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Isothermal annealing at various temperatures: effect of temperature change on the process kinetics observed

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Measurements of diverse process kinetics during isothermal annealing are often performed by repeated quenching to a much lower measuring temperature. The warming-up procedure, in order to continue the anneal, can drastically influence the physical process under consideration. The effect is caused by the increasing atomic mobility within the sample and by the changing instantaneous equilibrium values which the observed physical quantity aims at as the temperature rises. In this paper, short-range ordering (SRO) kinetics observed by resistivity measurement curves are calculated for ideal and real experimental conditions and compared with experimental results. It is shown that for not too short annealing times the effect can be compensated by a correction in the annealing times used. In this case results corresponding with an ideal annealing experiment are obtained. A lower and an upper limit of annealing time is observed, beyond which experiments yield pathological results and cannot be corrected.

1. Introduction

Usually the kinetics of a thermally activated process is investigated during isothermal annealing after a more or less sudden temperature change. In practice this temperature change is not infinitely fast, the beginning of the observed kinetics is not strictly isothermal but is influenced by the changing temperature. This way the ideal process kinetics being observed may be altered by the dependence on temperature of:

(i) The number of defects, which are responsible for a thermally activated process *via* diffusion (linked to the formation enthalpy of the defects).
(ii) The migration of the defects (linked to the migration enthalpy of the defects).
(iii) The final equilibrium value of the process, which is usually a function of temperature.
(iv) The physical quantity itself, which is used as a measure of the process under observation. For example, in the case of resistivity measurements the kinetics being observed are hidden behind temperature dependent phonon scattering.

To avoid these problems especially (iv), the investigation is often carried out by quenching the sample repeatedly from the actual annealing temperature to a low constant measuring temperature. This way, however, the temperature jump preceding each isothermal annealing period is considerably enlarged.

It is well known that the quenching rate is essential for the thermodynamical state of a quenched sample. To an even greater extent the annealing kinetics is influenced if the relaxation time τ_w of the thermal equilibration after a change of temperature from a low measuring temperature to the annealing temperature (warming-up) is of the same order of magnitude as the relaxation time of the physical process under investigation. For this case the finite process of thermal equilibration does not only mean a simple reduction of the effective annealing time [1], as often considered by researchers. In the present paper this warming-up effect on the process kinetics observed, is calculated for the example of SRO-kinetics as investigated by resistivity measurement and compared with recent experimental results on a Cu–16 at % Al alloy. The possibility of considering the effect of warming-up by correcting the actual annealing times is discussed.

2. Experimental realization of measuring isothermal annealing kinetics

2.1. Measurement at-temperature

Obviously the easiest method of realizing an investigation of isothermal annealing kinetics is to observe the kinetics at the annealing temperature before and after a small and sudden change in the annealing temperature. In this case the kinetics observed is influenced only by the temperature change from the previous annealing temperature T_0 to the actual annealing temperature T_a (temperature up-step for $T_a > T_0$, temperature down-step for $T_a < T_0$). However, as mentioned earlier an elevated and even changing, measuring temperature may reduce measuring accuracy. Furthermore, the changing phonon spectrum may influence the temperature dependence of the physical quantity observed (deviation from Mathiessen's rule for electrical resistivity) leading to some uncontrolled shift with temperature. This may particularly be a problem if possible equilibrium states of the system are investigated as a function of temperature (equilibrium line), as usual for SRO-investigations [2].

2.2. Low temperature measurement

If the measurement is carried out at a low measuring temperature one has an unavoidable finite period of thermal equilibration (warming-up) at the beginning of the isotherm and both a warming-up and a quenching period for each measured point of the annealing kinetics.

We restrict the present paper just to considering the effect of the warming-up process because:

(i) The quenching rate is usually greater than the warming-up rate by some orders of magnitude.
(ii) For the quenching process the high temperature region (high atomic mobility) is quickly passed, whereas for the warming-up process the temperature change becomes slower and slower in the region of high mobility as the temperature approaches the annealing temperature T_{a}.

For these reasons the warming-up process seems to be of fundamental importance for the results of measurements and the effect of quenching at least below a certain characteristic temperature can be neglected, especially if the quenching procedure is done in a reproducible way.

2.2.1. Low temperature measuring technique with repeated warming-up procedure from T_{m} to T_{a}

The most frequent method of an isothermal annealing experiment in connection with resistivity measurement is to frequently interrupt the annealing by quenching the sample to a low measuring temperature T_{m} and to subsequently continue the annealing at the actual annealing temperature T_{a} (Fig. 1a). In this case each measured point of the isotherm corresponds to the partially annealed frozen state by quenching the sample to the measuring temperature. Each single measurement is followed by a warming-up process from T_{m} to T_{a}. Apart from the complications of a large temperature change this method has the advantage of a high measuring accuracy (low measuring temperature) and a constant phonon spectrum. In the present paper we show the limits of this method and how the difficulties may be overcome.

2.2.2. Low temperature measuring technique with the characteristics of a single warming-up procedure from T_{m} to T_{a}

In Fig. 1b the following temperature programme is sketched: After an initial thermal equilibration at T_0 the sample is quenched for the measurement to T_{m}. This step is followed by the first annealing period at T_{a} and a measurement at T_{m}. Then again an annealing at T_0 is carried out until equilibrium is reached (the corresponding annealing time may be known from previous annealing experiments), which is followed by a quench and measurement at T_{m} before the next, prolongated annealing period at T_{a}. This way, any point of the isothermal curve can be measured for the same initial state corresponding to T_0 with the warming-up characteristics of just a single step from T_{m} to T_{a}. Obviously this method only works if the process to be investigated tends towards equilibrium states. In spite of the complicated method, this procedure was used in the present paper to study experimentally the influence of the warming-up procedure on the observed annealing kinetics.

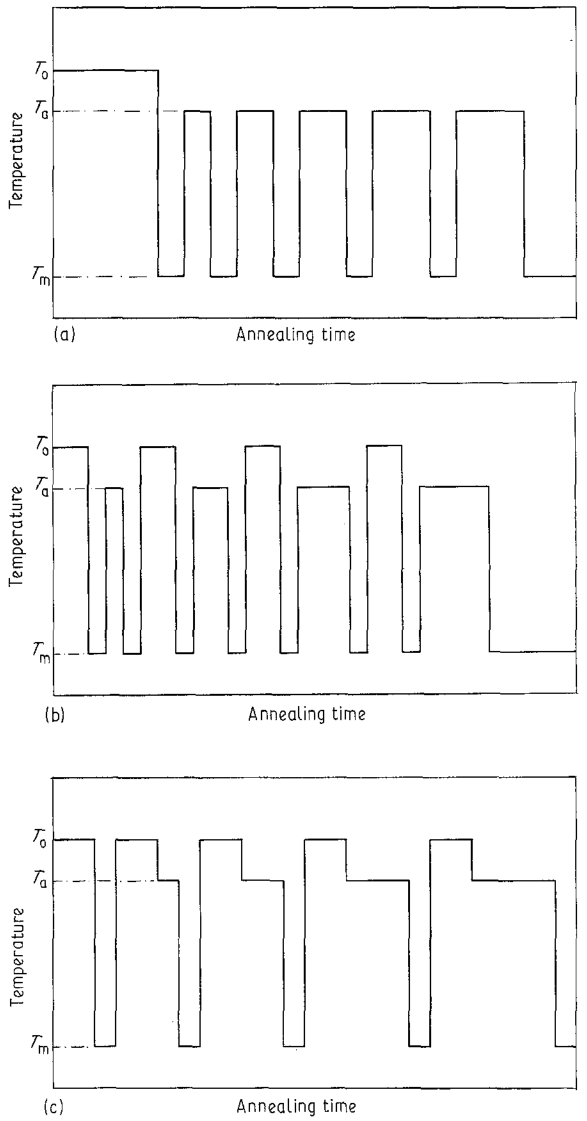

Figure 1 Temperature as a function of time in a down-step annealing experiment (schematic); (a) Starting from an initial equilibrium state, which corresponds to T_0, the annealing at T_{a} is frequently interrupted for measuring at a low constant temperature T_{m}, (b) after each annealing period at T_{a} and subsequent measurement at T_{m} the sample is again equilibrated at T_0 and measured at T_{m} to guarantee the re-establishment of the initial state. For each annealing period the thermal treatments of the previous annealing steps have to be repeated. The method is used to study a single warming-up procedure from T_{m} to T_{a} by means of a repeated quenching to the low measuring temperature T_{m}, (c) similar to (b), but immediate annealing at T_{a} after equilibration at T_0 without intermediate measurement at T_{m}. This way in spite of the low measuring temperature, as for an at-temperature measurement just the single temperature change from T_0 to T_{a} is involved in the observed kinetics.

2.2.3. Low temperature measuring technique with the characteristics of an at-temperature measurement

A method of avoiding both the elevated measuring temperature and the large warming-up step from T_m to T_a is sketched in Fig. 1c [3]: After an initial thermal equilibration at T_0 the sample is quenched for the measurement to T_m. To avoid influences by the large temperature change from T_m to T_a the sample is again annealed at T_0 until equilibrium is reached; then the temperature is abruptly changed to T_a for the first annealing period. After a quench and measurement at T_m the equilibrium is adjusted again at T_0; another period of annealing at T_a follows immediately and so on. By this procedure, in spite of the low measuring temperature T_m there is only the influence of the small temperature change from T_0 to T_a similar to the measurement at-temperature. On the other hand this method means that for each point measured the equilibrium at T_0 has to be first re-established and then the annealing kinetics at T_a run through up to that point. The amount of measuring time involved makes this method impracticable.

3. Calculation of experimentally observed kinetics

3.1. Kinetics of the processes involved

3.1.1. Thermal equilibration

For the warming-up period the time dependence of the specimen temperature is assumed to follow a simple exponential law with relaxation time τ_w; this means that we disregard a transitory over- and undershooting of the annealing temperature or an oscillatory behaviour. Thus

$$T(t) = T_a - (T_a - T_m)\exp(-t/\tau_w) \qquad (1)$$

where T_a is the annealing temperature, T_m is the measuring temperature, and τ_w is the relaxation time of thermal equilibration (warming-up relaxation time).

3.1.2. SRO-induced electrical resistivity

Theoretical considerations and a lot of experimental investigations show that there is a linear relation between the Warren–Cowley SRO-parameters and the residual electrical resistivity [4]. Therefore, changes of the SRO-parameters can be read directly from resistivity changes.

Consequently SRO-kinetics are often investigated by resistivity measurement: The sample is annealed at temperature T_0 until the resistivity reaches an equilibrium value $\rho_\infty(T_0)$. Then the annealing temperature is changed to T_a, which can be either higher than T_0 (temperature up-step annealing experiment) or lower (down-step).

By investigating sequences of such isothermal anneals for a number of alloys including the Cu–16 at % Al alloy treated in the present paper it has been shown that certain resistivity values belong to specific annealing temperatures as equilibrium values [2, 5, 6]. This has been interpreted as evidence for the thermodynamic stability of homophase alloys. It is therefore assumed for the following calculations that SRO-kinetics tend towards specific equilibrium values for long enough times of isothermal annealing.

The alloy systems AuAg, AuPd, AgAl [7–9], the systems CuAl and CuMn at certain concentrations [6, 10] are reported to show a more or less single exponential behaviour of the normalized SRO-relaxation process observed by electrical resistivity

$$\Delta\rho(t)/\Delta\rho_0 = \exp(-t/\tau_{\mathrm{SRO}}) \qquad (2)$$

where $\Delta\rho(t) = \rho(t) - \rho_\infty(T_a)$ is the measured resistivity minus the final equilibrium value, $\Delta\rho_0 = \rho(t_0) - \rho_\infty(T_a) = \rho_\infty(T_0) - \rho_\infty(T_a)$ is the total change of resistivity from the initial to the final value and τ_{SRO} is the characteristic time of SRO-relaxation.

For reasons of simplicity but without restricting the results the SRO-resistivity kinetics in the following are assumed to be a first order reaction obeying the following differential equation

$$d_{\rho}(t)/\mathrm{d}t = -\tau_{\mathrm{SRO}}^{-1}(T_a)(\rho(t) - \rho_\infty(T_a)) \qquad (3)$$

3.1.3. Atomic mobility

Since any microscopic rearrangement is brought about by jumps of the alloy atoms, the SRO-relaxation time depends on the concentration of vacancies and on the ability of these vacancies to move within the sample. The relaxation rate at a given temperature T_a is a linear function of the product of equilibrium vacancy concentration c_v and jump frequency ν_v

$$\tau_{\mathrm{SRO}}^{-1} = (1/m)c_{v,\infty}(T_a)\nu_v(T_a) \qquad (4)$$

where $c_{v,\infty} = c_0\exp(-(H_F/kT_a))$ is the equilibrium concentration of vacancies at temperature T_a, $\nu_v = \nu_0\exp(-(H_M/kT_a))$ is the jump frequency at T_a, H_F is the formation enthalpy of vacancies, H_M is the migration enthalpy, c_0, ν_0 are pre-exponential factors and m is the number of vacancy jumps during relaxation time τ_{SRO}.

The adjustment of the number of vacancies at a given temperature T_a was assumed to follow a first order reaction

$$\mathrm{d}c_v(t)/\mathrm{d}t = -\tau_v^{-1}(T_a)(c_v(t) - c_{v,\infty}(T_a) \qquad (5)$$

$$\tau_v^{-1} = \nu_v/m$$

3.2. Calculation of annealing kinetics

3.2.1. Ideal annealing kinetics

The conditions for an ideal annealing experiment are

$$\tau_w = 0 \text{ and } T(t) = T_a = \text{constant} \quad \text{for } t \geq 0$$

$$\tau_{\mathrm{SRO}}(T_a) = \text{constant}$$

$$\rho_\infty(T_a) = \text{constant}$$

In this case Equation 3 yields a single exponential function (Equation 2) as an analytical solution.

3.2.2. Consideration of realistic experimental conditions with a low measuring temperature

During an ideal isothermal annealing experiment at temperature T_a the observed physical quantity, in our

TABLE I Parameters of Cu–16 at % Al determined experimentally and used for numerical calculations.

	Annealing temperature, T_a (°C) 240	250	260	270	280	290	300
τ_w(s)	19.0	18.22		16.84	16.22	15.64	
τ_{SRO}(s)	1048.0	469.8		109.0	69.0	25.28	
$\frac{\Delta\rho_\infty}{\rho_{220}}$(%)	0.499	0.757	1.015	1.272	1.530	1.788	2.046

case the electrical resistivity $\rho(t)$, asymptotically approaches the final value $\rho_\infty(T_a)$. If there is a period of warming-up, as is unavoidable for a real experiment, the temperature $T(t)$ changes from the measuring temperature T_m to the annealing temperature T_a. Therefore $\rho(t)$ during each increment of time tends towards the respective equilibrium value $\rho_\infty(T(t))$ with a rate determined by the relaxation time $\tau_{SRO}(T(t))$. The SRO-relaxation time, too, depends on $T(t)$ *via* the changing concentration of vacancies and their jump frequencies. The equilibrium concentration of vacancies $c_{v,\infty}(T_a)$ at the annealing temperature T_a therefore has to be replaced by the actual concentration $c_{v,\infty}$ $(T(t)) = c_v(t)$. In the same way the jump frequency $v_v(T_a)$ has to be replaced by $v_v(T(t))$.

Fig. 2 shows this change of actual resistivity for a single warming-up period from T_m to T_a in a schematic way: During the temperature change from T_m to T_a there is a certain temperature T_v with $T_m < T_v < T_0$, around which the vacancies start to move, enabling changes in the degree of order. At the beginning of the warming-up the instantaneous equilibrium values of resistivity the system aims at (current equilibrium values, CEV $= \rho_\infty(T(t))$, correspond to temperatures near the measuring temperature T_m. For the case of an overall temperature up-step ($T_a > T_0$), this means a microstructural change away from the final value. This change is reversed just when the instantaneous resistivity corresponds to the instantaneous temperature as an equilibrium value ($\rho(t) =$ CEV). τ_w, the vacancy properties of the system, the annealing temperature T_a and the temperature difference between T_0 and T_a determine what happens for the case of a temperature down-step ($T_a < T_0$).

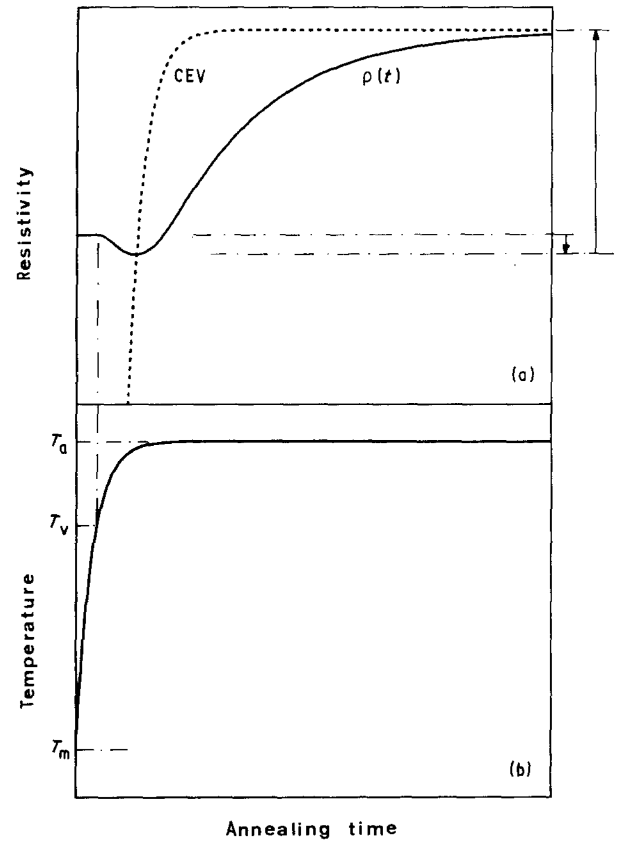

Figure 2 (a) Schematic plot of resistivity change during the warming-up procedure (full line), (b) change of actual annealing temperature with time. The instantaneous equilibrium values (CEV) are given by the dashed line.

For realistic experimental conditions, i.e., a finite warming-up relaxation time τ_w, Equation 3 in contrast to the ideal annealing case cannot be solved analytically because of the implicit time dependence of the relaxation rate τ_{SRO} and the CEV.

Solving Equation 3 one needs to know the implicit dependence on time of the CEV and of $\tau_{SRO}(T(t))$. For the present calculation $\rho_\infty(T)$ was taken from experimental results on Cu–16 at % Al under the simplifying assumption of a linear dependence on temperature (see Table I), which is a good approximation for many alloy systems. The solution of Equation 3 is now found step by step by first calculating the equilibrium concentration of vacancies and the jump frequency for the starting temperature T_m: $c_{v,\infty}(T(t=0)) = c_{v,\infty}(T_m)$; $v_v(T(t=0)) = v_v(T_m) = v_0\exp(-H_m/kT)$. These values together with the starting value of the vacancy concentration $c_v(t=0) = c_{v,\infty}(T_0)$ are inserted into Equation 5 in order to calculate the instantaneous vacancy concentration $c_v(t + dt)$ after a short time interval, dt. With $c_v(t + dt)$ and $v_v(t + dt)$, Equation 4 now yields the SRO-relaxation time τ_{SRO} $(t + dt)$ and using the starting value $\rho(t = 0) = \rho_\infty(T_0)$, Equation 3 gives the resistivity value $\rho(t + dt)$ at time $t + dt$, which serves as a starting value for the next step.

Things get even more complicated for the case of repeated warming-up procedure during an isothermal anneal (see Section 2.2.1): Here the annealing procedure is interrupted before an equilibrium value has been achieved; then the warming-up procedure starts again possibly first leading away from the final value.

Using the method sketched above, Equation 3 was solved numerically for different sets of starting and annealing temperatures with corresponding resistivity equilibrium values.

4. Experimental procedure

Cu–16 at % Al was produced by high frequency melting 99.999% Cu and 99.999% Al in graphite crucibles under a vacuum below 10^{-3} Pa. The material was rolled to sheets of 0.2 mm thickness with several intermediate anneals in vacuum. Serpentine-shaped samples were cut by spark erosion. Before the investigation the samples were homogenized at 750 °C for about 1 h. For more details on sample preparation see [6].

The annealing treatments were carried out in a bath of silicone oil (Baysilon PN200). The heat capacity of the sample holder was taken into account by slightly overheating the bath, thus achieving a relaxation time for the warming-up of the samples τ_w of less than 20 s (see Table I). This process has been studied directly by measuring the sample resistivity (at-temperature) as a function of time.

The method of using a bath for sample heating instead of directly heating the samples by means of electrical current has the advantage of a homogeneous temperature profile throughout the sample, independent of its geometrical shape. This we think is of essential importance, especially when kinetic processes are investigated.

Resistivity measurements were made by the standard potentiometric method relative to a dummy specimen in a stirred bath of liquid nitrogen with an accuracy of $\pm 3 \times 10^{-5}$.

5. Results

5.1. At-temperature measurement

In Fig. 3 the relative change in resistivity as measured at the annealing temperature, $T_a = 240\,°\mathrm{C}$ after a temperature increase of 20 °C is plotted as a function of annealing time. Because of the relative change in phonon scattering at the beginning of the isotherm due to the temperature change from T_0 to T_a, the very first part of the process kinetics cannot be detected by this method. Anyway, after thermal equilibration of the sample at T_a the observed kinetics correspond to an exponential process (full line). Therefore this measuring method yields correct process kinetics, if, in spite of, the high measuring temperature a high enough measuring accuracy can be met.

5.2. Single warming-up procedure ($T_m = 77$ K)

For the given experimental conditions and using plausible values for the vacancy activation enthalpies in Cu–16 at % Al ($\tau_0 = 3 \times 10^{-7}$, $c_0 = 2$, $m = 0.5$, $H_F = 1.05$ eV and $H_M = 0.8$ eV) the vacancy concentration within the sample during a warming-up procedure from T_m and subsequent isothermal annealing at T_a was computed as a first step towards the calculation of the annealing kinetics (Fig. 4).

At the beginning of the warming-up period the vacancy concentration is constant: Near the low measuring temperature T_m the rather low number of thermal vacancies is unable to contribute to atomic mobility and the surplus vacancies, which correspond to the previous annealing temperature T_0, remain frozen. With increasing temperature $T(t)$ the vacancy concentration starts to decrease due to the annealing out of those vacancies, which are now in excess, corresponding to the actual low temperature. In the case of a temperature up-step ($T_a > T_0$; curve (a) the equilibrium concentration $c_{v,\infty}(T_a)$ is higher than the initial value. After a minimum, the concentration of vacancies therefore starts to increase until the final value corresponding to T_a is reached. A similar behaviour is observed for a temperature down-step experiment ($T_a < T_0$; curve (b)).

Fig. 5 shows the normalized change in electrical resistivity as a function of annealing time for both, (a) temperature up-step and (b) temperature down-step experiment of $\Delta T = 10$ K. The points correspond to the experimental investigation carried out on Cu–16 at % Al at a constant measuring temperature of 77 K. As sketched in Section 2.2.2 for this investigation before each period of annealing the initial equilibrium state at T_0 had to be re-adjusted. As this procedure takes an increasing time for decreasing

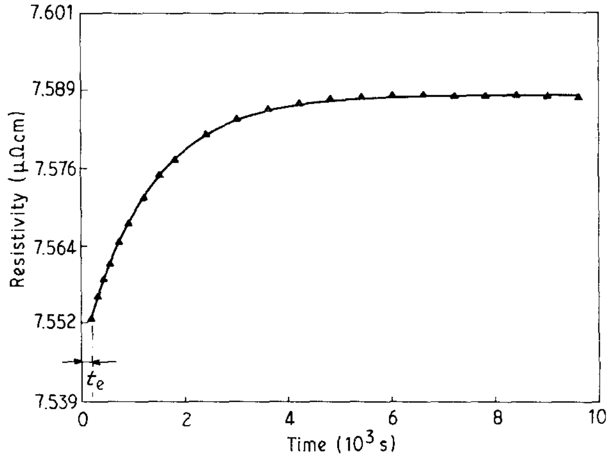

Figure 3 SRO-induced change of electrical resistivity with annealing time of Cu–16 at % Al after changing the annealing temperature from $T_0 = 220$ to $T_a = 240$ °C. Measuring temperature: $T_m = T_a$. The full line is the best-fit of an exponential function to the measured points. The measurement started after a time of equilibration $t_e \cong 10\tau_w \cong 190$s.

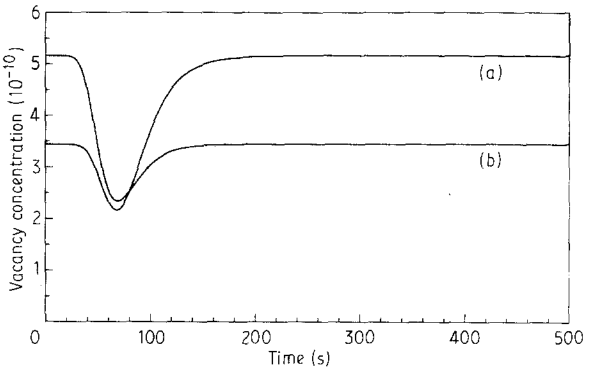

Figure 4 Change of vacancy concentration with annealing time during a single warming-up procedure from the measuring temperature $T_m = 77$ K to the annealing temperature $T_a = 280$ °C (curve (a)) and $T_a = 270$ °C (curve (b)), respectively. The initial temperature, T_0, before the temperature change was 270 and 280 °C, respectively. Parameters used see Table 1 and Section 5.2.

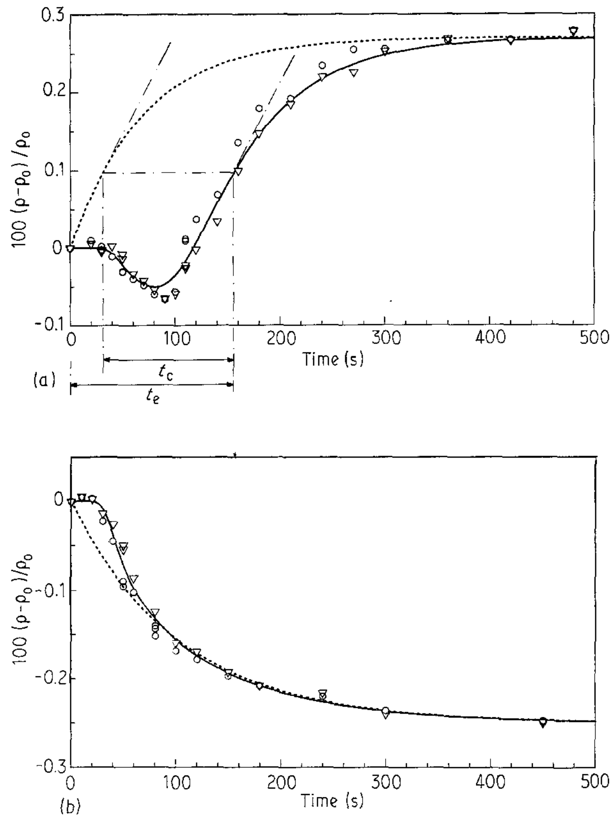

Figure 5 Relative change of SRO-induced electrical resistivity with annealing time for a single warming-up period; (a) $T_0 = 270\,°C$, $T_a = 280\,°C$; (b) $T_0 = 280\,°C$, $T_a = 270\,°C$. Points are measured at 77 K. As sketched in Section 2.2.2 before the annealing intervals of increasing length, the sample was thermally equilibrated again at T_0 and measured at 77 K. Ideal process kinetics (single exponential function) is given by dashed line. The full line is the result of a numerical calculation described in Section 3.2.2 with parameters of Table 1 and Section 5.2. After an annealing time at T_a of $t_e \cong 10\tau_w$ the real process shows the same time law as the ideal process (compare tangents to both curves for annealing times t_e and $t_e - t_c$, respectively, given in (a)).

values of T_0, this temperature was chosen high enough (280 and 270 °C, respectively) to allow a reasonable duration of the experiments.

In Fig. 5a (temperature up-step) the resistivity at the beginning remains constant due to the instantaneous low temperature ($T \simeq T_m$): The vacancies are immobile and therefore no change in SRO from its equilibrium value at T_0 is possible. This is followed by a decrease in resistivity. The system tends towards degrees of SRO, which correspond to lower temperatures. Only when the actual SRO-state meets the CEV, an increase of resistivity results. The kinetics of an ideal annealing experiment is given by the dashed line for comparison.

In Fig. 5b the change in resistivity as a function of annealing time is plotted for a temperature down-step experiment. In this case the initially constant resistivity decreases more than the ideal case (dashed line) as soon as the atoms become mobile. This is a consequence of the CEV lying in the same direction as the final value but corresponding to even lower temperatures; this means a greater driving force towards lower resistivity values than for the ideal case.

The full curves in Fig. 5a, b are calculated in the way described in Section 3.2.2 using the parameters given in Table I and Section 5.2. A very good correspondence is obtained in spite of the difficult experimental conditions and the simplifying assumptions for the kinetics of warming-up. This fact corroborates the calculations done for the single warming-up procedure and so yields the basis for calculating the resistivity change during a repeated warming-up procedure.

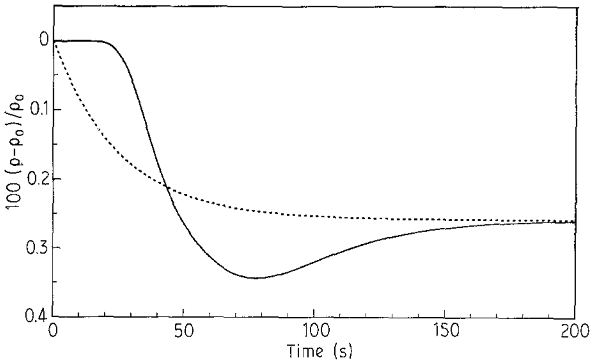

Figure 6 Relative change of SRO-induced resistivity as a function of annealing time, calculated for a temperature down-step experiment from 300 to 290 °C. Parameters used see Table I and Section 5.2. Ideal process kinetics is given by the dashed line for a comparison.

That the effect for a temperature down-step experiment can be similarly drastic as for an up-step experiment when τ_{SRO} comes close to τ_w at high annealing temperatures is shown in Fig. 6. In this case the atoms of the sample are quite mobile in a temperature range, where the CEV still corresponds to temperatures lower than T_a. Therefore the final equilibrium value, which corresponds to T_a, is crossed and asymptotically adjusted from resistivity values lower than T_a, although $T_0 > T_a$.

5.3. Repeated warming-up procedure ($T_m = 77$ K)

The change in vacancy concentration during an isothermal annealing experiment with repeated interruptions is shown in the lower parts of Fig. 7a, b. For the first annealing period the vacancy concentration changes as calculated for the single warming-up process: Surplus vacancies first anneal out, before the number of thermal vacancies increases to its equilibrium value at the new annealing temperature T_a. A similar behaviour with a slight change in the minimum of c_v is observed for each of the following interruptions.

The upper parts of Fig. 7a, b show the normalized resistivity change versus annealing time as the result of numerical calculations for a temperature up-step and a temperature down-step experiment, respectively. For both cases the annealing intervals are chosen 10 times larger than τ_w to guarantee a thermal equilibration of the samples within each interval. The points of interruption, where the quench to T_m is carried out (given by full circles) constitute curves which deviate considerably from an exponential behaviour (dashed line).

That the deviation is greater for smaller annealing intervals is shown in Fig. 8a, b for the extreme case of the first annealing interval being considerably shorter

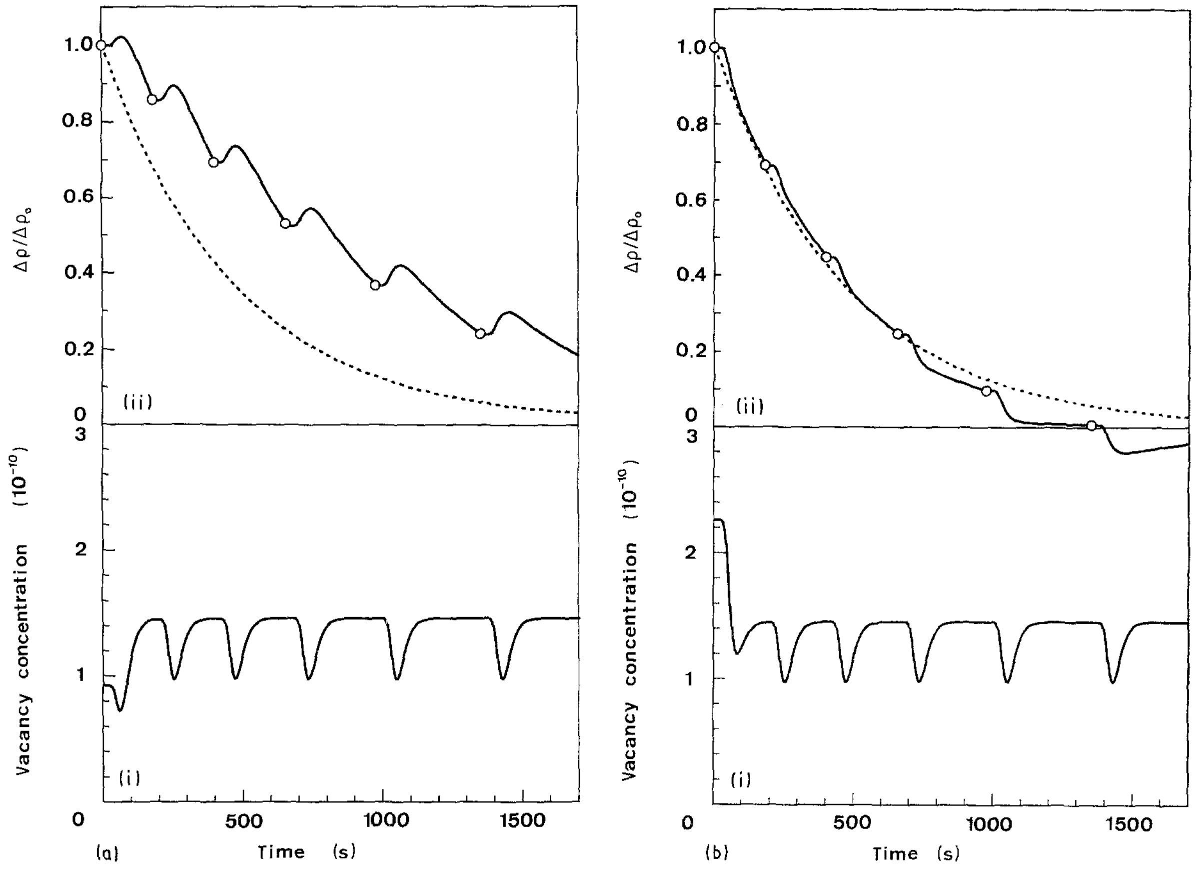

Figure 7 Isothermal annealing experiment with repeated interruptions: (i) Change in vacancy concentration, (ii) normalized resistivity change versus total annealing time at T_a as calculated for repeated quenching to the measuring temperature $T_m = 77$ K (see Section 3.2.2). Parameters used see Table I and Section 5.2. The corresponding curve for ideal process kinetics is given by the dashed line. (○) points of interruption with quenching to T_m and subsequent warming-up to T_a, which similar to experimental conditions constitute a curve of low measuring temperature. (a) $T_0 = 240$ °C, $T_a = 250$ °C; (b) $T_0 = 260$ °C, $T_a = 250$ °C.

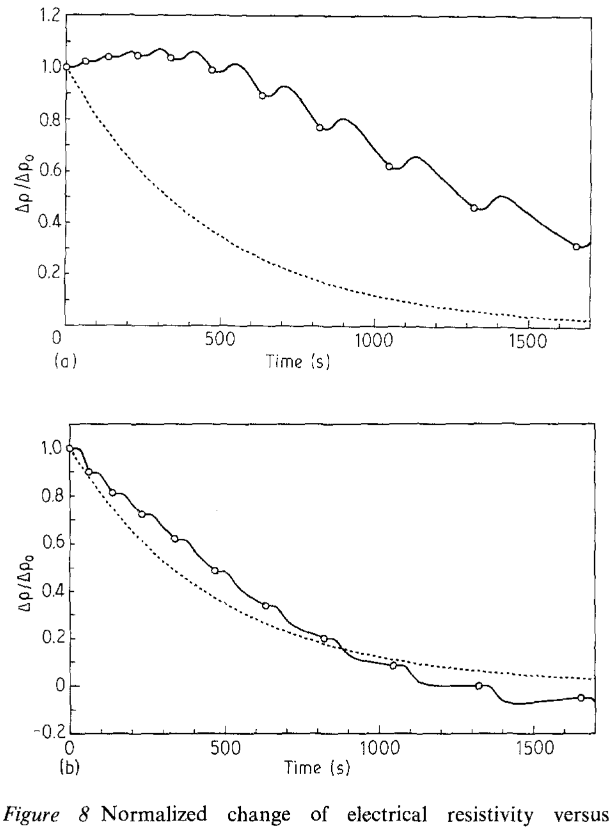

Figure 8 Normalized change of electrical resistivity versus annealing time as calculated. Length of first annealing interval at T_a: $t_1 = 3.5\tau_w = 64$ s. The annealing interval increases in time by a factor of 1.2. The curve for ideal process kinetics is given by the dashed line. (○) points of interruption with quenching to $T_m = 77$ K. (a) $T_0 = 240$ °C, $T_a = 250$ °C; (b) $T_0 = 260$ °C, $T_a = 250$ °C.

than the total time of equilibration. It is observed that pathological results may be obtained in such a case, depending on the sequence of annealing intervals.

In Fig. 9 the normalized relative change of resistivity as measured on Cu–16 at % Al by repeated quenching to $T_m = 77$ K is plotted as a function of annealing time. The influence of the repeated warming-up procedure on the observed result of an annealing experiment as already shown numerically (Figs 7 and 8) leads to a considerable difference between experimentally observed (full squares) and ideal kinetics (dashed line).

6. Discussion

Obviously the points measured at the beginning of an isothermal annealing experiment are most important for investigating the kinetics of a physical quantity approaching equilibrium, at first because the relative error in measurement increases with increasing annealing time; secondly, properties of the moving defect, which is responsible for the atomic mobility, may be obtained from the initial slope of the resistivity change [11]. Therefore it is important for a high resolution to measure many points at the beginning of the experiment just after the temperature change. These conditions of a high measuring accuracy are in contrast to the results of the present paper where it is observed that measuring after a short annealing interval may change the result in a drastic way. Therefore

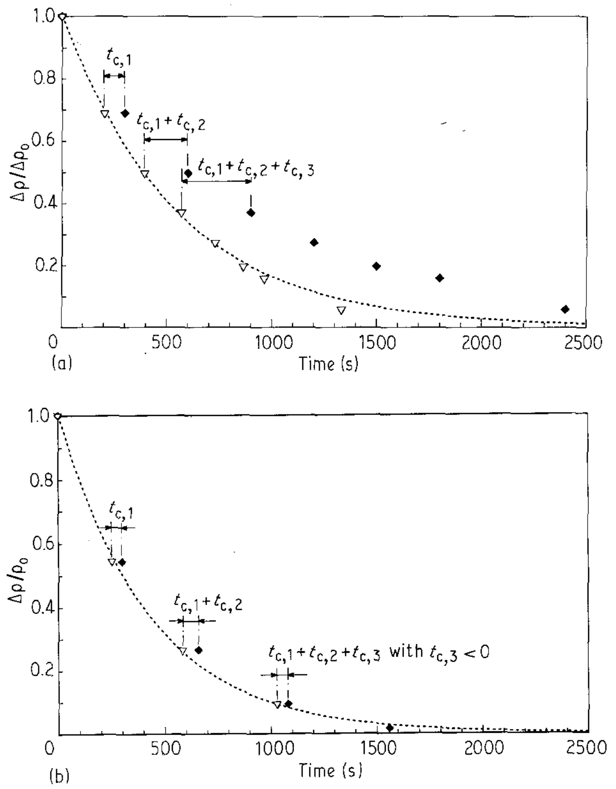

Figure 9 Normalized change of resistivity versus annealing time as measured by repeatedly quenching to the measuring temperature $T_m = 77$ K. (a) $T_0 = 240\,°C$, $T_a = 250\,°C$; (b) $T_0 = 260\,°C$, $T_a = 250\,°C$. (◆) original measuring points; (△) after correcting the annealing time by subtracting from each annealing time, t_i, the correction time $\sum t_{c,i}$, given in chapter 6, Equation 9. Ideal process kinetics is given by the dashed line.

great care has to be taken to study the experimental conditions used.

The experimental results of at-temperature measurements show that after a certain time of thermal equilibration, t_e, of the sample, which depends on the experimental conditions, the observed kinetics correspond to the ideal process kinetics. That the results for annealing times shorter than t_e are not reliable in the present case is not only a consequence of the process kinetics changing with changing temperature, but also of considerable changes in the phonon scattering. For an adequate correction of the annealing times used see below.

If the measurement is carried out at a low measuring temperature $T_m \ll T_0, T_a$ there is a considerably larger influence of the warming-up procedure on the observed annealing kinetics: In this case as shown in Figs 5 and 6 a change in the sign of the resistivity may be observed. Because of the thermal activation of the process kinetics (atomic mobility) the relation $\tau_{\text{process}}/\tau_w$, which is essential for the magnitude of the effect, depends on temperature. However, for the temperature range where experiments are performed preferentially, τ_{process} is just a few times τ_w, giving rise to the above problems.

On the other hand the good correlation of calculated and measured results suggests that the warming-up effect can be corrected adequately.

In spite of the warming-up effect after a certain annealing time, t_e (equilibration time), the real kinetics within a given accuracy obey the same time law as the ideal kinetics (see Fig. 5a, b). This takes places when the actual temperature $T(t)$ becomes equal to the final temperature T_a that is $T(t_e) = T_a$. This is valid for low temperature as well as at-temperature measurements. Now one can try to use this fact for a correction of the annealing times, then treating the kinetics as if performing an ideal experiment. A correction time, t_c is defined by (compare Fig. 5)

$$(\Delta\rho/\Delta\rho_0)(t_e)|_{\text{real}} = (\Delta\rho/\Delta\rho_0)(t_e - t_c)|_{\text{ideal}}, \quad (6)$$

which can be used for a correction of the annealing intervals to get ideal annealing kinetics: Subtracting t_c from the values t actually used in a real experiment yields an annealing curve, which merges with the curve of a comparable ideal experiment as soon as the temperature has reached the final value T_a, that is for $t > t_e$.

Obviously resolving a difference between the actual temperature, $T(t)$, and the final temperature, T_a, is a question of measuring accuracy. As the slope of the equilibrium line (step height) for Cu–16 at % Al is found to be about $2.5 \times 10^{-4}\,K^{-1}$ [6], the measuring accuracy of $\pm 3 \times 10^{-5}$ means a temperature resolution of about 0.1 K. t_e therefore was determined using the condition $|T(t_e) - T_a| = 0.01$, which is much below the measuring accuracy. This condition is fulfilled sufficiently for $t_e \cong 10\tau_w$.

The above procedure can also be used for correcting an isotherm with repeated interruptions. But, such a correction only makes sense if all the annealing intervals are chosen long enough to allow the samples to become thermally equilibrated (compare Fig. 8), which means that the corrected realistic curve merges with the ideal curve for each annealing interval. This gives the equilibration time, t_e, as a lower limit for each annealing interval. Further, for each annealing interval of the repeated interruptions a new correction time, t_c, has to be determined.

In Fig. 10 such a correction is shown for the case of a temperature up-step experiment from 240 to 250 °C (Fig. 10a) and a temperature down-step experiment from 260 to 250 °C (Fig. 10b). It can be observed that after shifting the various parts (single warming-up procedures) of the curves corresponding to each annealing interval for an adequate time, t_c, to shorter annealing times both curves follow the same time law as for the ideal case.

Two main features can be observed from Fig. 10:

(i) The correction time, t_c, for the annealing intervals increases with decreasing distance from the final equilibrium value. If the process under investigation is already near to the final equilibrium value immediately before the interruption to the measuring temperature, the degree of SRO during the subsequent warming-up procedure drifts away, strongly from the final value.

(ii) For $T_a < T_0$ (temperature down-step experiment) t_c becomes negative, that means the actual measured annealing time has to be enlarged in order to get the correct kinetics. This is due to the fact that, for a temperature down-step the instantaneous resistivity

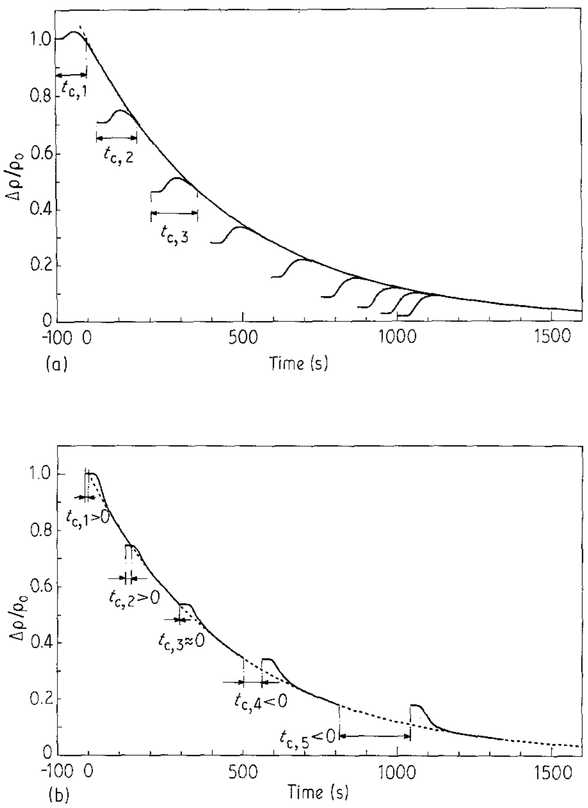

Figure 10 Normalized change of electrical resistivity with total annealing time as calculated using corrected annealing times given in chapter 6. Ideal process kinetics are given by the dashed line. (a) $T_0 = 240\,^\circ\mathrm{C}$, $T_a = 250^\circ$; (b) $T_0 = 260\,^\circ\mathrm{C}$, $T_a = 250\,^\circ\mathrm{C}$. Correction times, $t_{c,i}$, as indicated.

values $\rho(t)$ during the warming-up process are more distant from the CEV than from the final equilibrium values ρ_∞: This means a transitory acceleration of SRO-adjustment. If the actual state of the sample after several annealing intervals is already near the equilibrium state the acceleration leads to an under-shooting of the final equilibrium value (compare Fig. 7b) and any correction of the measured data is impossible beyond this annealing time.

We have been able to find a functional dependence of t_c on the relative change in resistivity, which yielded satisfying results for the kinetics

$$t_c = a\tau_w(T_a) + b\exp(-c\ln(\Delta\rho/\Delta\rho_0)_m) \quad (7)$$

where $(\Delta\rho/\Delta\rho_0)_m$ is the normalized measured resistivity change and a, b, c are fit parameters. Equation 6 means an exponential increase of the correction time, t_c, with the annealing time (compare Equation 2) if an exponential time law for the process kinetics is assumed

$$t_c = a\tau_w + b\exp(c't) \quad (8)$$

with $c' = c\tau_{SRO}^{-1}(T_a)$.

From an isothermal annealing experiment a set of data (t_i, R_i) is obtained, where the R_i are the normalized measured resistivity values at the times t_i. Corrected pairs of data can be obtained by substituting $t_{\mathrm{new},i}$ for t_i

$$t_{\mathrm{new},i} = t_i - \sum_{k=0}^{i-1} (a\tau_w(T_a) + b\exp[-c\ln(R_k)]) \quad (9)$$

For the present experimental conditions (see Tables I and Section 5.2) the calculation yielded independently of the starting and annealing temperatures: a = 4; b = + 25 or b = − 25, depending on temperature up-step or down-step, respectively; $c = 1$. With these parameters a correction time was calculated leading to a very good correspondence with ideal process kinetics as long as $(\Delta\rho/\Delta\rho_0) > 0.1$, that is for annealing times shorter than about 2.5 times τ_{SRO}. This limit does not mean a severe restriction in comparison to the accuracy in the normalized data representation of $\Delta(\Delta\rho/\Delta\rho_0) = \pm 0.08$ (corresponding to a measuring accuracy of $\pm 3 \times 10^{-5}$ for a temperature change of 10 K).

The experimental curves measured by repeated interruption of the annealing treatment have been corrected in the way just described. The points of corrected annealing times (open triangles) are given in Fig. 9, together with the points of original annealing times (full squares). It can be seen that a satisfying correlation with the ideal process kinetics (dashed line) results for the points where the annealing is interrupted if corrected annealing times are used.

7. Conclusions

(i) There is a pronounced influence of the warming-up procedure on the observed annealing kinetics for a single warming-up, as well as for a repeated warming-up procedure, especially if the measuring temperature $T_m \ll T_0, T_a$.

(ii) The effect can be predicted from calculations with a satisfying correlation to the experimental. It depends on the relation of $\tau_{\mathrm{process}}/\tau_w$, that is, on the annealing temperature and on the annealing time.

(iii) The effect can be compensated by an adequate correction of annealing times if the single annealing interval is kept longer than $10\tau_w$ and for repeated quenching to a low measuring temperature as long as the overall corrected annealing time is shorter than $2.5\tau_{\mathrm{process}}$.

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