

17Cr-4Ni-4Cu Precipitation Hardening Stainless Steel

(The Fourth Report)

Tempering Process of 17Cr-4Ni-4Cu-0.07C Steel*

Mainly on the precipitation rate of Cu-rich phase and anomalous length change observed at the temperature between 500°C and 550°C

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The tempering process of the cast 17%Cr-4%Ni-4%Cu-0.07%C precipitation hardening type stainless steel and especially the anomalous length change in the isothermal tempering process at about 510°C were studied through dilatometric, magnetic and X-ray analyses, and the following results were obtained. (1) At a temperature lower than 350°C, only the precipitation of carbide is recognized. The amount of saturation contraction per unit length due to carbide precipitation in the isothermal tempering process, a_c , is 1.82×10^{-4} at 350°C. As we have previously reported⁽¹⁾, at a higher temperature than about 300°C this carbide is metastable $(\text{Fe, Cr})_3\text{C}$, θ phase, and it is replaced by more stable alloy carbide at a temperature higher than 510°C. (2) The precipitation of Cu-rich phase, playing the leading part in the age-hardening, becomes active at the temperature of about 370°C. It is reasonable to assume that, above 350°C, a_c increases linearly up to about 3.66×10^{-4} at 500°C, the greatest value of a_c corresponding to the complete precipitation of carbide, as the isothermal tempering temperature rises, and remains unchanged at a tempering temperature higher than 500°C. Thus it is shown that the precipitation rate of Cu-rich phase follows an equation of the type; $\dot{l} = K(a-l)t^m$, where: l = an amount of contraction per unit length of a specimen at time t , caused by the precipitation of Cu-rich phase, during the isothermal tempering at $T^\circ\text{K}$, a = the amount of saturation contraction per unit length of the specimen at $T^\circ\text{K}$, attributable to the precipitation of the Cu-rich phase, K = a temperature-dependent rate constant, m = a constant. (3) a increases linearly as the isothermal tempering temperature rises, from 0 at 370°C up to 1.5×10^{-5} at 510°C, and remains unchanged at a higher temperature than 510°C. (4) The results of experiments indicate $m = -0.84$, showing that the precipitation of Cu-rich phase is extremely rapid at the beginning. (5) The reaction rate constant K varies with temperature as follows; $K = K_0 \exp(-Q/RT)$, where: K_0 = a constant independent of temperature, Q = the activation energy for the proceeding of the precipitation of Cu-rich phase, R = universal gas constant, T = absolute temperature. The experimental results showed $K_0 = 2.5$ and $Q = 5.3 \times 10^8$ cal/°K mol. (6) The lattice spacings of α - and γ -phase at 15°C were 2.867Å and 3.586Å respectively. The mean thermal expansion coefficient of α -phase is $1.20 \times 10^{-5}/^\circ\text{K}$ and that of γ -phase is $1.89 \times 10^{-5}/^\circ\text{K}$. (7) After the solution treatment of 880°C \times 2 hours \rightarrow water-quenching to room temperature, the matrix of the hardened steel contains the retained austenite, γ_R , of about 13 wt% of a specimen. This γ_R decomposes as the tempering temperature is raised beyond 500°C. At 500°C about 40% of γ_R decompose and at 510°C about 90% of γ_R decompose. (8) In the isothermal tempering process of the as-water-quenched material at 550°C, $\alpha \rightarrow \gamma$ transformation gets into an action after about 3×10^4 seconds, and at 600°C, it does after about 1×10^8 seconds. (9) As a general tendency,

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the higher the isothermal tempering temperature was, the larger the contraction per unit length of a specimen was. But, the amount of contraction per unit length in the isothermal tempering process at 510°C is smaller than that at 500°C, and in the case of isothermal tempering at 550°C, the contraction per unit length in the early period of the tempering is smaller than that at 500°C, reversing the situation in the later period. This anomaly can be explained with above-mentioned results.

Introduction

The martensitic transformation temperature (M_s point) of 17-4PH type stainless steel, which has been developed as the precipitation-hardening steel, is strongly affected by the solution treatment temperature (S.T. temperature)⁽²⁾; when the S.T. temperature rises higher than 1020°C, M_s point gets down lower than room temperature. Accordingly, the steel of this type is regarded as a good controlled-transformation aging steel.

After a usual solution treatment, such as 880°C × 2 hours → W.Q., the structure of this steel is composed of a large amount of martensite, some retained austenite (γ_R) and a small quantity of δ -ferrite, while their ratio changes remarkably according to chemical composition and S.T. temperature. In the tempering process of this steel, it is sure that the precipitation of Cu-rich phase is remarkable, but the precipitation of a very small amount of carbide can not be neglected⁽¹⁾.

We have noticed that the dimensional change of this steel is very anomalous in the tempering process at the temperature between 500°C and 550°C. In this report, the tempering process of this steel, together with this anomaly, will be discussed in detail.

Materials and Procedures

The samples used in the experiments are the cast 17-4PH type stainless steel with base composition of 17%Cr-4%Ni-4%Cu, and were taken out of the same heat used in the study reported in the third thesis⁽¹⁾. The process of preparation is the same with that in the first report⁽²⁾. Its chemical analyses are given again in the next table.

Chemical Analyses of Sample (wt%)

C	Si	Mn	Cr	Ni	Cu
0.07	0.51	0.60	17.18	4.55	4.27

The experimental procedures used are mainly dilatation tests, magnetic analyses with ballistic-galvanometer technique and X-ray analyses et al.

The length-change of the material in the isothermal tempering process,

excluding the thermal expansion, were measured as follows. In the first place, a specimen was sufficiently aged at 400°C and carbide were fully precipitated. Then it was heated at the rate of 5°C/min and the heating dilatation curve was obtained. As we have previously mentioned in the third report⁽¹⁾, the precipitation of Cu-rich phase occurs at the temperatures higher than about 370°C. Therefore, it may safely be said that, at least, at the temperatures lower than 350°C, this curve shows the pure thermal expansion. Thus, using this dilatation curve in the above-mentioned temperature range, we obtained the value of $1.29 \times 10^{-5}/^{\circ}\text{K}$ for the mean coefficient of thermal expansion of the steel. If the specimen does not suffer precipitations or transformations, this mean thermal expansion coefficient may be applicable up to 600°C as the first approximation. Accordingly, the difference between the length of the sample calculated with this mean thermal expansion coefficient and the measured value may be considered as the change in length due to tempering- or aging-reaction itself excluding thermal expansion above 400°C. Thus, we get the isothermal tempering length-changes, excluding the thermal expansion, for 455°C, 480°C, 500°C, 510°C, 550°C and 600°C.

Besides, it was ascertained by preliminary magnetic analyses that τ_R did not decompose at the temperatures lower than 490°C. Accordingly, as to the length-changes in the isothermal tempering process at 455°C and 480°C, the differential dilatation curves were measured using the annealed sample, which was completely aged at the respective temperature, as the standard. This is the same method as described in the third report⁽¹⁾ to obtain the saturation contraction per unit length of the material. The result was compared with that through the above mentioned method. Both the results showed satisfactory agreement within the experimental error, showing the adequateness of the above mentioned method.

The dimensions of the samples used for magnetic and dilatation tests were 5mm ϕ \times 80mm, and that for X-ray analyses were 20mm ϕ \times 5mm and 20mm \times 25mm \times 1mm. Samples were solution treated for 2 hours at 880°C and then water-quenched to room temperature, prior to a desired tempering, unless it had a proviso. All heat treatments above room temperature were done in a vacuum furnace of about 5×10^{-5} mmHg.

Results and Discussions

Saturation Contraction Value observed in Isothermal Tempering below 510°C

Fig. 1 shows the relation between a saturation contraction per unit length after aging and a aging temperature. As previously mentioned in the third report⁽¹⁾, small saturation contraction values observed in the isothermal tempering below 350°C are caused by the precipitation of carbide, and the rapid increase of the

Saturation Contraction per Unit Length of tempered 17-4PH Steel

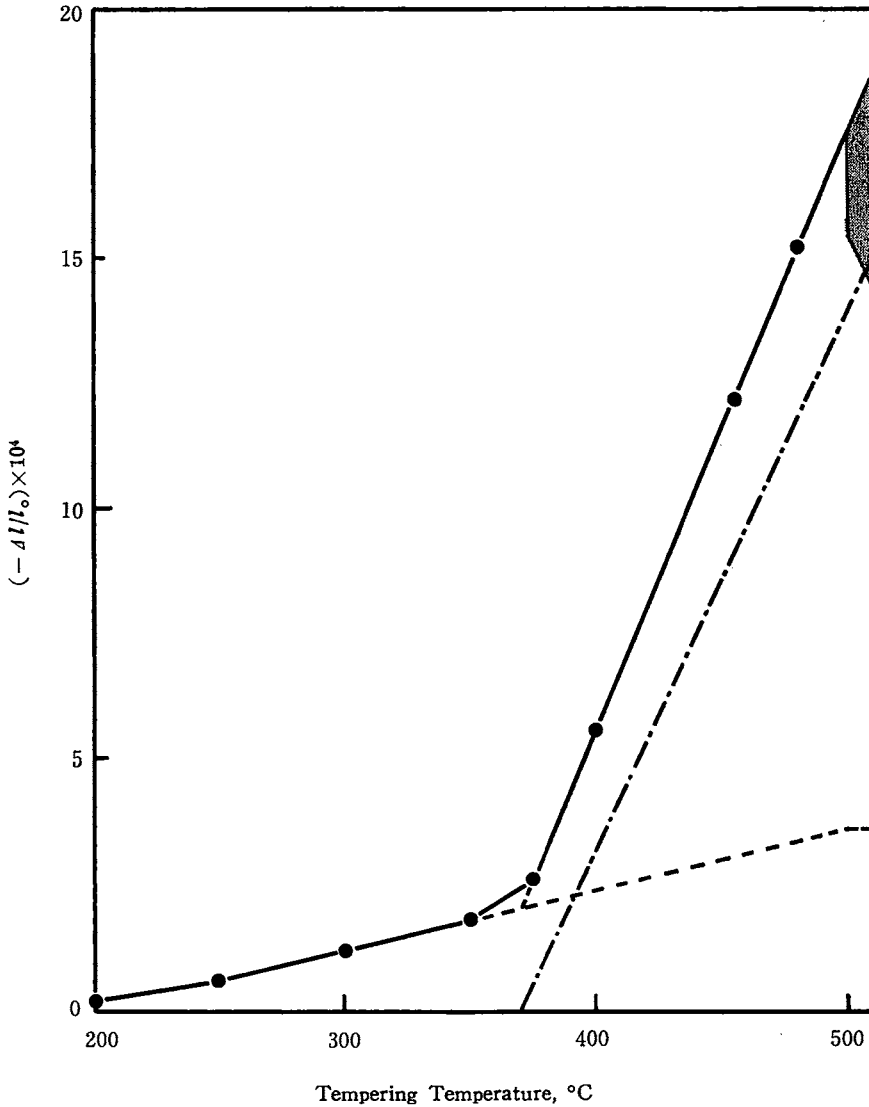


Fig. 1

saturation contraction, which begins at about 370°C, may be regarded as the precipitation of Cu-rich phase. The saturation contraction values below 480°C depended only on the aging temperature, namely they were not affected by a small change in the solution treatment temperature and refrigeration condition. On the other hand, at the aging temperature higher than 510°C, the saturation contraction value at a given aging temperature varied considerably according to preceding thermal treatment condition. This will be discussed later.

Now, as reported in the first report⁽²⁾, the main diffraction line ($2\theta=68.6^\circ$ with $\text{Cr-K}\alpha$) of the material, subzero-treated for 5 hrs at -100°C , splits into one

strong line ($2\theta=68.7^\circ$) and one weak line after the aging at 480°C for 20 hrs, and the diffraction angle of this weak line ($2\theta=67.1^\circ$) indicates that it is resulted from the precipitated Cu-Ni solid solution with about 25 at% Ni. Using this results, we obtained the value of about 1.5×10^{-3} for the saturation contraction per unit length when Cu was precipitated completely. Considering that a small contraction caused by the precipitation of carbide must be added to this calculated value, this value may be sufficient to explain the result shown in Fig. 1. That is, from a viewpoint of the contraction per unit length it may be appropriate to deduce that the precipitated Cu-rich phase is Cu-Ni solid solution with about 25 at% Ni.

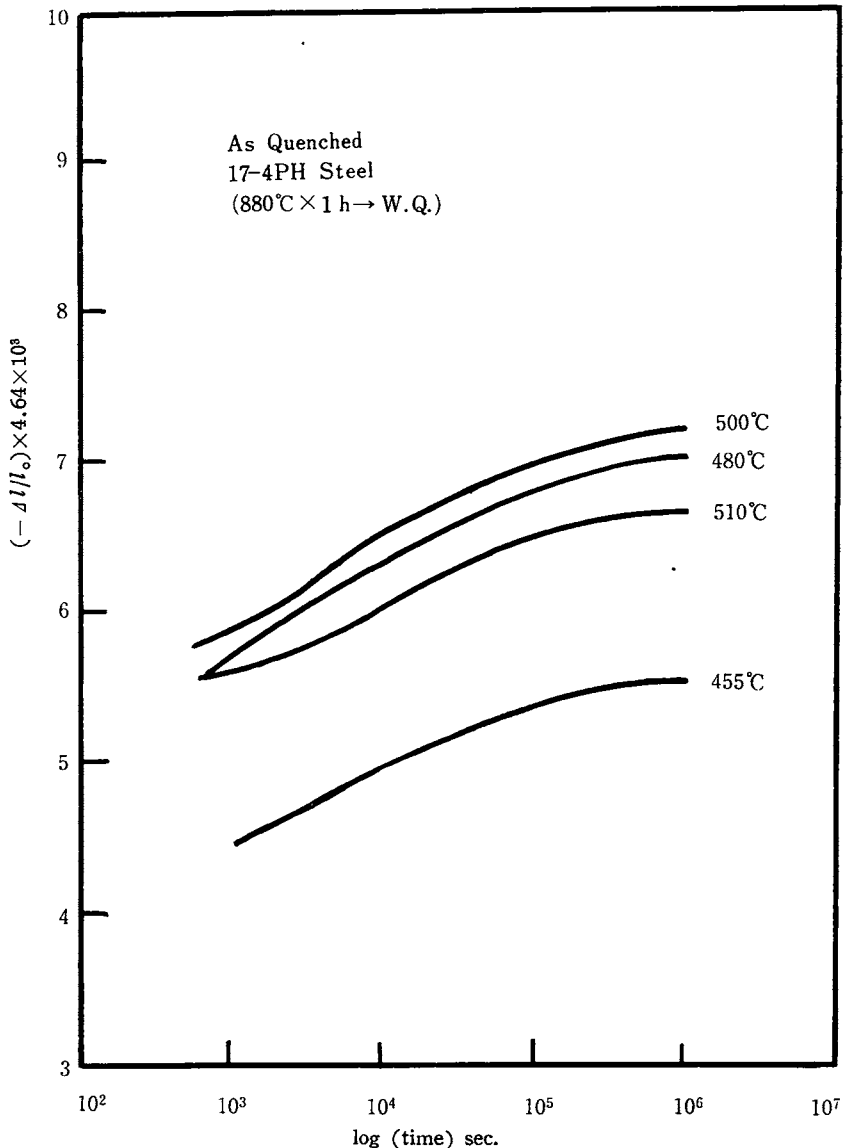


Fig. 2

Contraction during Isothermal Tempering at various Temp.

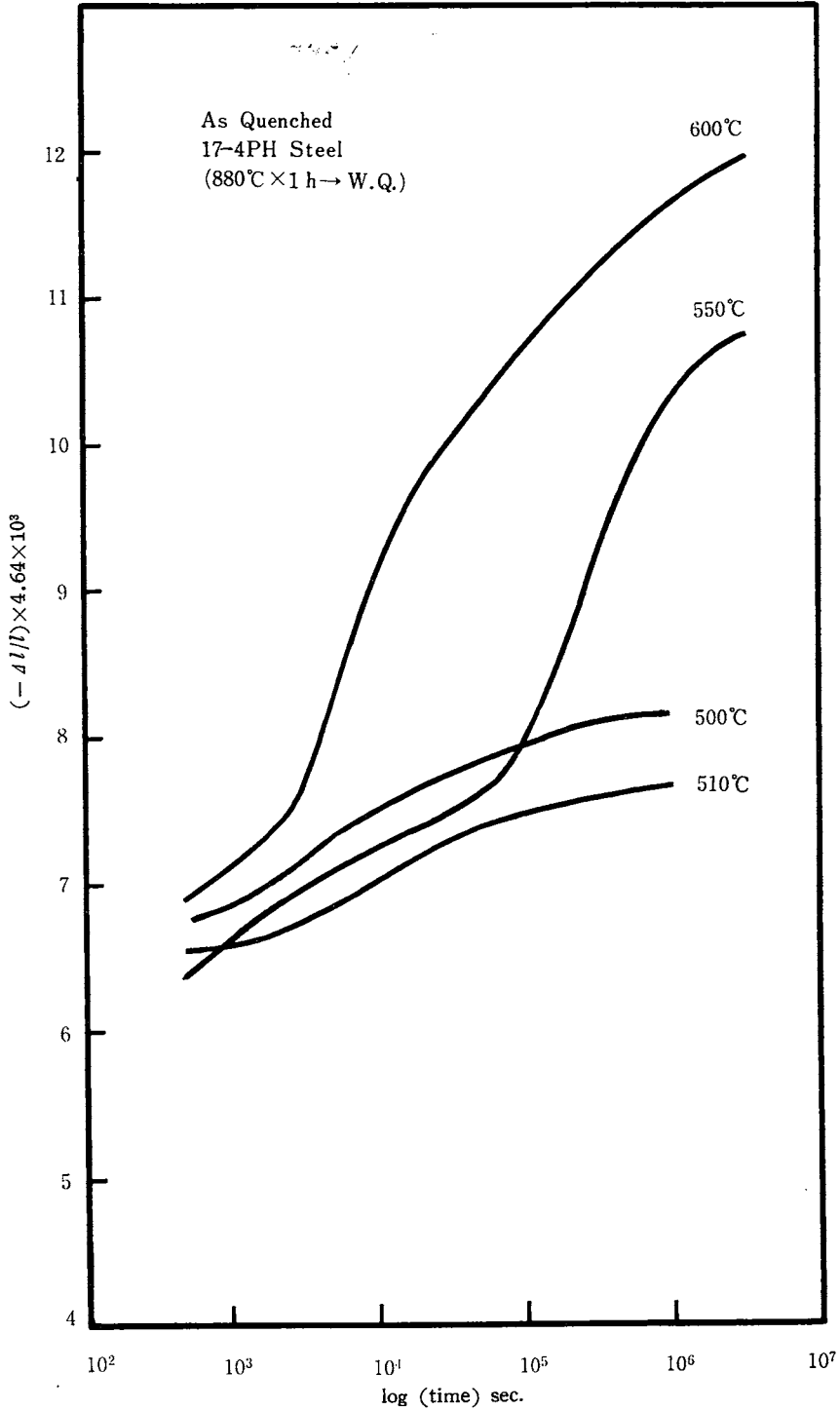
Contraction during Isothermal
Tempering at various Temp.

Fig. 3

Contraction observed in Isothermal Tempering Process

Fig. 2 and Fig. 3 show the contraction per unit length in the isothermal tempering process at 455°C, 480°C, 500°C, 510°C, 550°C and 600°C. Time was measured immediately after the material reached to a desired temperature. Since a few minutes are required before the desired temperature is reached, in the discussion about the length-changes in isothermal tempering process, it is necessary to compensate the contraction occurred in this transitional period by an appropriate formula. Practically, it is very difficult to do so. However, this is a problem only in the early period of tempering, and after the lapse of long period the small discrepancies at the original point of time make little or no difference in the form of curves denoting the relation between time and change in length, that is, the time correction may be neglected. This is a reason why, in Fig. 2 and Fig. 3, initial parts of the curves are eliminated.

As shown in these figures, generally speaking, the higher the isothermal tempering temperature is, the larger the contraction per unit length is. However, a remarkable anomaly is observed at temperatures ranging from 500°C to 550°C; the contraction per unit length at 510°C tempering is smaller than that at 500°C tempering, and in the case of isothermal tempering at 550°C, the contraction per unit length in the early period is smaller than that at 500°C tempering reversing the situation in the later. As mentioned above, this anomaly in the observed length-change is not resulted from the inappropriateness or neglect of time-correction. It is sure that it is a characteristic property of this material. This problem will be discussed later in detail.

Magnetic Analyses of Isothermal Tempering Process

Fig. 4 and Fig. 5 show the magnetization curves of this material isothermally tempered at 450°C and 510°C. The time was measured immediately after the desired temperature was reached, and the heating rate was 5°C/min. When a specimen, which is solution-treated at 880°C for 2 hours and then water-quenched to room temperature, is isothermally tempered at 450°C, the change of the magnetization is not observed. On the other hand, when it is kept at 510°C, a small increase of magnetization is observed as the tempering proceeds. This small increase of the magnetization, however, can not be observed in the specimen subzero-treated for 5 hours at -100°C. While, it is more remarkable when the specimen is solution-treated at 960°C. As previously reported⁽²⁾, the material solution-treated at 960°C contains a large amount of γ_R , as compared with the material solution-treated at 880°C. And, when the material is subzero-treated for 5 hours at -100°C immediately after water-quenching from 880°C \times 2 hours, we can scarcely observe γ_R in its structure. Putting together this result and the fact

that the decomposition of τ_R is accompanied with a increase of magnetization, it can be concluded that τ_R decomposes during the isothermal tempering at 510°C. As previously mentioned and shown in Fig. 1, when the material is isothermally tempered at a given temperature higher than 500°C, the saturation contraction value varies considerably according to the preceeding thermal treatment. Now, it will be concluded reasonably that this variety of saturation contraction value is attributable to a difference in the amount of τ_R contained in the material. Such an interpretation is supported by the fact that the contraction per unit length increases with decreasing amounts of τ_R contained in the material. Such an

Magnetization Curves on Isothermal Tempering
of as-quenched 17-4PH Steel.

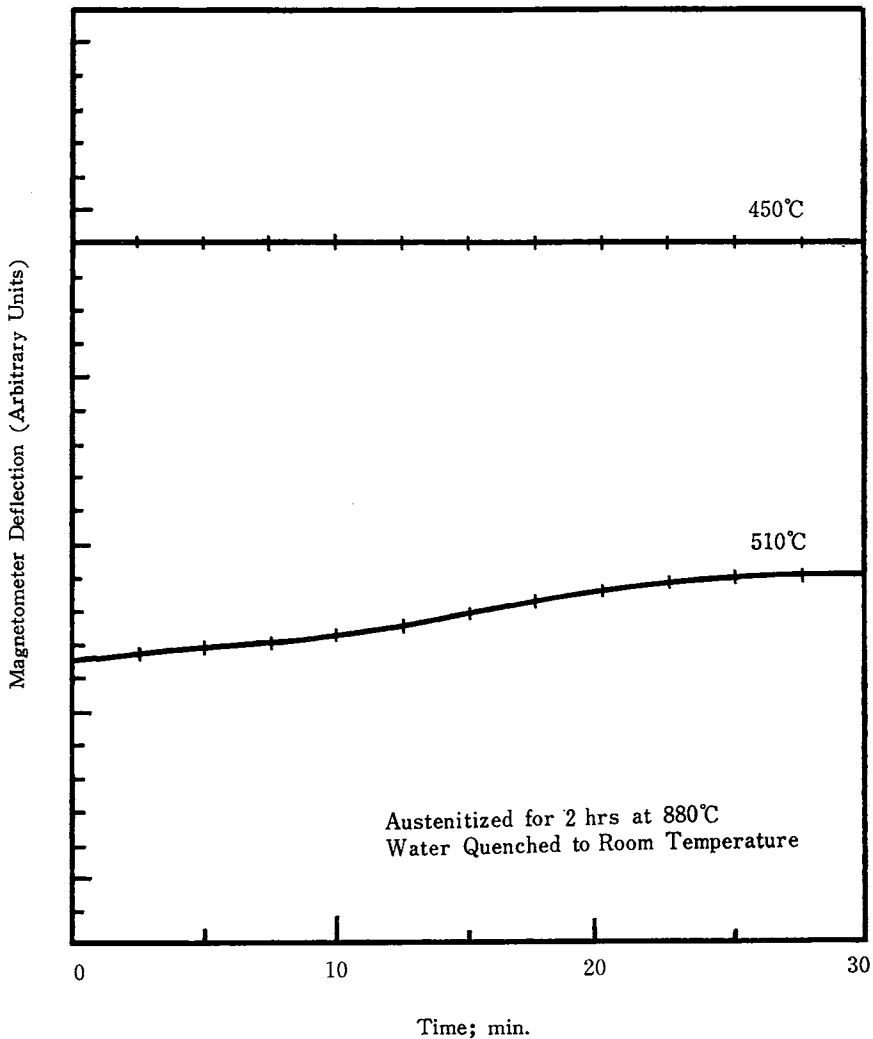


Fig. 4

example is given in Fig. 11, which shows the length-change during the isothermal tempering at 500°C: that is, the amount of contraction of subzero-treated material, which scarcely contains γ_B , is larger than that of as-water-quenched material,

Magnetization Curves on Isothermal Tempering
as-quenched 17-4PH Steel at 510°C

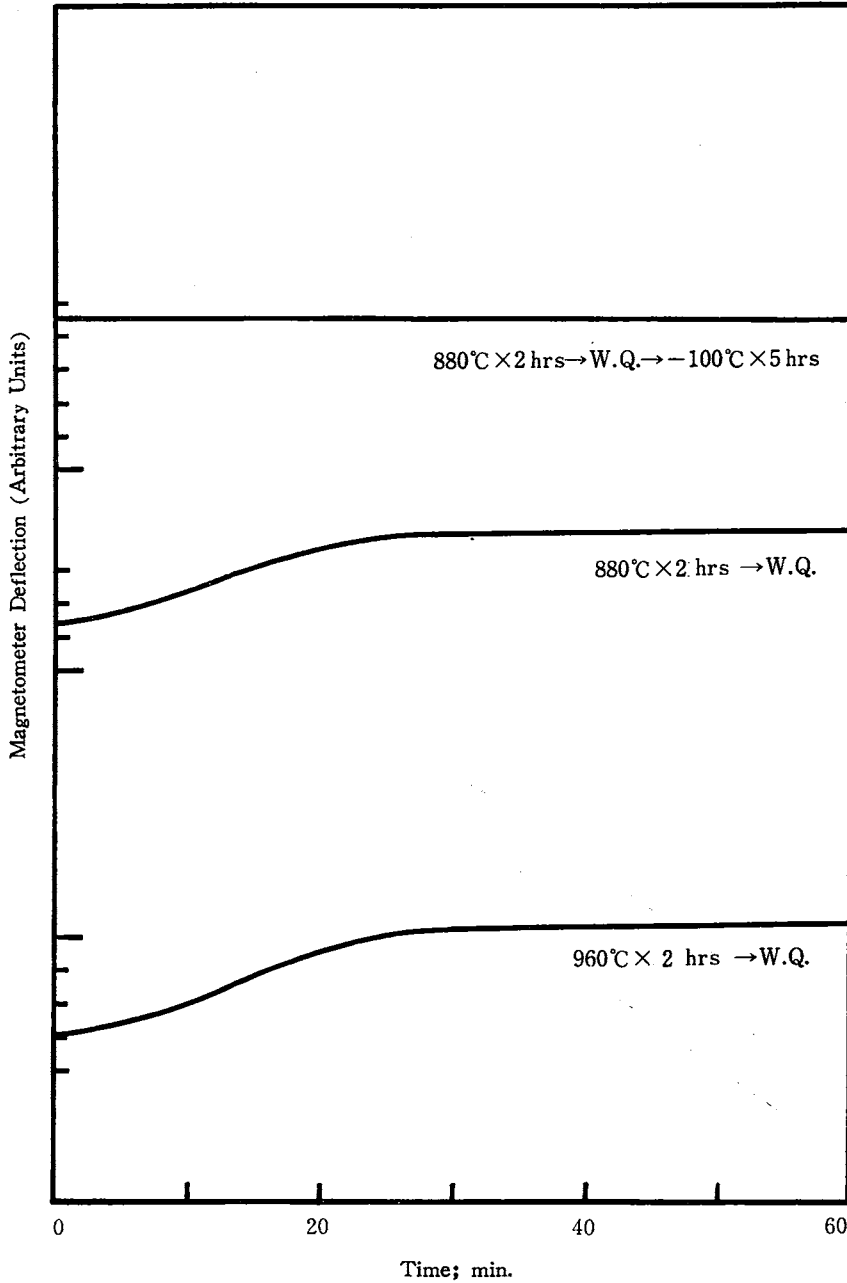


Fig. 5

which contains considerable amount of r_R . In due consideration of the results given in Figs. 1, 4, 5 and 11, the decomposition of r_R seems to get into an action at about 500°C. From a viewpoint mentioned above, it will be considered that the anomalous contraction rate, observed in the isothermal tempering process at 510°C, is attributable to the decomposition of r_R .

Now, as reported in the first report⁽²⁾, with the heating rate of 5°C/min, this steel suffers A_3 transformation at 570°C~580°C, and as is well known, this transformation is accompanied with the contraction. Consequently, the anomalous behavior appeared in the contraction curve of the material isothermally tempered

Temperature Dependence of α 17-4PH Lattice Spacing

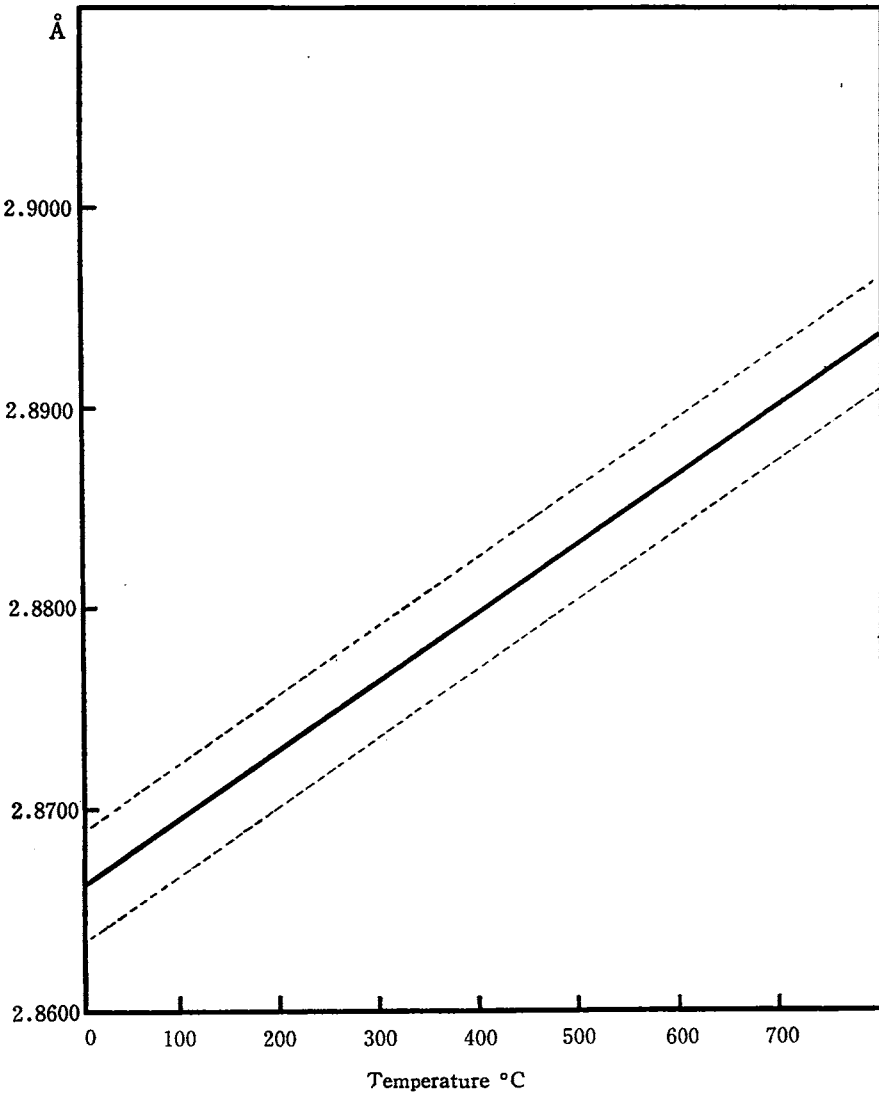


Fig. 6

at 550°C may be interpreted as follows; in the early period of tempering, the curve is lower than that tempered at 500°C because of complete decomposition of γ_B , and in the latter period it is higher than that at 500°C because A_3 transformation occurs gradually. However, to discuss this point in detail, it is necessary to get a quantitative relation between dilatation and decomposition of γ_B , and between contraction and $\alpha \rightarrow \gamma$ transformation.

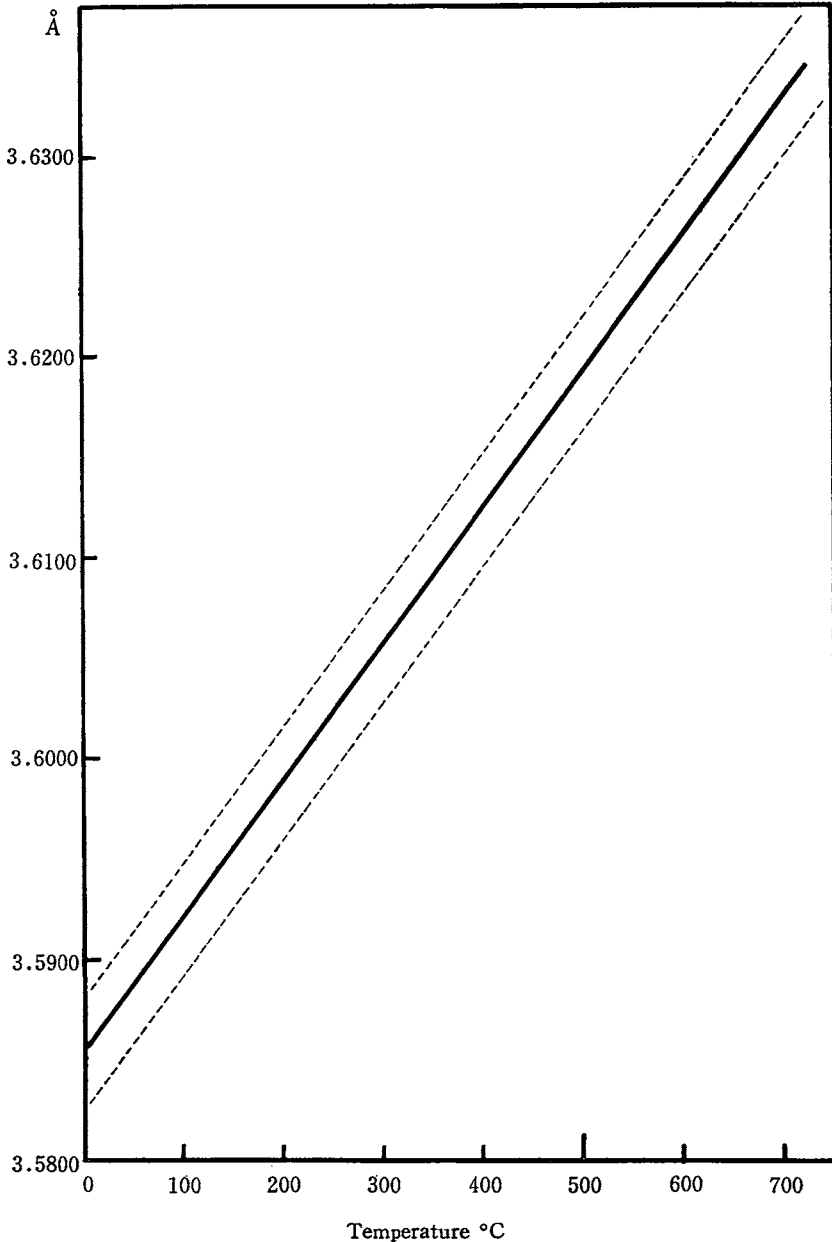
Temperature Dependence of γ 17-4PH Lattice Spacing

Fig. 7

Lattice Spacings of α - and γ - Phase as a Function of Temperature

Fig. 6 shows lattice spacing of α -phase in 17-4PH Type stainless steel as a function of temperature, and Fig. 7 shows that of γ -phase. They were obtained through a X-ray diffractometer equipped with a high-temperature camera, and the dotted line indicates the limit of experimental error. The lattice parameters of α - and γ -phase at 15°C were 2.867 Å and 3.586 Å respectively, and their mean thermal expansion coefficients, obtained through these X-ray diffraction experiments, were $1.20 \times 10^{-5}/^{\circ}\text{K}$ and $1.89 \times 10^{-5}/^{\circ}\text{K}$ respectively.

Kinetic Treatment of Isothermal Tempering

As already mentioned above, the contraction of the material accompanying the isothermal tempering at a temperature lower than 350°C is caused by carbide precipitation, and that at a temperature higher than 400°C is caused mainly by precipitation of Cu-rich phase and partially by precipitation of θ -phase. Below 350°C, the amount of saturation contraction per unit length, α_c , caused by carbide precipitation, increases linearly with the rising of isothermal tempering temperature, as shown in Fig. 1. Above 400°C, it is difficult to separate these two kinds of contraction, but, as a first approximation, α_c is assumed to have the same tendency as described above, and is indicated by the dotted line in Fig. 1. However, taking the carbon content of the material (0.07% C) into account, the greatest value of α_c , which is caused by the complete precipitation of carbide, must be about 3.66×10^{-4} . On the above-mentioned dotted line, this value corresponds to a value at about 500°C. Here, we made a 2nd assumption that, above 500°C, α_c takes a definite value of 3.66×10^{-4} . Thus, α_c takes the value as follows; 3.08×10^{-4} at 455°C, 3.41×10^{-4} at 480°C and 3.66×10^{-4} above 500°C, and with the scale graduated on the ordinate shown in Figs. 2, 3, 10, 11, 12, 13 and 14 these values are replaced by 1.43, 1.58 and 1.70 respectively.

Now, according to the author's study on the tempering process of high chromium steel⁽⁸⁾, the precipitation of θ carbide is completed within 15 minutes at the latest, at the tempering temperature higher than 400°C. In due consideration of the above-mentioned result, and deducing from the increasing rate of contraction during the isothermal tempering at 350°C, it may be permitted to consider that the precipitation of θ carbide in the tempering process of 17-4PH Type stainless steel proceeds nearly at the same rate as in the chromium steel. Consequently, above 455°C, it may be assumed reasonably that the contraction caused by the precipitation of θ phase is saturated within 10^8 seconds at latest.

Moreover, as previously mentioned, in this steel, r_R does not decompose at the temperature lower than 490°C. Accordingly we have a following relation for the isothermal tempering process of the material below 490°C (763°K);

$$l_m - a_c = l \quad (1)$$

where: l_m = an amount of contraction per unit length of the material observed at any time t , during the isothermal tempering at $T^\circ\text{K}$ lower than 763°K (490°C), a_c = as already mentioned, the amount of saturation contraction per unit length at $T^\circ\text{K}$, caused by the precipitation of carbide, l = an amount of contraction per unit length at time t , attributable to the precipitation of Cu-rich phase, during the isothermal tempering at $T^\circ\text{K}$.

After a long lapse of time, l is equal to a , the amount of saturation contraction per unit length of the material, attributable to the Cu-rich phase precipitation. The relation between a and T is given in Fig. 1 with dash-dotted line. Here, we must remember that the equation (1) is valid only below 490°C (763°K). While, as shown in Fig. 1, a - T curve starts from 370°C (643°K) and increases with the rising temperature linearly up to 490°C (763°K). So, we have assumed that this linear relation holds as yet so far as a reaches the greatest value, 1.5×10^{-3} , obtained through X-ray diffraction analyses as described previously. Thus, the greatest value of a corresponds to the isothermal tempering at about 510°C (783°K), and above this temperature it may be safely said that a remains unchanged. Accordingly it may be reasonably assumed that a is expressed in the form as follows;

$$a = 1.07 (T - 643) \times 10^{-5} \text{ at } 643^\circ\text{K} (370^\circ\text{C}) \leq T^\circ\text{K} \leq 783^\circ\text{K} (510^\circ\text{C}),$$

$$a = 1.5 \times 10^{-3} \text{ at } T^\circ\text{K} \geq 783^\circ\text{K} (510^\circ\text{C}) \text{ and}$$

$$a = 0 \text{ at } T^\circ\text{K} \leq 643^\circ\text{K} (370^\circ\text{C}).$$

If the precipitation of Cu-rich phase may be assumed to proceed by nucleation and growth, and the change in unit length, caused by this reaction, may be assumed to be proportional to the extent of the reaction, then the isothermal contraction curve for such a process would follow a general differential equation of the type pointed out by H.K.Hardy and T.J.Heal⁽⁴⁾

$$\frac{dl}{dt} = K(a-l)t^m \quad (2)$$

where: K = a temperature-dependent rate constant, m = a constant. In the integral form, equation (2) becomes

$$\log \cdot \log \frac{a}{a-l} = (m+1) \log t + \log \frac{K}{2.3(m+1)} \quad (3)$$

If $\log \cdot \log a/(a-l)$ is plotted as a function of $\log t$ for the isothermal tempering process at 455°C and 480°C , a straight line with a slope of $m+1=0.16$ is observed as given in Fig. 8, showing the validity of this formulation at these temperature at the least. Again, in the isothermal tempering process at 500°C , the linear

Rate Equation for Cu-rich Phase Precipitation in 17-4PH Steel.
(Isothermal Tempering)

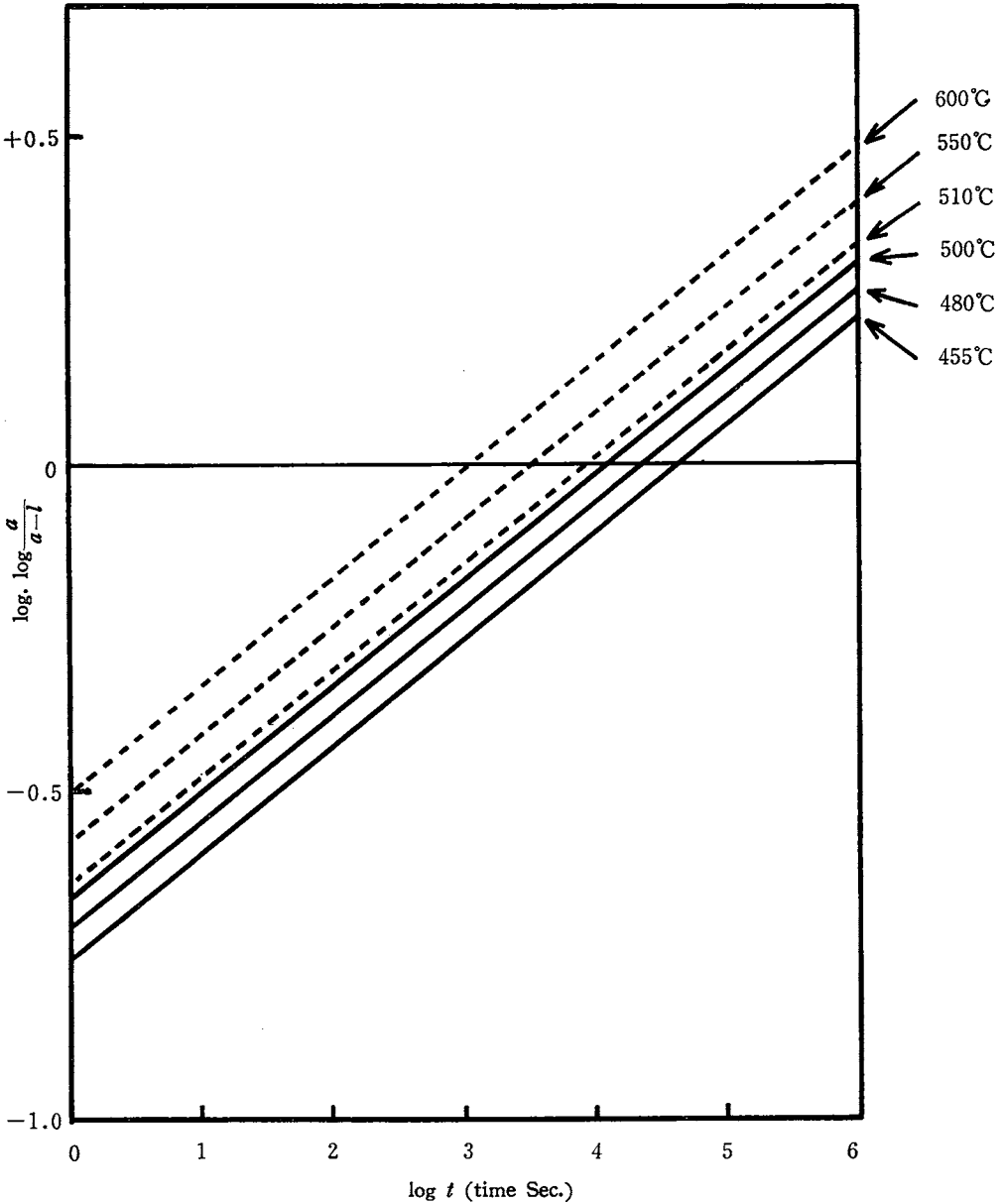


Fig. 8

relation between $\log \cdot \log a/(a-l)$ and $\log t$ is hold for the material which is subzero-treated for 5 hours at -100°C and can scarcely contain the retained austenite r_R . This means that the equation (3) and therefore the equation (2)

Temperature Dependence of Rate Constant "K"
for Cu-rich Phase Precipitation in 17-4PH Steel

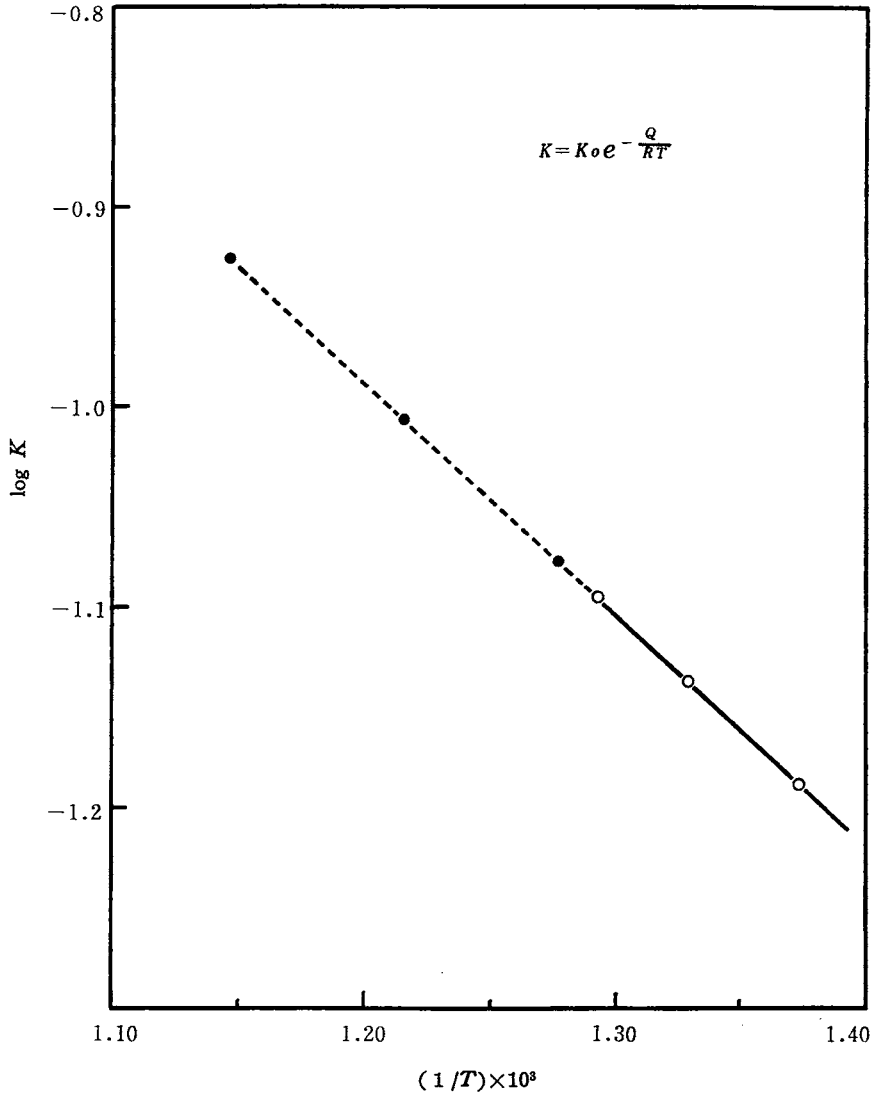


Fig. 9

is applicable for the precipitation process of Cu-rich phase.

Now, K reflects the temperature dependence of the reaction rate, and may follow the usual exponential form;

$$K = K_0 e^{-\frac{Q}{RT}} \quad (4)$$

Length Changes in 455°C and 480°C Isothermal Tempering
of 17-4PH Steel

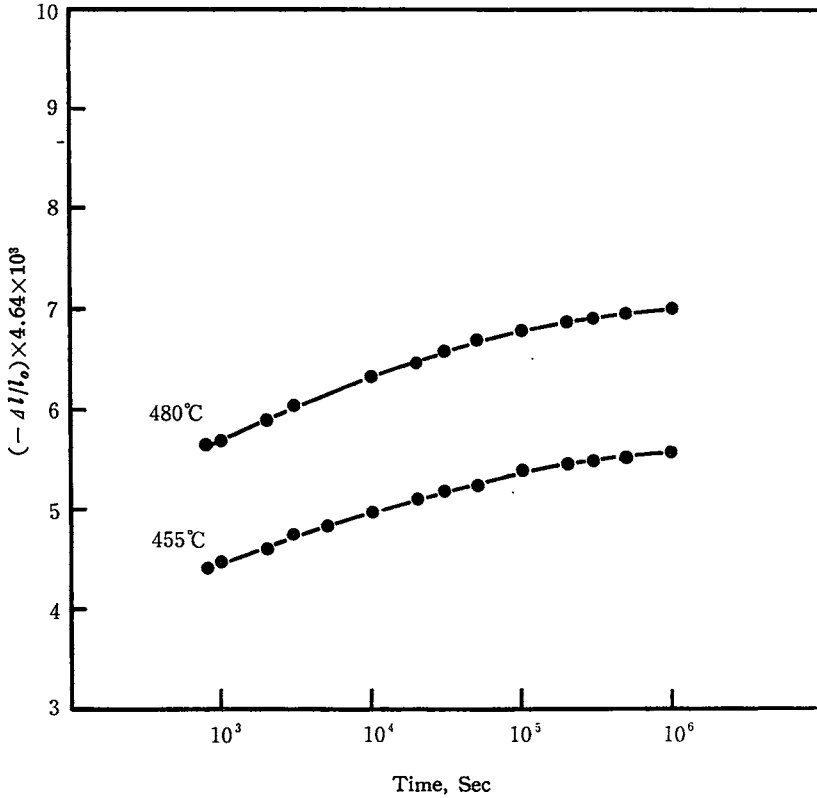


Fig. 10

where: K_0 =a constant independent of temperature, Q =activation energy in this process, R =universal gas constant, T =absolute temperature. From the values at the points where lower two solid straight lines cross the ordinate of $\log t=0$ in Fig. 8, $\log K/2.3(m+1)$ and therefore the values of K at 455°C and 480°C can be calculated. Using these values of K , the values of K_0 and Q were calculated as follows;

$$K_0=2.5$$

$$Q=5.3 \times 10^8 \text{ cal/}^\circ\text{K mol}$$

Again, using the values of K_0 and Q mentioned above, and following the equation (4), the value of K at 500°C, and accordingly the value of l at 500°C, was calculated. Thus, we can obtain the value of $l+a_c$ at 500°C, and the result is given in Fig. 11 with solid line. As shown in the figure, this result approximately coincides with the observed value for the subzero-treated material indicated by open circle. A small discrepancy may be attributable to the decomposition of a

Length Changes in 500°C Isothermal Tempering of 17-4PH Steel

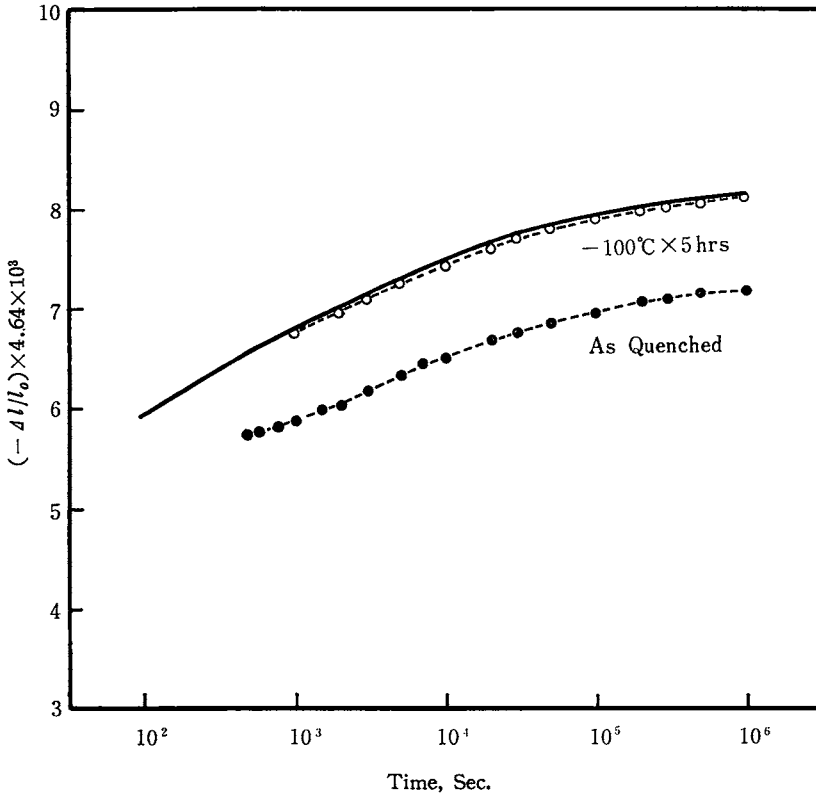


Fig. 11

very little τ_B , still retained in the subzero-treated material. Accordingly, it may be safely said that the isothermal contraction due to the precipitation of Cu-rich phase is represented by the Equation (2), (3) and (4) with $m = -0.84$, $K_0 = 2.5$ and $Q = 5.3 \times 10^8$ cal/°K mol.

A negative quantity for m indicates that the reaction is extremely rapid at the beginning and that there is no incubation period. The same characteristics were found for the carbide reaction in the tempering process of chromium steel⁽⁸⁾⁽⁵⁾ and this may indicate that the usual nucleation and growth mechanism does not apply in these case.

The above mentioned value of Q may be rather small compared with the usual activation energy for the diffusion. As previously reported⁽⁸⁾ a thing of this kind was found with plain carbon steel and chromium steel, and various explanations have been given so far. To make this problem clear, and to get the correct meaning of m , the further resarches are indispensable, and now they are in progress.

If the tempering temperature rises higher than 500°C τ_B begins to decom-

Length Changes in 510°C Isothermal Tempering of 17-4PH Steel

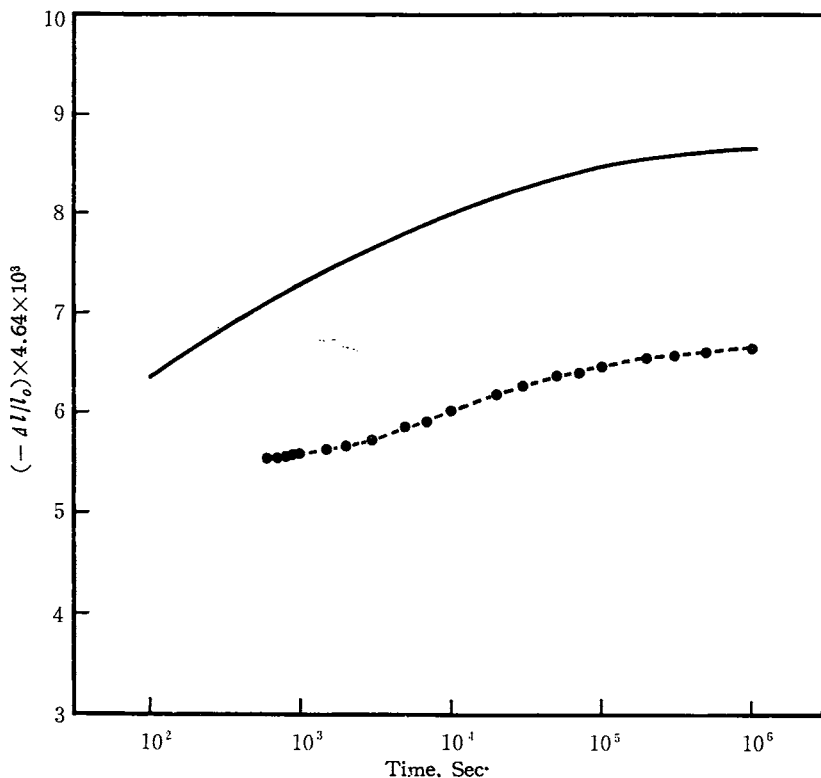


Fig. 12

pose, and above 550°C A_3 transformation begins to proceed, so that, at a higher temperature than 500°C, in the observed value of the isothermal contraction, a length change due to the A_3 ($\alpha \rightarrow \gamma$) transformation and the decomposition of γ_R should be included. Accordingly, it is impossible to get the precipitation rate of Cu-rich phase at this temperature range experimentally. But, it may be permitted to assume as a first approximation that the relations represented by the Equations (2), (3) and (4) are applicable up to about 600°C, though they were obtained from the isothermal tempering process of the material at the lower temperature than 500°C. Thus, the values of K at 510°C, 550°C and 600°C are obtained through the procedure as shown in Fig. 9, and they are indicated by solid circle in the figure respectively. Then, using Equation (3), the relations between $\log \cdot \log a/(a-l)$ and $\log t$ for the isothermal tempering at 510°C, 550°C and 600°C were obtained. They are given in Fig. 8 with dashed lines. In this way, we can deduce the value of l at higher temperature than 500°C.

Thus we can calculate an amount of contraction per unit length, R , at time t later than 10^3 sec, attributable to the precipitation of Cu-rich phase and carbide during the isothermal tempering of the as-water-quenched material

Length Changes in 550°C Isothermal Tempering
of 17-4PH Steel

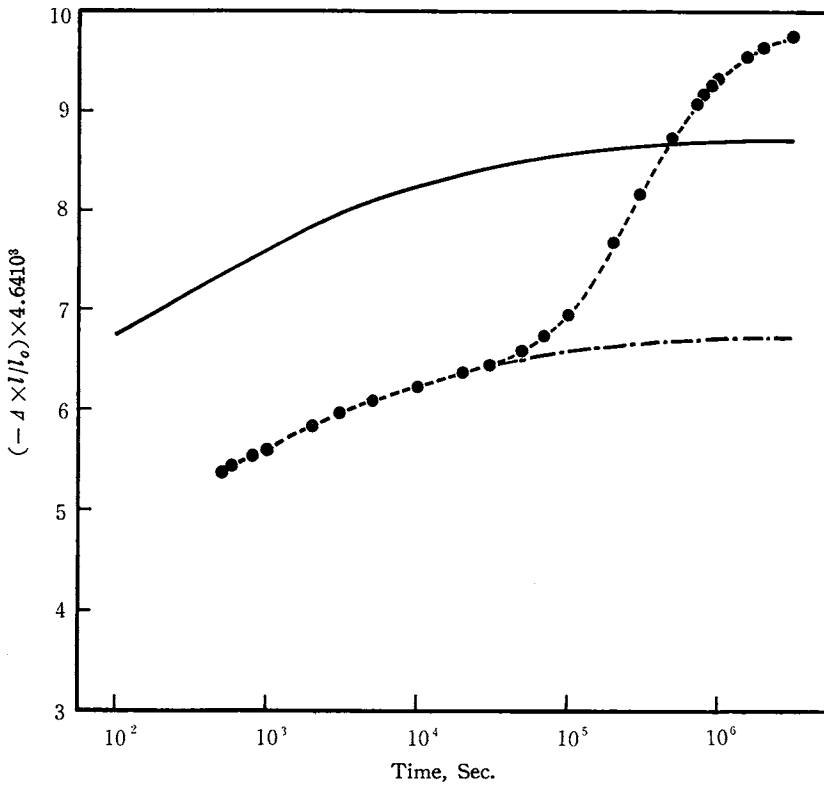


Fig. 13

at the temperature range between 455°C and 600°C.

$$R = l + a_c$$

Below 490°C, and accordingly at 455°C and 480°C, R should be identical with l_m .

The calculated values R for the isothermal tempering at 455°C and 480°C are given in Fig. 10 with solid lines, and, as shown in the figure, fairly correspond with the observed values indicated by solid circles.

The observed total change in the unit length of the material, D , and the calculated value, R , for the isothermal tempering at 500°C, 510°C, 550°C and 600°C are shown as a function of time in Fig. 11, 12, 13 and 14 respectively, where values of D are indicated by solid circles and R is given with a solid line.

The difference between D and R at 500°C and 510°C gives the expansion due to the decomposition of γ_R .

At the tempering temperature of 550°C and 600°C, the decomposition of γ_R is completed during the very early stage of tempering. Again, it may be said that the rapid increase of D shown in Fig. 13 and 14 corresponds to the beginning of $\alpha \rightarrow \gamma$ transformation. Displace R -curve down upon D -curve in parallel with

Length Changes in 600°C Isothermal Tempering
of 17-4PH Steel

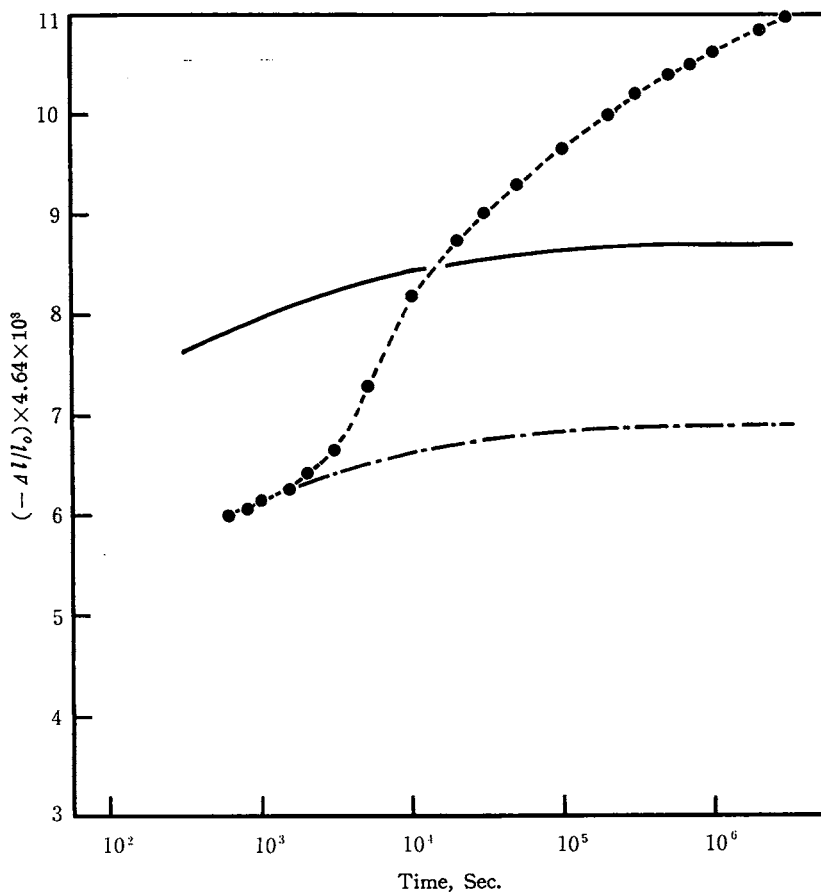


Fig. 14

ordinate so as to make the initial part of R -curve overlap that of D -curve, and the result obtained is R' -curve denoted by dot-dash in these figures. Then, the difference between D and R' gives the contraction due to $\alpha \rightarrow \gamma$ transformation.

Using the amounts of $D-R'$, obtained from Fig. 13 and Fig. 14, together with the results shown in Fig. 6 and Fig. 7, we can get the relations between a percentage of $\alpha \rightarrow \gamma$ transformation and a time t in the isothermal tempering process of this steel at 550°C and 600°C, and they are shown in Fig. 15. Again, using the amounts of " $R \rightarrow R'$ parallel displacement", obtained from Fig. 13 and Fig. 14, we can deduce an amount of r_R contained in the as-water-quenched material. The result obtained is as follows: when 17%Cr-4%Ni-4%Cu-0.07%C steel is solution-treated for 2 hrs at 880°C and then water-quenched to room temperature, the amount of r_R contained is about 13% of total weight of the specimen. This value nearly coincides with that derived through X-ray analyses. Accordingly, it may be said reasonably that the above-mentioned " $R \rightarrow R'$ parallel displacement"

$\alpha \rightarrow \gamma$ Transformation during The Isothermal Tempering
of as-water-quenched 17-4PH Steel

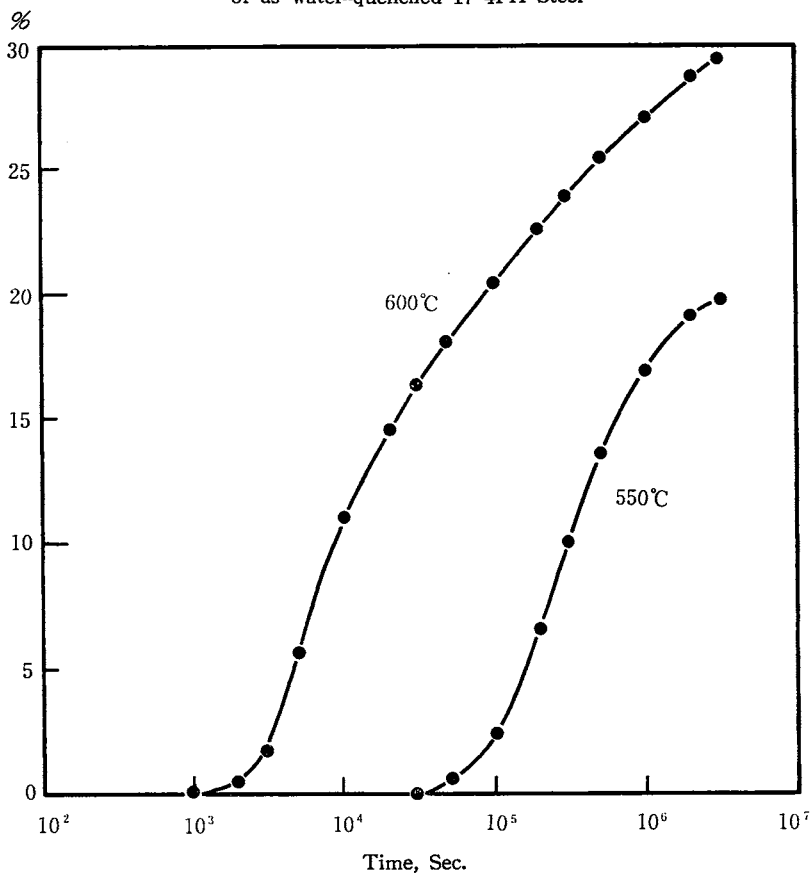


Fig. 15

operation is regarded as appropriate.

Of course, there may be some question in our above-mentioned opinions that the precipitation of Cu-rich phase still proceeds while $\alpha \rightarrow \gamma$ transformation goes into an action. If it is assumed that the precipitation of Cu-rich phase is completed prior to the opening of $\alpha \rightarrow \gamma$ transformation, then the above-mentioned procedures must be changed as follows: $D-R'$ is replaced with $D-R'_0$ with the proviso that R'_0 is the value of R' where R' -curve branches off from D -curve. Accordingly, in this case, in Fig. 15, 600°C-curve is shifted upwards within 4.5 units of the ordinate, and 550°C-curve is shifted upwards within 1.6 units of the ordinate remaining their starting point unchanged. This means that 600°C-curve in Fig.15 includes a relative error of about 15% and 550°C-curve in the same figure includes a relative error of about 10%, at the most. However, it is sure that more researches are required to get a correct conclusion, and they are in progress. Here, suffice it to say that Fig. 15 shows a general tendency of $\alpha \rightarrow \gamma$

Decomposition of τ_R during The Isothermal Tempering
of as-water-quenched 17-4PH Steel

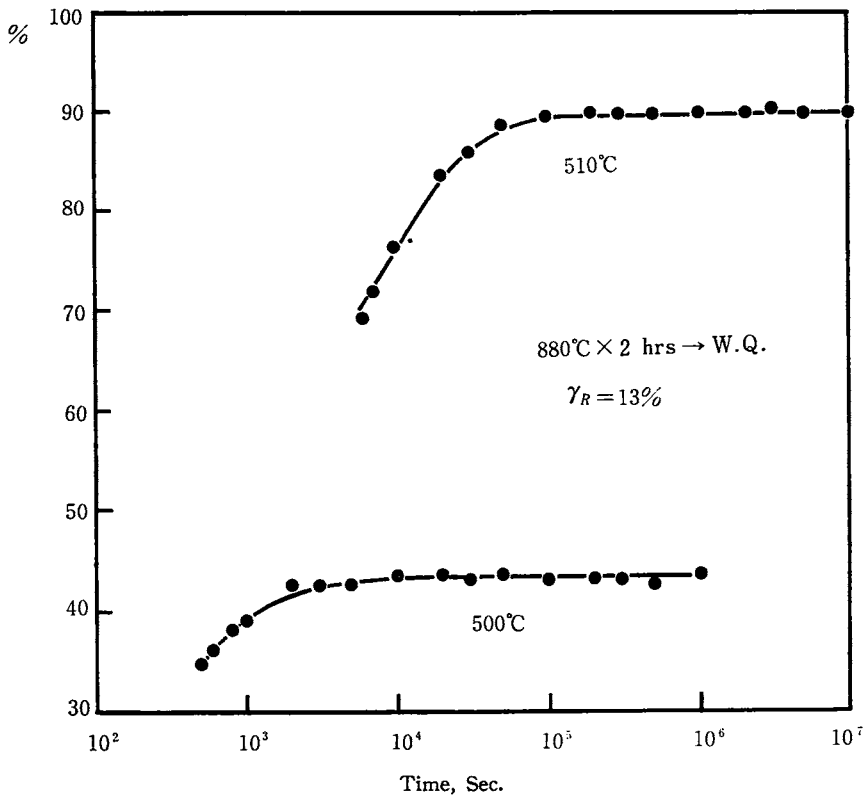


Fig. 16

transformation rate of the material at 550°C and 600°C.

Fig. 16 shows the decomposition rate of τ_R , in the isothermal tempering process of the as-water-quenched material at 500°C and 510°C, obtained from the results given in Figs. 6, 7, 11 and 12, where the amount of τ_R contained in the as-quenched structure is about 13% of total weight of the specimen.

Conclusion

The authors studied the isothermal tempering process of the cast 17%Cr-4%Ni-4%Cu-0.07%C stainless steel, and obtained the following results.

1. Below 350°C, only the precipitation of carbide is recognized. The saturation contraction per unit length due to carbide precipitation in the isothermal tempering at 350°C is 1.82×10^{-4} .

2. The precipitation of Cu-rich phase becomes active at the higher temperature than about 370°C, and its rate follows a general differential equation of the type;

$$\frac{dl}{dt} = K(a-l)t^m$$

or in the integrated form,

$$\log \cdot \log \frac{a}{a-l} = (m+1) \log t + \log \frac{K}{2.3(m+1)}$$

where: l = an amount of contraction per unit length of a specimen at time t , caused by the precipitation of Cu-rich phase, during the isothermal tempering at $T^\circ\text{K}$, a = the amount of saturation contraction per unit length of the specimen at $T^\circ\text{K}$, attributable to the precipitation of the Cu-rich phase, K = a temperature-dependent rate constant, m = a constant.

3. a was expressed in the form as follows;

$$\begin{aligned} a &= 1.07(T-643) \times 10^{-5} && \text{at } 643^\circ\text{K}(370^\circ\text{C}) \leq T^\circ\text{K} \leq 783^\circ\text{K}(510^\circ\text{C}), \\ a &= 1.5 \times 10^{-5} && \text{at } T^\circ\text{K} \geq 783^\circ\text{K}(510^\circ\text{C}) \text{ and} \\ a &= 0 && \text{at } T^\circ\text{K} \leq 643^\circ\text{K}(370^\circ\text{C}) \end{aligned}$$

4. The results of the experiments showed $m = -0.84$. A negative quantity for m indicates that the precipitation of Cu-rich phase is extremely rapid at the beginning and that there is no incubation period.

5. The reaction 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 form;

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

where: K_0 = a constant independent of temperature, Q = the activation energy for the proceeding of the precipitation of Cu-rich phase. The experimental results showed $K_0 = 2.5$ and $Q = 5.3 \times 10^3$ cal/ $^\circ\text{K}$ mol.

6. The lattice spacings of α - and γ -phase are 2.867 Å and 3.586 Å respectively at 15°C, and their mean thermal expansion coefficients are $1.20 \times 10^{-5}/^\circ\text{K}$ and $1.89 \times 10^{-5}/^\circ\text{K}$ respectively.

7. After the solution treatment of 880°C × 2 hours → water quenching to room temperature, the amount of austenite retained in the matrix of the hardened steel was about 13 wt% of a specimen, and this retained austenite γ_R decomposes as the tempering temperature is raised beyond 500°C. At 500°C and 510°C, about 40% and about 90% of γ_R decompose respectively.

8. In the isothermal tempering process of the as-water-quenched material at 550°C, $\alpha \rightarrow \gamma$ transformation gets into an action after about 3×10^4 sec, and at 600°C, it does after about 1×10^3 sec.

9. The anomalous length change in the isothermal tempering process at the temperature between 500°C and 550°C can be explained with above-mentioned results.

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