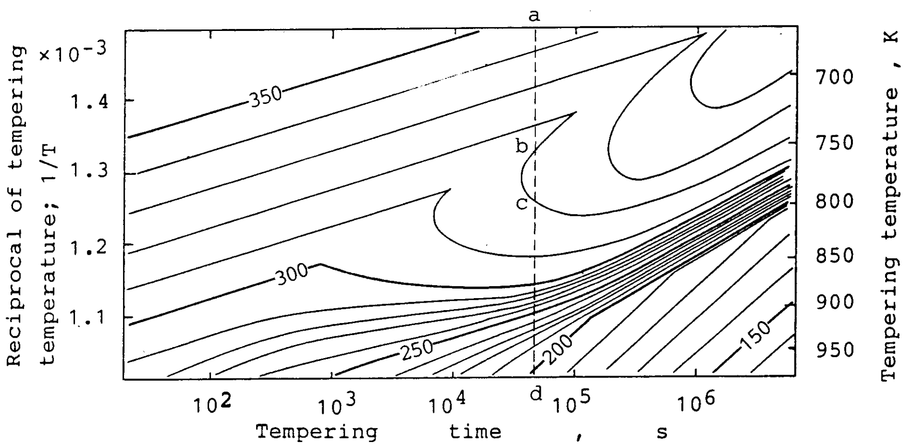

Fig.12 The-time-temperature-hardness diagram of HT80 steel

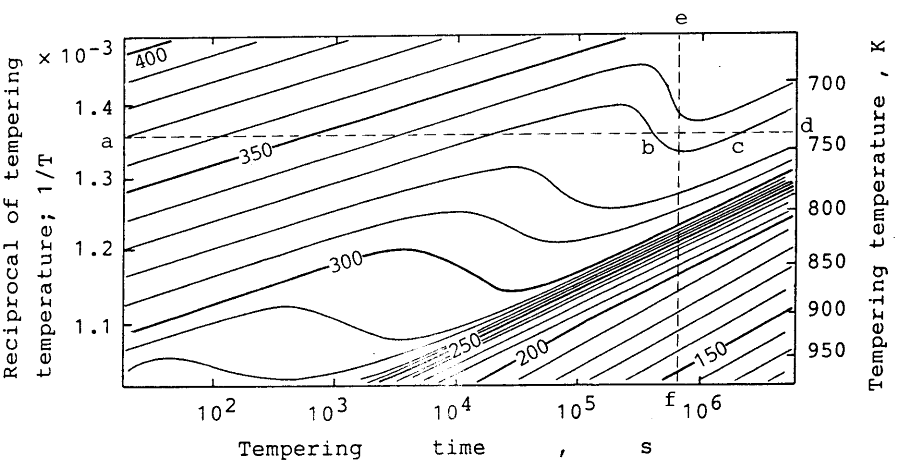

Fig.13 The time-temperature-hardness diagram of 1/2Mo steel

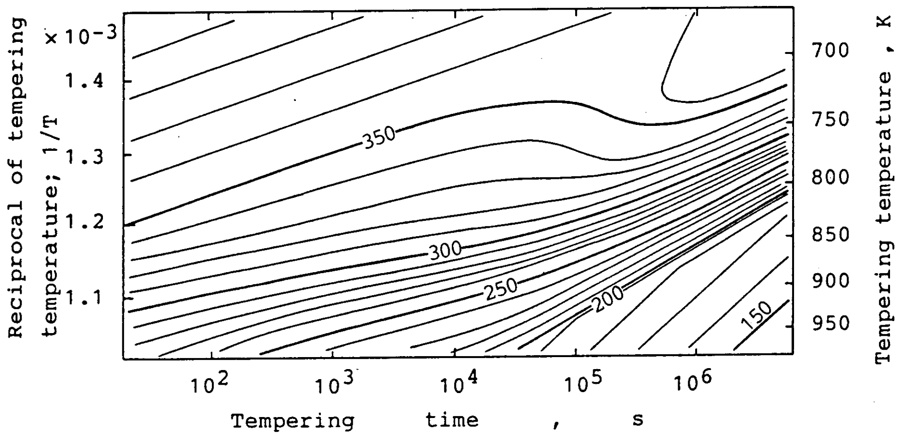

Fig.14 The time-temperature-hardness diagram of 1Cr-1/2Mo steel

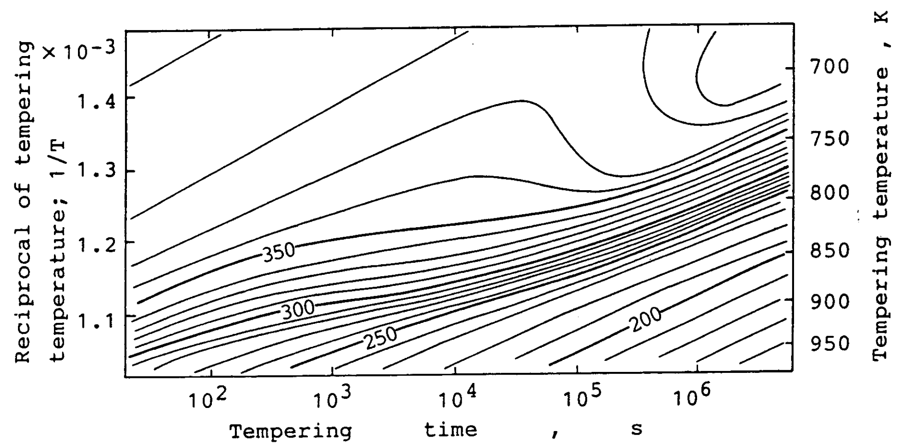

Fig.15 The time-temperature-hardness diagram of 2 1/4Cr-1Mo steel

secondary hardening will be recognized with advancing tempering time at a constant temperature. An example of the secondary hardening section is shown as the part of bc in the line ad in Fig.13. If the tempering is performed with increasing temperature for the same time, only the delay of softening will be observed, as shown in Fig.13 (line ef).

In the cases of HT80, 1Cr-1/2Mo and 2 1/4Cr-1Mo steels, which contain chromium, the types of level lines are different by the tempering temperature. In the higher temperature range (lower side of figures), level lines are type III. Therefore, in such higher temperature range, the secondary hardening will be not recognized, and the remarkable delay of softening will be scarcely recognized. In the lower temperature range, the level lines belongs to type I. This deflextion of level line is most remarkable in HT80 steel. The secondary hardening will be recognized with increasing temperature for a constant tempering time beyond 10^4 s in this steel, as shown by the part bc in Fig.12.

The steep softening occurs at the final stage of region II for all steels. The precipitation of carbide of alloying element has a significant effect on the irregular change of hardness in region II. In the steels containing both chromium and molybdenum, molybdenum carbide, M_2C and/or chromium carbide, M_7C_3 precipitate during tempering, according to the combination of chromium and molybdenum contents [7]. Vanadium carbide, V_4C_3 precipitates in HT60 and HT80 steels, which contain vanadium of 0.03 and 0.04%, respectively [8]. In the steels, in which no chromium carbide precipitates, molybdenum carbide exists stably in the whole tempering range, while in the steels with chromium, molybdenum carbide becomes unstable due to the presence of chromium. The steels of 1Cr-1/2Mo and 2 1/4Cr-1Mo contain small amount of molybdenum comparing with chromium contents. From the results concerning carbide precipitation, the following can be suggested.

a) Molybdenum carbide, M_2C causes the secondary hardening during tempering of lower temperature-longer time and higher temperature-shorter time.

b) Chromium carbide, M_7C_3 causes the secondary hardening during tempering of lower temperature-longer time.

The different dependency of hardness is considered due to the combined effect of carbide forming elements. This problem must be investigated further.

6.Conclusions

The changes of hardness during tempering were investigated using seven types of commercial steels. The results are summerized as followings.

1) The tempered hardness of carbon steels is linear to the reciprocal of tempering temperature in kelvin and the logarithm of tempering time. Therefore, the tempering parameter, λ can be applied for expressing the hardness of carbon steels.

2) The tempered hardness of carbon steels is inversely proportional to the conventional tempering parameter, P.

3) In the range, in which the secondary hardening occur, the change of hardness is irregular and depends on the combination of alloying elements. However, for the other ranges, the tempering parameter, λ is available for expressing the hardness.

4) The time-temperature-hardness diagrams are proposed for showing the tempered hardness of the steels in which the secondary hardening occurs.

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