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## Tempering of Chromium Steels

(The Fifth Report)

### Contraction accompanied with Isothermal Tempering (mainly on the proceeding rate of the first stage).\*

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The tempering process of 8% Cr steel (0.6% C) was studied in terms of contraction in the process of isothermal tempering, and these results together with those in the previous reports were considered synthetically. The conclusions obtained are as follows: (1) The growth of  $\epsilon$ -carbide at the first stage of tempering process reaches its saturation point at 250°C and produces the contraction of  $255 \times 10^{-5}$  per unit length. (2) The proceeding of the first stage in the tempering follows Hardy and Heal's equation, that is,  $da/dt = K(A-a)t^m$ , where  $a$  = contraction per unit length for  $t$  (time),  $A$  = saturation value of  $a$ ,  $K$  = rate constant (function of temperature), and  $m$  = constant. (3) The results of the experiment showed  $m = -0.73$ . (4) The rate constant was indicated as  $K = K_0 \times e^{-Q/RT}$ , where  $K_0$  = constant independent of temperature,  $R$  = universal gas constant,  $T$  = absolute temperature,  $Q$  = activation energy in this process. (5) The results of the experiments showed:  $K_0 = 5.0 \times 10^3$ ,  $Q = 1.17 \times 10^4$  cal/°K. mol. (6) The validity of the conclusion in the previous reports that in the intermediate tempering process between the temperature range of  $\epsilon$ -carbide and that of  $\theta$  phase there exists  $\chi$ -carbide was reaffirmed.

### Introduction

It is generally admitted that the first tempering stage of chromium steels with Cr content up to about 5% as well as that of plain carbon steel proceeds in the following form; martensite  $\rightarrow$  transition precipitate + less tetragonal martensite, and that this transition precipitate passes the stage of  $(\text{Fe}, \text{Cr})_3\text{C}$  into ultimately stable alloy carbide  $(\text{Cr}, \text{Fe})_7\text{C}_3$ . The author recognized<sup>(1)</sup> that this relation in the process holds true in Cr-steel with Cr content up to about 13%. (In plain C-steel and low Cr-steel it ends in the rather simple carbide reaction, that is, transition precipi-

\* A part of this research was presented at the Semiannual Conventions of Japan Institute of Metals, held 4 times between April, 1959 and October, 1960.

tate  $\rightarrow \theta$  phase). It is also generally accepted that transition precipitate which is precipitated from martensite is  $\epsilon$ -carbide. However, there has been no accepted theory so far about whether this  $\epsilon$ -carbide turns into  $\theta$  phase directly or  $\epsilon$ -carbide passes the intermediate phase and then transforms into  $\theta$  phase. In the case of plain carbon steel, overlapping this carbide reaction the retained austenite ( $r_R$ ) is decomposed and the change of physical properties due to the carbide reaction becomes obscure, that was one of the important reasons why there has been no standard theory for this carbide reaction. The author paid his attention to the fact that decomposition of  $r_R$  in hardened high chromium steels occurs at the temperature higher than 550°C and carried on fundamental researches on the tempering processes of chromium steels on one hand and went on studying them in comparison with those of plain carbon steel on the other hand: thus he reached the conclusion that a new different phase must be introduced into the intermediate tempering stage between  $\epsilon$ -carbide and  $\theta$  phase. Its details were shown in the previous reports.<sup>(1)~(4)</sup> The author named this new phase  $\chi$ -factor tentatively, but judging from the results of magnetic analyses and X-ray diffraction analyses he reached the conclusion that it is highly probable that it is nothing but ' $\chi$ -carbide' itself, as is mentioned in the previous report.<sup>(4)</sup>

The first stage of the tempering process of plain carbon steel has nearly been made clear by now,<sup>(5)</sup> but there have been some divergent opinions<sup>(6)~(9)</sup> about how to deal with the activation energy, and about the mechanism of this tempering stage there has been no established theory. In order to discuss the mechanism of the first stage of the tempering process in the right way it is quite natural that the proper understanding of the first stage should be indispensable. As was pointed out in the previous reports,<sup>(1)~(4)</sup> the results of the author's tests show that the first stage of the tempering process begins with the precipitation of  $\epsilon$ -carbide, (which is the same with the results of other reports published so far) but it closes just before the formation of  $\chi$ -carbide, and not right before the precipitation of  $\theta$  phase. Judging synthetically from the results of the previous reports,  $\epsilon$ -carbide is considered to begin to be precipitated at the room temperature and start growing at the tempering around 120°C, getting to the saturation point at around 250°C.

Kinetic treatment of the first stage in the tempering process of chromium steel with approximate 10% chromium content has never been reported up to the present.

In this study the author measured the change of length which goes with the isothermal tempering of the chromium steel (8% Cr, 0.6% C) with dilatometer, re-examined the results of the previous reports, and made researches on the proceeding rate of the first stage in the tempering process.

### Materials and Procedures

The samples used in the experiment are the same R80C6 steel as in the first report<sup>(1)</sup> and their dimension is 5 mm $\phi$   $\times$  80 mm. The hardening conditions are the

same with those mentioned in the first report. The changes in length excluding the thermal expansion which accompany the isothermal tempering were measured as follows: first, mean thermal expansion coefficients were calculated from the cooling curves of the alloy steel, and obtained the following values;  $1.30 \times 10^{-5}/^{\circ}\text{C}$ , at the temperature lower than  $300^{\circ}\text{C}$ , and  $1.33 \times 10^{-5}/^{\circ}\text{C}$  at the lower temperature than  $500^{\circ}\text{C}$ . The difference between the length of the sample calculated with this mean thermal expansion coefficient and the measured value is the change in length due to the carbide reaction itself excluding thermal expansion. Needless to say, it is possible that deformation due to the release of macro strain produced by hardening may occur as the temperature rises up, but these can be eliminated by the repetition of experiment several times. As to the some temperatures, its differential dilatation curve was measured using the annealed sample as a standard, and the result was compared with that through above mentioned method. Both the results showed satisfactory agreements within the experimental error. All the heat treatments were carried on in vacuum.

In the isothermal tempering it is open to discussion how to deal with the reaction which proceeded before the required temperature was reached. In other words, how to decide the starting point of time is a question. However, after the lapse of long period the small discrepancies at the original point of time make little or no difference in the form of the curves denoting the relation between time versus change of length. Accordingly, in order to avoid the uncertainty at the starting period of the tempering process, in this report the author did not discuss this part and confined himself to the study of the later period when a certain amount of time has elapsed after the opening time.

It is generally reported that the precipitation of  $\epsilon$ -carbide starts at the early period and its growth begins at the later period of the tempering process. As was pointed out in the previous report,  $\epsilon$ -carbide seems to start growing at around  $120^{\circ}\text{C}$ . Consequently, in the discussion about the rate of growth of  $\epsilon$ -carbide the appropriate results can be obtained when it is considered excluding the early part of the isothermal tempering curve at the temperatures higher than  $120^{\circ}\text{C}$ . As a matter of fact in this experiment the isothermal tempering at the temperatures higher than  $150^{\circ}\text{C}$  was measured up to 100 hours.

### Results and Discussion

Fig. 1 shows the relations between the time and the change in the length of the samples accompanied with the following tempering processes: first the hardened R80C6 steel was isothermally tempered for 100 hours at  $150^{\circ}\text{C}$  and after the lapse of 100 hours since then the temperature was rapidly raised to  $180^{\circ}\text{C}$ , at which temperature it was isothermally tempered for 100 hours, and then with the same procedure it was tempered for 100 hours at  $210^{\circ}\text{C}$ ,  $240^{\circ}\text{C}$ ,  $250^{\circ}\text{C}$ ,  $270^{\circ}\text{C}$ ,  $300^{\circ}\text{C}$ ,  $330^{\circ}\text{C}$ ,  $360^{\circ}\text{C}$ ,  $390^{\circ}\text{C}$ ,  $440^{\circ}\text{C}$  and  $490^{\circ}\text{C}$  respectively. The ordinate in the diagram denotes

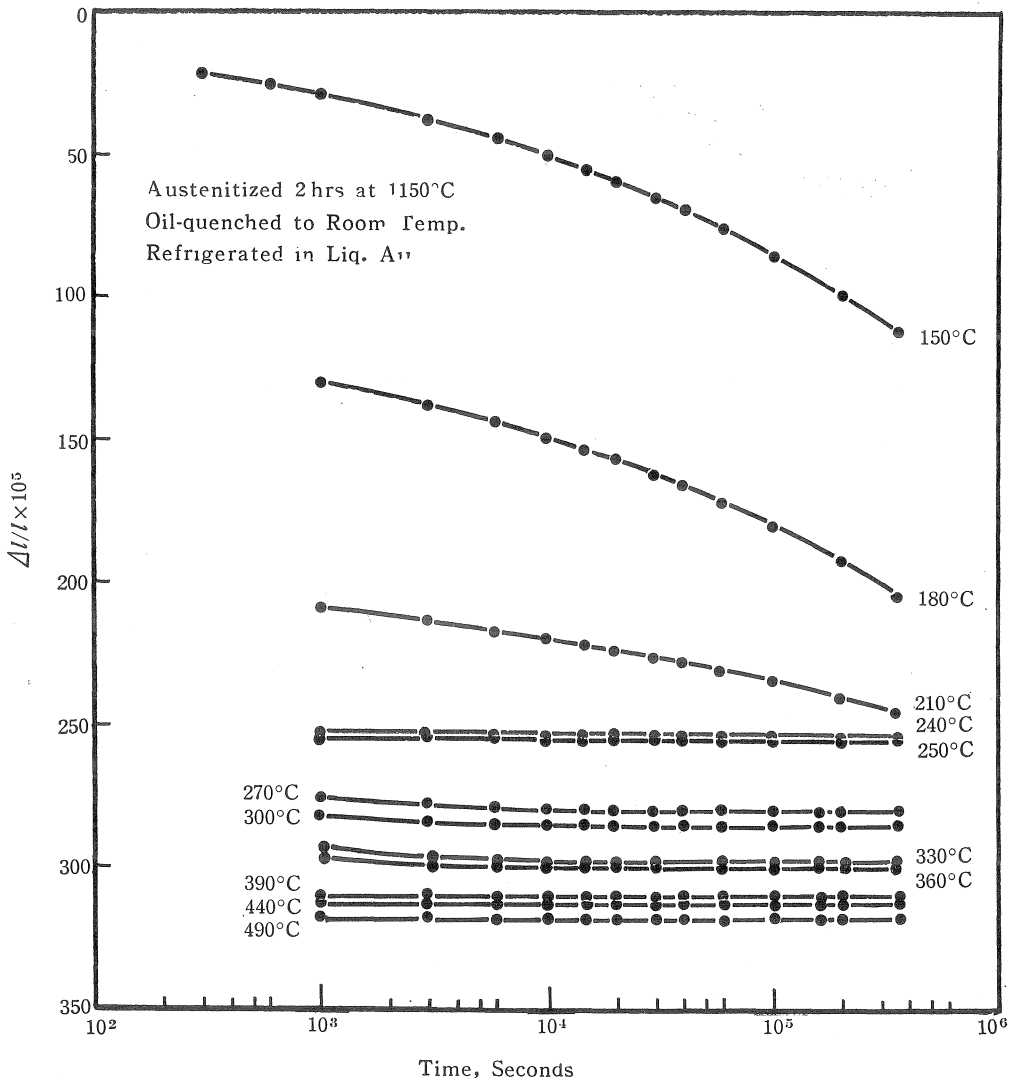


Fig. 1 Length Changes on Step-by-step Isothermal Tempering of R80C6 Steel

the change of length per unit length excluding the thermal expansion. As is seen in the diagram, contraction increases gradually as tempering proceeds, but the appearance of its progress shows noticeable difference between that at lower temperature than 250°C and that at higher temperature than 250°C. It means that there must certainly be some reaction that reaches the saturation point at 250°C in the tempering process. This coincides completely with the author's view in the previous reports that the growth of  $\epsilon$ -carbide reaches the saturation point at around 250°C.

In the isothermal tempering curves at the temperature higher than 250°C, a

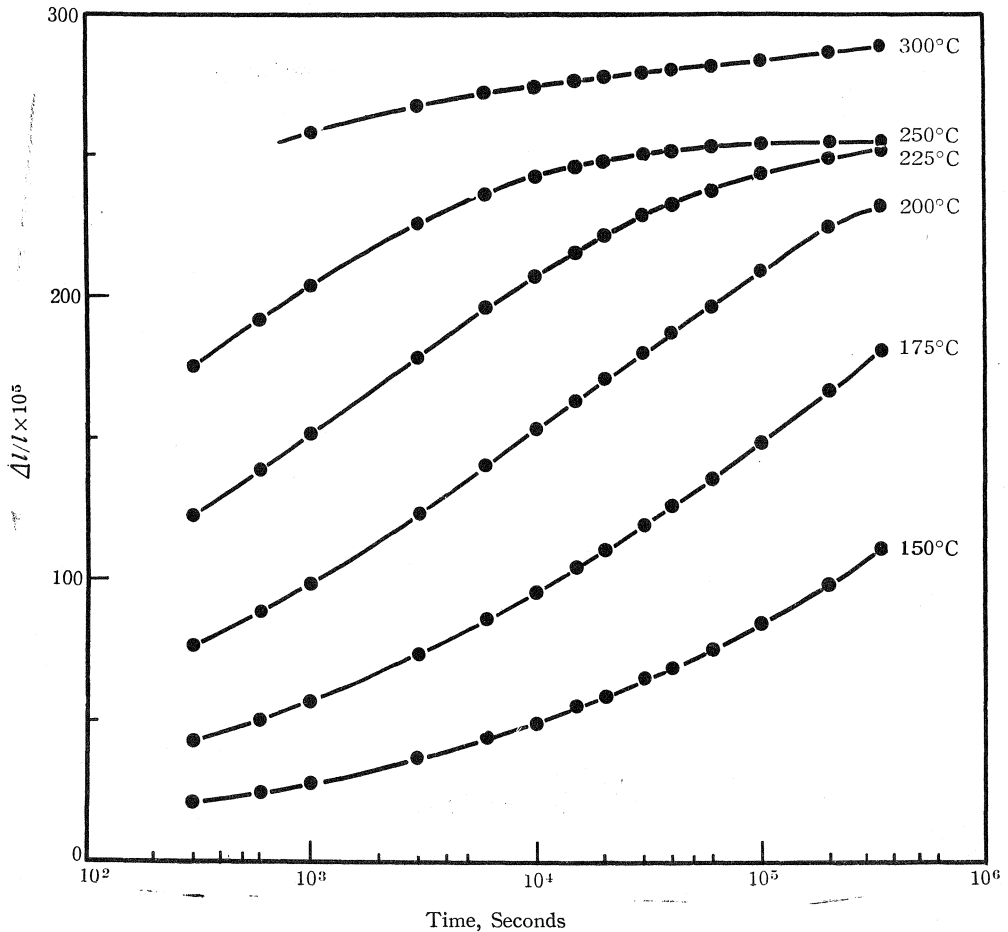


Fig. 2 Length Changes on Isothermal Tempering of R80C6 Steel

tendency to split into some small group is seen, and each group corresponds with the range of  $\chi$ -carbide and that of  $\theta$  phase respectively; consequently in terms of the contraction which accompanies the isothermal tempering, the conclusion in the previous reports that the existence of  $\chi$ -carbide can be justified was verified.

Fig. 2 shows the contraction curves when hardened chromium steels were isothermally tempered at various temperatures; but as was mentioned above, in order to discuss the growth of  $\epsilon$ -carbide, the contraction curves at the temperature range lower than 250°C serve the purpose. Now, in the isothermal tempering between 150°C and 250°C, at the early period the nucleus of  $\epsilon$ -carbide is precipitated, and this can be considered to grow; to this process the following equation pointed out by Hardy and Heal<sup>(10)</sup> is applicable;

$$\frac{da}{dt} = K(A - a) t^m \dots\dots\dots(1)$$

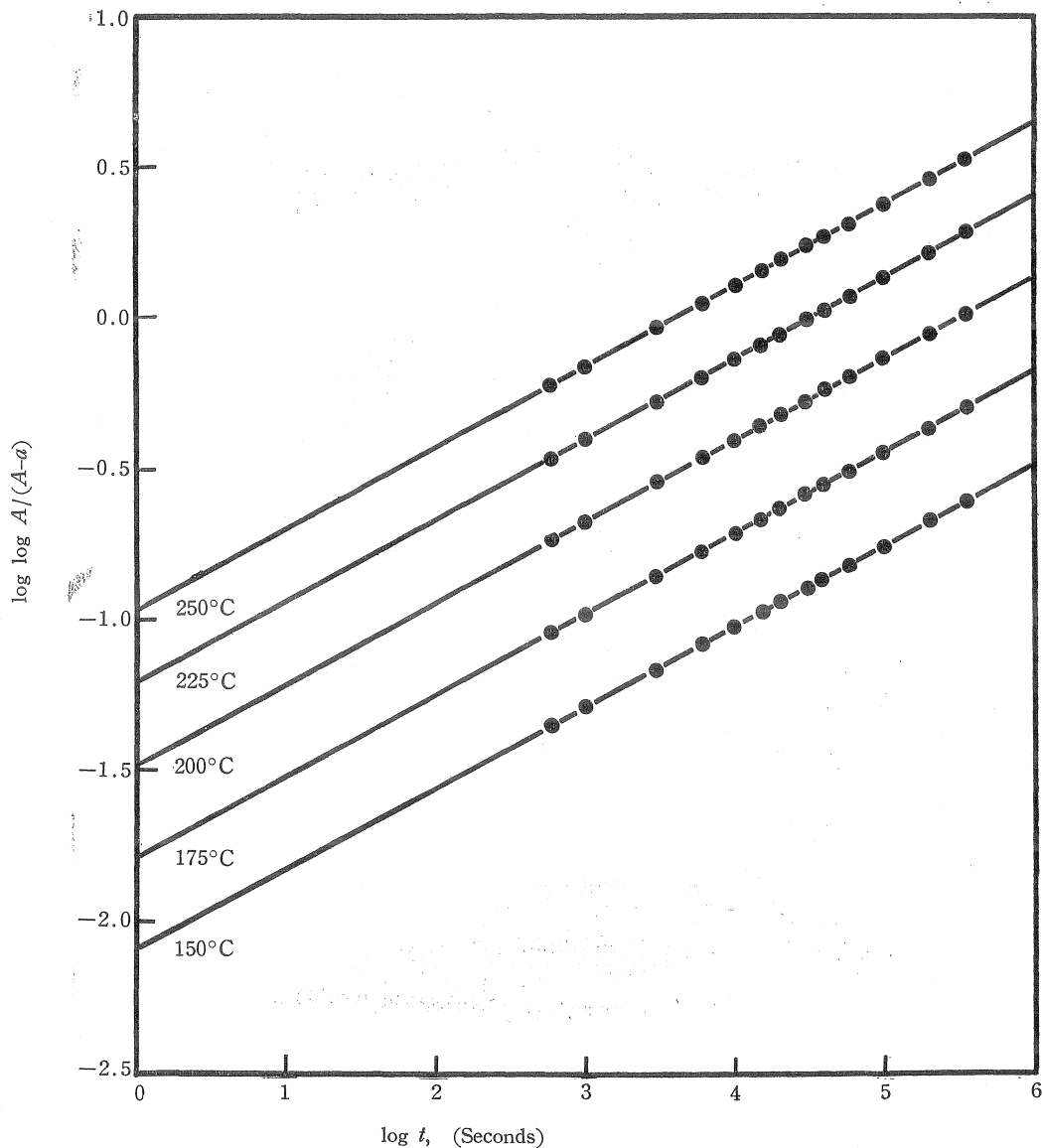


Fig. 3 Rate Equation for First Stage of Tempering of R80C6 Steel

where  $a = \frac{\Delta l}{l_0}$ ,  $\Delta l$  = amount of contraction,  $l_0$  = length of the sample at  $t = 0$ ,  $A$  = saturation value of  $a$ ,  $t$  = time,  $K$  = rate constant,  $m$  = constant. Considering the experimental contraction value at 250°C,  $255 \times 10^{-5}$  was adopted as the value of  $A$ . The composition of  $\epsilon$ -carbide produced at the first stage of tempering may be considered as always constant, and therefore the value of  $A$  can be assumed to be constant irrespective of temperature at lower than 250°C. This assumption coincides with that applied to plain carbon steel by C. S. Roberts et al.<sup>(5)</sup>, and it can be considered approximately valid.

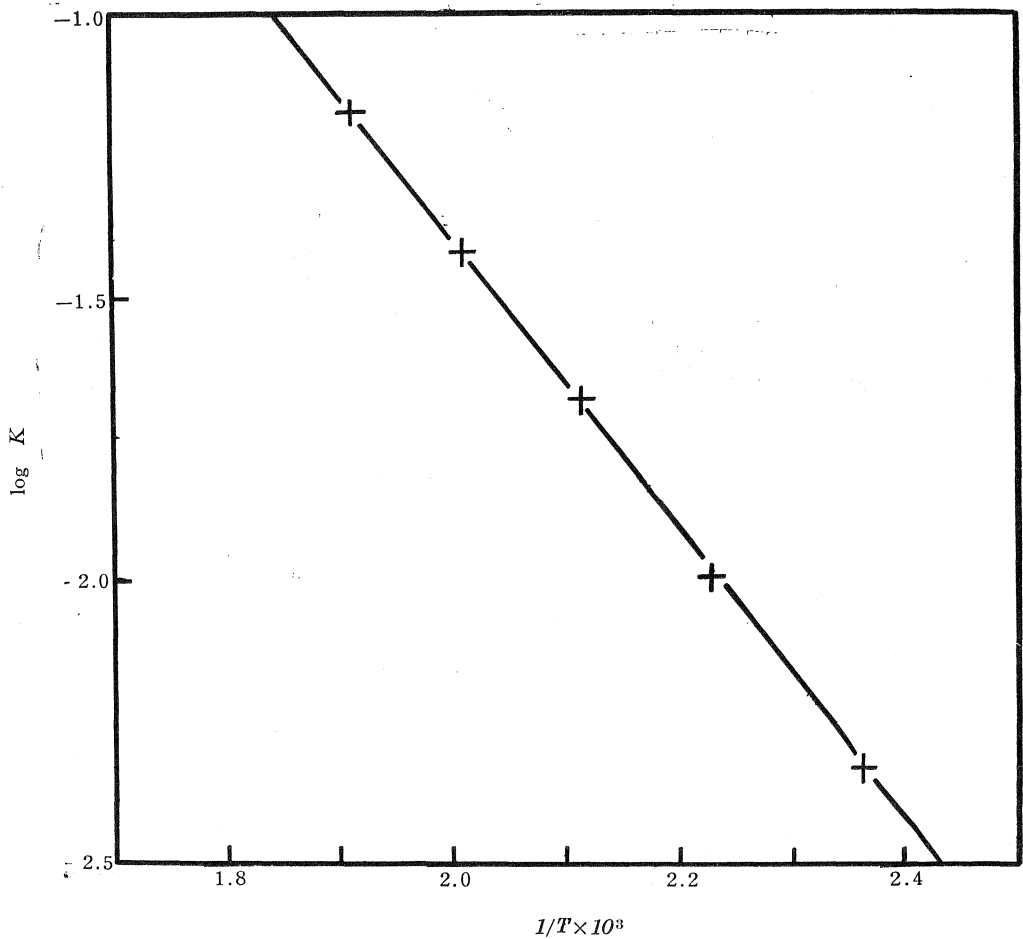


Fig. 4 Temperature Dependence of Rate Constant "K" for 1st Stage of Tempering, R80C6 Steel

The equation (1) is expressed in the following integrated formula :

$$\log. \log \frac{A}{A-a} = (m+1) \log t + \log \left( \frac{K}{2.3(m+1)} \right) \dots \dots (2)$$

Fig. 3 shows the relation between  $\log. \log \frac{A}{A-a}$  and  $\log t$  with the aid of  $A = 255 \times 10^{-5}$ ; this relation presents itself as a straight line at the respective tempering temperature between 150°C and 250°C; this means that the equation (2) holds true and therefore the equation (1) also holds good.

From the inclination of the straight lines in Fig. 3,  $m+1$  were calculated:  $m+1$  showed approximately definite values, viz, 0.266, 0.273, 0.266, 0.273 and 0.266 at the respective isothermal tempering temperature 150°C, 175°C, 200°C, 225°C and 250°C. Taking experimental errors into consideration, the mean value of these,  $m+1 = 0.27$ , therefore  $m = -0.73$  were adopted; this value is appropriate and valid in comparison with that obtained by Roberts et al<sup>(5)</sup> for plain carbon steel,

From the value at the point where each straight line crosses the ordinate of  $\log t = 0$  in Fig. 3,  $\log \left( \frac{K}{2.3(m+1)} \right)$  and therefore the value of  $K$  can be calculated. Each tempering temperature showed different value of  $K$ ; but taking the absolute temperature as  $T$ , the linear relation could be found between  $\log K$  and  $1/T$  as was shown in Fig. 4. This shows that the rate constant  $K$  can be expressed in the equation:

$$K = K_0 e^{-\frac{Q}{RT}} \dots \dots \dots (3)$$

where  $K_0$  = constant independent of temperature,  $Q$  = activation energy in this process,  $R$  = universal gas constant.

This relation is a general equation which holds true with the rate constants of various reactions. From Fig. 4 the values of  $K_0$  and  $Q$  were calculated as follows:

$$K_0 \approx 5.0 \times 10^3$$

$$Q \approx 1.17 \times 10^4 \text{ cal/}^\circ\text{K}\cdot\text{mol}$$

The activation energy for the diffusion of C in  $\alpha$ -Fe has been expressed in  $2 \sim 3.6 \times 10^4$  cal/ $^\circ\text{K}\cdot\text{mol}$ <sup>(5)</sup><sup>(11)</sup>: compared with this value, the above mentioned value of  $Q$  is remarkably small. A thing of this kind was found with plain carbon steel, and various explanations<sup>(5)</sup><sup>(6)</sup><sup>(9)</sup> have been given so far. But more results of researches in various fields are necessary to derive a right model of the mechanism of the first stage in the tempering process of chromium steels. For example, in our experiments mainly the growth of  $\epsilon$ -carbide has been studied, but more detailed data about the precipitation of the nucleus of  $\epsilon$ -carbide at the first stage of tempering process are indispensable for the further research. The effect and influence of the amount of chromium content upon the diffusion of carbon in martensite also requires further detailed investigations. Accordingly, in this report the author confined himself to reporting that the activation energy at the first stage in the tempering process of chromium steels with 8% Cr content (0.6% C), at least in the period of growth of  $\epsilon$ -carbide, was found to be  $Q = 1.17 \times 10^4$  cal/ $^\circ\text{K}\cdot\text{mol}$ .

### Conclusion

The author studied the tempering process of 8% Cr steel (0.6% C) in terms of length changes in the process of isothermal tempering and obtained the following conclusions.

- (1) The growth of  $\epsilon$ -carbide at the first stage of the tempering process reaches its saturation point at 250°C.
- (2) When the growth of  $\epsilon$ -carbide reaches its saturation, the contraction of  $255 \times 10^{-5}$  per unit length occurs.
- (3) The proceeding of the first stage in the tempering process follows Hardy and Heal's equation, that is,

$$\frac{da}{dt} = K (A - a) t^m$$

where  $a = \frac{4l}{l_0}$ ,  $4l$  = amount of contraction,  $l_0$  = length of sample at  $t = 0$ ,  $A$  = saturation value of  $a$ ,  $t$  = time,  $K$  = rate constant,  $m$  = constant.

(4) The results of the experiments showed  $m = -0.73$ .

(5) The rate constant  $K$  varies with temperature: indicating the absolute temperature as  $T$  and universal gas constant as  $R$ , it can be expressed in the following equation;

$$K = K_0 e^{-\frac{Q}{RT}}$$

where  $K_0$  is the constant independent of temperature, and  $K_0 = 5.0 \times 10^3$ , and  $Q$  is the activation energy for the proceeding of the first stage in the tempering process, and  $Q = 1.17 \times 10^4$  cal/°K·mol.

(6) The validity of the conclusion in the previous reports that in the intermediate tempering stage between the range of  $\epsilon$ -carbide and that of  $\theta$  phase, there exists  $\chi$ -carbide was proved and reaffirmed in the light of the results of measurement of contraction accompanying the process of isothermal tempering.

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