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METHODS OF NON-ISOTHERMAL KINETIC ANALYSIS BY DSC CURVES

AN INVESTIGATION ON LATTICE REORGANIZATION IN COPPER

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ABSTRACT

Various analytical methods of non-isothermal kinetics have been applied to DSC curves to determine the kinetic parameters ruling the lattice reorganization (primary recrystallization) of prestrained pure copper.

The techniques by Borchardt and Daniels, and Rogers and Smith have been modified to make them suitable for complex phenomena other than *n*th-order reactions.

The results supplied by the new formulas are consistent with the data previously obtained under isothermal conditions. The same applies to the other methods tested, provided an accurate temperature calibration be made to correct the thermal lag of the calorimetric sensors.

Such a calibration is of prime importance when DSC peak shifts are analyzed as a function of heating rate.

INTRODUCTION

Isothermal measurements carried out by high-sensitivity calorimeters to study thermally activated processes suffer severe limitations whenever the materials employed have to be quickly preheated to working temperature.

Serious difficulties, in fact, are encountered both in enthalpic and kinetic analysis during the first stages of the process, due to baseline perturbations and to the thermal inertia of the instrument.

It was previously shown in one of these cases, namely the recrystallization of deformed metals, that stored energy released by pure copper can be easily determined through the DSC technique, by a method which is able to detect the effects produced by some tens of ppm of foreign elements added to the pure metal[1,2]. Moreover, DSC measurements were carried out on specimens partially recrystallized at constant temperature to determine their residual contents of stored energy, so as to obtain a picture of isothermal heat evolution during recrystallization, avoiding the drawbacks of isothermal calorimetry.

One object of the present work is to check different theoretical formulations for non-isothermal kinetics and to point out that activation energy of recrystallization in metals can be determined by the DSC curves of stored energy release.

Furthermore, an evaluation of the effect produced on the thermograms by the thermal inertia of the DSC apparatus is considered possible in the present favourable experimental conditions (high conductivity of copper, good geometrical reproducibility of the specimens, constancy of specific heat throughout the lattice-reorganization process).

Finally, an attempt will be made to adapt some kinetics theories for *n*th-order reactions to complex kinetics in solids and to apply the new expressions to the study of recrystallization kinetics in copper.

EXPERIMENTAL

(*a*) *Materials and methods*

The study of the thermal effect connected with recrystallization has been carried out on pure copper (99.999%, of the firm Koch-Light) deformed by rolling (reduction in thickness of 85%) and submitted to heating at a constant rate in an apparatus for quantitative differential thermal analysis (DuPont DSC cell connected with a 900 differential thermal analyzer).

The purity of the protective atmosphere during DSC runs and the constancy of shape and weight of the specimens proved to be of prime importance[1,2] to obtain a good reproducibility of the thermograms (within 3% of area). A 4 l h^{-1} flux of argon depurated on Al amalgam, Ca chips at 700°C and Zr powder at 1000°C was used to prevent any oxydation of copper. A thin sheet of rhodium (0.1 mm) has been introduced between the constantan sensor and the copper specimen to avoid solid state diffusion at the higher temperatures tested

Rolled sheets of copper have been punched to obtain the deformed specimens in the shape of discs of 4.5 mm in diameter, 0.96 mm in thickness and 132 to 135 mg in weight after electrolytic polishing.

(*b*) *Calibration*

The correspondence between the recorded temperature and the sample temperature, and between the area of the thermogram and the energy has been calibrated by submitting to DSC runs a few milligrams of pure metals which absorbed 2 to $6 \cdot 10^{-2}$ cal during melting. A recrystallized sample drilled in the center of its upper face down to the core has been used as a support for melting metals, in order to reproduce the heat transfer path from the specimens to the thermo-electric disc.

The energy calibration curve, giving cal cm^{-2} at the various temperatures, fitted the experimental points with a maximum deviation of 6%.

After a first test which produced a good contact between the melting metal and the support, the melting temperature was reproducible within ±1°C. In this way calibration curves of the "real temperature" of the specimen (i.e., the melting points reported in the literature) were obtained as a function of the temperature recorded by the instrument at different heating rates between 5 and 70°C min^{-1}. The delay in the calorimetric response depends, as foreseeable, on temperature and heating rate. In the present experimental conditions the recorded temperature exceeds the real one by 4°C at 150°C and by 17°C at 400°C for the lower heating rate (5°C min^{-1}), whereas the difference is stronger for higher heating rates, passing, for instance, from 12°C at 150°C to 26°C at 400°C when temperature increases linearly at 70°C min^{-1}. In the temperature range examined (150 to 400°C) the temperature correction to be made on the thermograms increases with specimen temperature in an almost linear way for all the heating rates adopted (5 to 70°C min^{-1}).

The fact that the DSC curve is a delayed picture of the real thermokinetics has been confirmed by quenching tests that stopped an energy evolution in course and were followed by a new heating run to determine the residual contents of stored energy.

A quick admission of liquid nitrogen, sucked inside the DSC cell at the peak temperature, was able to quench recrystallization at a rate of 90°C min^{-1} (as monitored by the sample thermocouple) or possibly higher, as the specimen screened the thermoelectric disc from liquid nitrogen and its vapours.

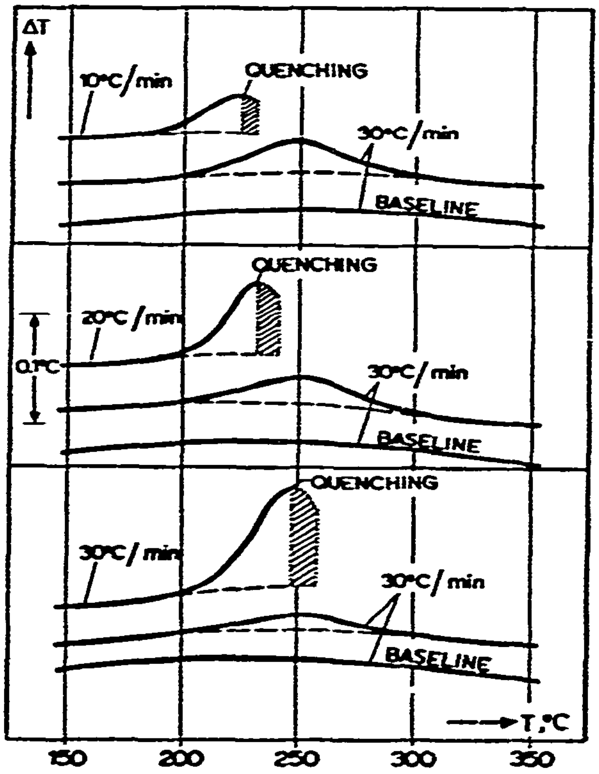

Fig. 1. Quenching tests on prestrained copper heated at different rates. Upper curves refer to a first DSC run interrupted at T_M. Middle curves show the residual contents of stored energy in a second heating run after quenching, and dashed areas indicate the heat evolution not recorded because of instrumental inertia. Baselines taken in a third run after recrystallization are also reported.

Some examples of quenching tests during heating at different rates are reported in Fig. 1, where three successive DSC runs on a same specimen show the trend of stored energy release interrupted at T_M, the residual energy contents after quenching (always recorded at the same rate, 30°C min^{-1}, for quantitative comparison) and finally the baseline behaviour of the fully recrystallized specimen.

The symmetrical shape of DSC peaks does not change with heating rate, as will be referred later on, thus the areas of the half peaks recorded in the first runs correspond to a same amount of energy release. They only differ because the sensitivity of the instrument depends on the heating rate and is enhanced by a heating-rate increase.

The second runs clearly show that the higher the heating rate before quenching, the lower the residual contents of stored energy retained by the specimens. In the present conditions of a relatively high quenching rate, such difference could hardly be attributed to changes in quenching effectiveness. It is more reasonable to attribute them to the differences in the response time of the DSC apparatus, detected by the melting tests at the various heating rates. The samples would thus reach different stages of energy evolution beyond the peak, which are not yet recorded at the moment of quenching (dashed portions of Fig. 1, deduced from the residual energy contents).

When peak temperature T_M is recorded by the instrument, the true condition of the sample is therefore the one corresponding to the end of the dashed curve and the real T_M has already occurred at a lower temperature.

Such a calibration confirms fairly well the trend of the curves of the real temperature obtained by melting tests, and only gives a rather stronger temperature correction. This fact leads to surmise that the thermal geometry of the melting metal–copper support system might be improved by a more sophisticated circular distribution of the melting metal around the center of the copper support. The importance of temperature calibration and its accuracy will be discussed in the next section.

RESULTS AND DISCUSSION

The fractions of stored energy released during linear temperature rises have been determined on the DSC peaks recorded at various heating rates. These α values are reported in Fig. 2 as a function of the specimen temperature calibrated by the melting tests.

Different analytical methods of non-isothermal kinetics have been applied to the results mentioned above in order to obtain the kinetic parameters of recrystallization.

(a) *Dependence of peak temperature on heating rate*

A pronounced symmetry has always been displayed by the thermograms of the differential temperature in several DSC runs under different heating-rate conditions.

Therefore the temperature of half recrystallization (transformed fraction $\alpha = 0.5$) coincides quite well with the peak temperature T_M, i.e., the flex point in the curves of Fig. 2, and this occurs independently of heating rate.

The requirement is thus met of a constant transformed fraction at peak

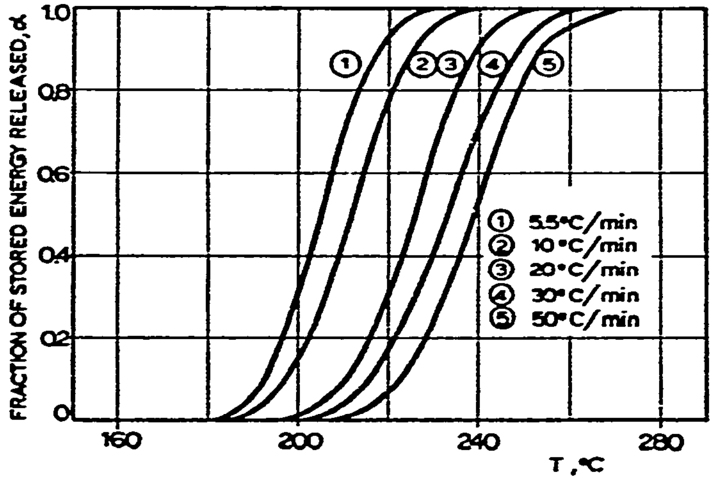

Fig. 2. Stored-energy release as a function of temperature: fractions of stored energy released by pure copper (99.999%) 85% cold-rolled submitted to linear temperature rises at different rates between 5.5 and 50 °C min^{-1}.

temperature to obtain a correct value of activation energy from the relationship between absolute peak temperature T_M and heating rate ϕ, as discussed by Ozawa[3] and Rogers and Smith[4].

Figure 3 shows how the experimental points linearly fit the logarithmic plots of ϕ (Ozawa's method)[3] or ϕ/T_M^2 (Kissinger's method)[5] as a function of the reciprocal absolute peak temperature.

The effect of temperature calibration on the slope of the straight lines (derived by the least square method) is shown in the same figure, where the trend of the curve corrected by the quenching tests is only approximatively indicated by the dashed line, because of the limited number of heating rates tested.

While the approximations contained in Kissinger's and Ozawa's methods lead to similar values of activation energy E (see Table 1), it must be remarked that a temperature calibration by melting tests furnishes an activation energy 25% higher and a further increase of around 11% may be deduced from the quenching tests. What is more, the temperature corrections adopted make the E value become consistent with the one previously obtained by the isothermal method and reported in Table 1 for comparison.

As Ozawa pointed out[3], the relationship between heating rate and peak temperature only holds for DSC curves (and not for DTA), in virtue of their derivative character with respect to the thermal effect detected. On the other hand the position of the thermoelectric sensors outside the sample, and their consequent thermal lag which increases with heating rate, is an intrinsic characteristic of DSC apparatus. Therefore Kissinger's and Ozawa's plots always lead to underestimate activation energy if a calibration of sample temperature is neglected. The error is around 30% in the present study on copper specimens, but it might be higher for similar amounts of materials of lower conductivity.

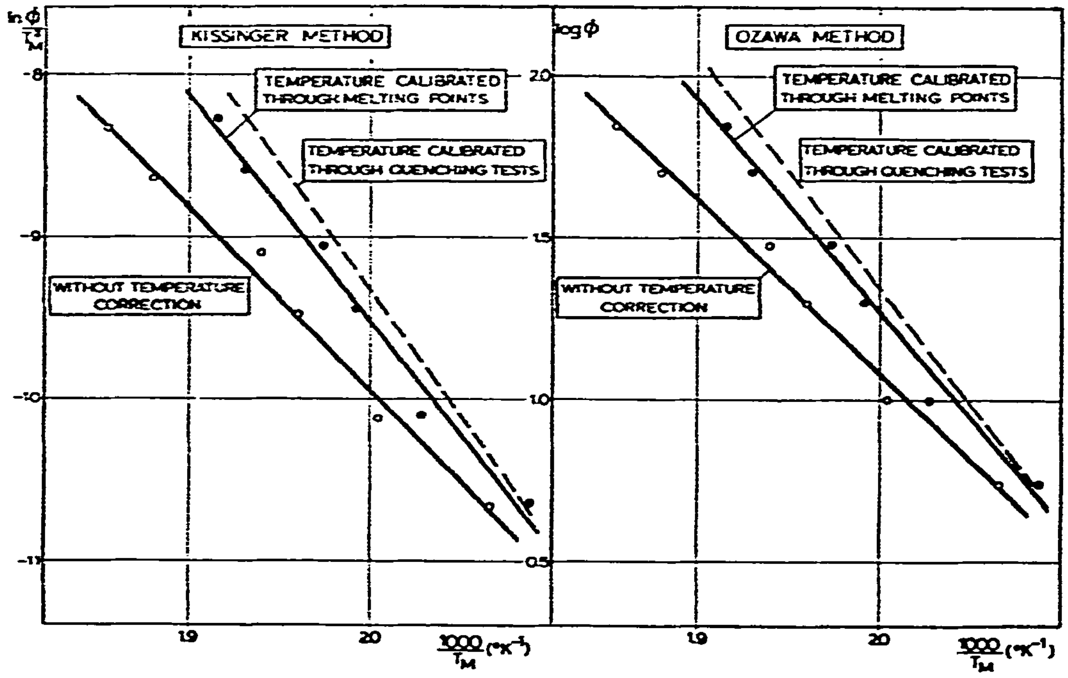

Fig. 3. Kissinger and Ozawa plots showing dependence of peak temperature T_M on heating rate ϕ for DSC curves of deformed copper. ○, peak temperatures recorded by the instrument; ●, — — — effect of temperature calibration on the trend of the curves.

Such considerations can account for the low values of activation energy reported in literature when the results of this method are compared with those obtained otherwise[4,6].

A peculiar characteristic of Kissinger's and Ozawa's plots, that marks them off from the other methods of non-isothermal kinetics, is their ability to supply activation energy data independently of any assumption of a kinetic model. Rate equation need only be of a very general type:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = Ze^{-E/RT}f(\alpha) \tag{1}$$

as is also required to determine E by the isothermal method, where $\log t$ is plotted versus $1/T$ for the same transformed fraction α.

It is worth noting, with respect to the recrystallization process examined, that straight lines with a slope practically coincident with that of the curve in Fig. 3 are obtained in Ozawa's plot for different values of constant α (even other than 0.5), so that the activation energy is constant (standard deviation of less than 1 kcal mol^{-1}) throughout the whole DSC peak of stored energy evolution. An examination of the isothermal data previously collected[1] confirms such a result, thus indicating that in 85% deformed copper the complex lattice reorganization, taking place through nucleation and boundary migration, seems to be ruled by a single value of activation energy.

(b) Single peak analysis

All the methods concerned with the analysis of a whole DSC peak either require the choice of a specific function of the transformed fraction in an explicit form or assume that the investigated process be of *n*th order.

Referring to methods of the former type, Zsakó[7] and Šatava and Škvára[8,9] pointed out that the integration of rate eqn (1) under conditions of a constant heating rate $\phi = \mathrm{d}T/\mathrm{d}t$, giving:

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \int_{T_0}^{T} \frac{k(T)}{\phi}\,\mathrm{d}T = \frac{ZE}{R\phi}\,p\left(\frac{E}{RT}\right) = \frac{ZE}{R\phi}\,p(x) \qquad (2)$$

may be transformed into a logarithmic expression independent of temperature:

$$\log g(\alpha) - \log p(x) = \log\left(\frac{ZE}{R\phi}\right) \qquad (3)$$

In the temperature range where recrystallization of copper occurs and for an activation energy of 30 kcal mol^{-1}, Doyle's approximation of $\log p(x) = -2.315 - 0.4567x$ coincides particularly well (-1.2% of error in the slope when plotted vs. $1/T$) with the true values of $\log p(x)$ tabulated by the same author[10].

Therefore the introduction of Doyle's approximation in relationship (3) giving:

$$\log g(\alpha) = -0.4567\left(\frac{E}{RT}\right) - 2.315 + \log\left(\frac{ZE}{R\phi}\right) \qquad (4)$$

is justified for an analysis of the results of the present work, as already assumed when $\log \phi$ has been plotted vs. $1/T$ according to Ozawa. The expressions of $g(\alpha)$ for various mechanisms acting in solid-state processes have been extensively reviewed by Šesták[12]. The efficacy of such relationship in accounting for copper recrystallization data has been checked on the present results by plotting $\log g(\alpha)$ against $1/T$, as suggested by Šatava[11]. The table of Fig. 4 reports the linearity interval, the activation energy and the preexponential factor Z calculated from the above-mentioned plots relative to mechanisms reasonably involved in recrystallization.

As seen, the linearity interval never extends beyond 60% of energy released and its extention scarcely helps in detecting the best $g(\alpha)$. In this case, the activation energy value furnishes a criterion for choice, since only Johnson–Mehl–Avrami's equation with the exponent $r = 2/3$ gives a result of 29.8 kcal mol^{-1}, in good agreement with the data obtained by methods independent of a kinetic model (isothermal measurements, Kissinger's and Ozawa's plots).

The same choice of $g(\alpha) = [-\ln(1-\alpha)]^{2/3}$ is also supported by the 11.27 value found for $\log Z$ since the preexponential factor for thermally activated processes in solids is stated as falling within the field of 10^{10}–10^{14} sec^{-1} (refs. 12 and 13).

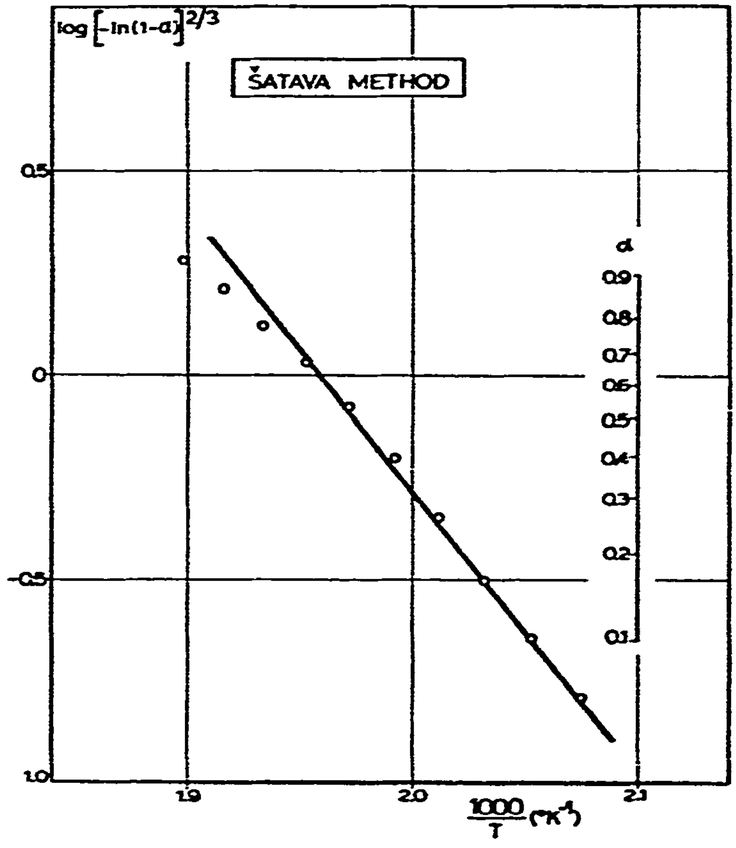

Fig. 4. Šatava plot of log g(α) vs. $1/T$ for DSC curves of deformed copper heated at 30°C min^{-1}. The α-function of Johnson–Mehl–Avrami's kinetics $f(\alpha) = (1-\alpha)[-\ln(1-\alpha)]^{1/3}$ has been used to obtain the integral values reported on the ordinate as a logarithm. The corresponding values are reported in the same figure to evidentiate the linearity interval. The results of an application of this method for other kinetic models are reported in the table on page 9 below.

Actually, recrystallization kinetics has been hitherto best described isothermally by Johnson–Mehl–Avrami's kinetics for nucleation and crystal growth, even though their analytical expression has proved to be failing in the later stages of the process[14,15].

The same applies to the present case, as results in Fig. 4, where log g(α) for needle type growth of random nuclei is reported as a function of $1/T$.

Šatava's method therefore indicates that the kinetic theory for phase transformations in metals by Johnson–Mehl–Avrami is a good approach for a kinetic study of recrystallization, but also shows its limits of validity.

In the lack of a completely satisfying theory to account for the stored energy fractions released in the whole temperature range where energy evolution occurs, an attempt has been made to express f(α) as a two-function product, according to the suggestion by Šesták and Berggren for empirical kinetics[16].

(c) *Empirical kinetics: extension of Rogers and Smith's, and Borchardt and Daniel's methods*

It has been mentioned above, while discussing the single-peak analysis, that some methods are concerned with *n*th-order reactions. These treatments are not suitable for the present recrystallization study, since the analysis of the thermograms according to the method by Šatava has clearly shown that a single function like $f(\alpha) = (1-\alpha)^n$ cannot agree with the experimental data. It is claimed, however, by Šesták and Berggren that $f(\alpha)$ in solids may be expressed as follows:

$$f(\alpha) = \alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p \tag{5}$$

and that only one or two exponents, out of the three *m*, *n* and *p*, need be determined, since no more than two α-functions are required for a complete description of $f(\alpha)$ in all the cases examined until now[16].

The kinetic treatments by Rogers and Smith[4], and by Borchardt and Daniels[17] may then be adapted to all the types of kinetics in solids by substituting expression (5) to the simpler function $f(\alpha) = (1-\alpha)^n$ employed for *n*th-order reactions.

Let us thus assume as a starting kinetic equation

$$\frac{d\alpha}{dt} = k(T)\alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p \tag{6}$$

Kinetic equation[a]	*Interval of linearity (%)*	*E (kcal mol^{-1})*	*Log Z*[b]	*Standard*[c] *deviation*
Diffusion				
$\alpha^2 = kt$	20	84.5	35.29	0.015
$(1-\alpha)\ln(1-\alpha)+\alpha = kt$	33	86.7	36.01	0.016
$\|1-(1-\alpha)^{1/3}\|^2 = kt$	33	89.8	36.83	0.021
$(1-2/3\alpha)-(1-\alpha)^{2/3} = kt$	33	87.7	35.85	0.017
Phase boundary react.				
$\|1-(1-\alpha)^{1/2}\| = kt$	33	44.1	17.21	0.009
$\|1-(1-\alpha)^{1/3}\| = kt$	33	44.9	17.40	0.010
Random nucleation				
$\|-\ln(1-\alpha)\| = kt$	60	44.7	17.81	0.022
$\|-\ln(1-\alpha)\|^{2/3} = kt$	60	29.8	11.27	0.014
$\|-\ln(1-\alpha)\|^{1/2} = kt$	60	22.4	8.04	0.011
$\|-\ln(1-\alpha)\|^{1/3} = kt$	60	14.9	4.86	0.007
$\|-\ln(1-\alpha)\|^{1/4} = kt$	60	11.2	3.30	0.005
Power law				
$\alpha^{1/4} = kt$	47	10.0	2.79	0.005
$\alpha^{1/3} = kt$	47	13.4	4.15	0.007
$\alpha^{1/2} = kt$	33	20.9	7.38	0.004
$\alpha = kt$	33	41.9	16.46	0.007
$\alpha^{3/2} = kt$	33	62.8	25.67	0.011

[a] The case models reported are extensively reviewed by Šesták[12]. [b] *Z* is expressed in sec^{-1}. [c] For the experimental points with respect to the least squares line.

In this case the b deflection of the DSC curve from baseline, according to Rogers and Smith[4], becomes:

$$b = \mathrm{A}Z\mathrm{e}^{-E/RT}\alpha^{m}(1-\alpha)^{n}[-\ln(1-\alpha)]^{p} \tag{7}$$

where A is the total area under the DSC curve*.

Differentiating eqn (7) with respect to time, and taking into account that $b = \mathrm{A}(\mathrm{d}\alpha/\mathrm{d}t)$, we have:

$$\frac{\mathrm{d}b}{\mathrm{d}t} = b^2\left[\frac{m}{\mathrm{A}\alpha} - \frac{n}{\mathrm{A}(1-\alpha)} + \frac{p}{\mathrm{A}(1-\alpha)[-\ln(1-\alpha)]} + \frac{E}{RT^2}\frac{\mathrm{d}T}{\mathrm{d}t}\frac{1}{b}\right] \tag{8}$$

hence:

$$\frac{(1-\alpha)}{b^2}\frac{\mathrm{d}b}{\mathrm{d}t} - \left[\frac{m(1-\alpha)}{\mathrm{A}\alpha} + \frac{p}{\mathrm{A}[-\ln(1-\alpha)]}\right] = \frac{\phi E}{b\cdot RT^2}(1-\alpha) - \frac{n}{\mathrm{A}} \tag{9}$$

This equation coincides with the original relationship given by Rogers and Smith when $m = p = 0$. The plot of the left side of (9) against $1-\alpha/b\cdot T^2$ should then furnish a straight line with $\phi E/R$ slope and $-n/\mathrm{A}$ intercept at the origin.

If it is considered that $\mathrm{d}b/\mathrm{d}t = 0$ at the peak temperature T_{M}, the frequency factor Z can be obtained from eqn (8) or (9) by substituting for b its value expressed in relationship (7):

$$Z = \frac{\phi E}{RT_{\mathrm{M}}^2}\,\mathrm{e}^{E/RT_{\mathrm{M}}}[n\alpha_{\mathrm{M}}^{m}(1-\alpha_{\mathrm{M}})^{n-1}[-\ln(1-\alpha_{\mathrm{M}})]^{p} - \\ - m\alpha_{\mathrm{M}}^{m-1}(1-\alpha_{\mathrm{M}})^{n}[-\ln(1-\alpha_{\mathrm{M}})]^{p} - p\alpha_{\mathrm{M}}^{m}(1-\alpha_{\mathrm{M}})^{n-1}\cdot[-\ln(1-\alpha_{\mathrm{M}})]^{p-1}]^{-1} \tag{10}$$

Borchardt and Daniels' method, too, can be generalized by starting again from eqn (6) to express the reaction rate. But since the above-mentioned authors[17] refer to the initial and actual number of reacting moles (N_0 and N) it is more convenient to rewrite eqn (6) in the following form:

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = k(T)N_0\alpha^{m}(1-\alpha)^{n}[-\ln(1-\alpha)]^{p} = \\ = \mathrm{k}(T)N_0\left(1-\frac{N}{N_0}\right)^{m}\left(\frac{N}{N_0}\right)^{n}\left[-\ln\frac{N}{N_0}\right]^{p} \tag{11}$$

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*The calibration coefficient used to calculate the heat effect from peak area is taken as independent of temperature in Rogers and Smith's theory. When such a condition is not fulfilled, but the calibration coefficient has a small and almost linear variation in the temperature range covered by the process investigated, its mean value in this temperature range may be taken as a constant (as considered in Borchardt and Daniel's treatment).

On the other hand, reaction rate and moles present at time t are related by Borchardt and Daniels to the differential temperature ΔT, to the specific heat of the sample C_p and to the heat transfer coefficient K':

$$-\frac{\mathrm{d}N}{\mathrm{d}t}=\frac{N_0}{K'\mathrm{A}}\left(C_p\frac{\mathrm{d}\Delta T}{\mathrm{d}t}+K'\Delta T\right)$$

and $N=N_0-(N_0/K'\mathrm{A})\,(C_p\Delta T+K'a)$, where a is the area under the DSC curve swept out at time t.

Therefore, the introduction of these two expressions in eqn (11) enables one to calculate the rate constant in the following form:

$$\mathrm{k}(T)=$$

$$=\frac{\frac{1}{K'\mathrm{A}}\left(C_p\frac{\mathrm{d}\Delta T}{\mathrm{d}t}+K'\Delta T\right)}{\frac{1}{K'\mathrm{A}}(C_p\Delta T+K'\mathrm{A})^m\left[1-\frac{1}{K'\mathrm{A}}(C_p\Delta T+K'a)\right]^n\left[-\ln\left(1-\frac{1}{K'\mathrm{A}}(C_p\Delta T+K'a)\right)\right]^p} \tag{12}$$

Equation (12) is reduced to the original relationship by Borchardt and Daniels for nth-order reactions when $m=p=0$, but may also be employed in a simpler form when the conditions $C_p\cdot\mathrm{d}\Delta T/\mathrm{d}t \ll K'\Delta T$ and $C_p\Delta T \ll K'a$ are experimentally met. In this case, in fact, the smaller terms may be neglected and eqn (12) for the rate constant becomes:

$$\mathrm{k}(T)=\frac{\Delta T/\mathrm{A}}{\left(\frac{a}{\mathrm{A}}\right)^m\left(\frac{\mathrm{A}-a}{\mathrm{A}}\right)^n\left[-\ln\frac{\mathrm{A}-a}{\mathrm{A}}\right]^p}=\frac{\Delta T/\mathrm{A}}{\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p} \tag{13}$$

Equations (9), (10) and (12), or (13), can then be used to determine the kinetic parameters of processes with a known empirical f(α). The determination of this α-function for the recrystallization of copper and its introduction in the new formulas is dealt with in the following section.

(*d*) *Determination of $f(\alpha)$ and empirical kinetics of recrystallization*

There are some indications from a DSC study of recrystallization on copper–oxygen alloys[18] that an analysis of DSC peaks according to Rogers and Smith, and Borchardt and Daniels gives rise to linear plots. Even though recrystallization cannot be framed in a scheme of nth-order transformation, the fractions of stored energy released by copper specimens heated at a rate of 30 °C min^{-1} also in the present case fit a straight line in a diagram derived from Rogers and Smith's theory (upper curve of Fig. 5).

The 1.7 reaction order deduced from the intercept value at the origin, or one slightly smaller ($n=1.6$) as will be discussed later on, would seem correct, since a

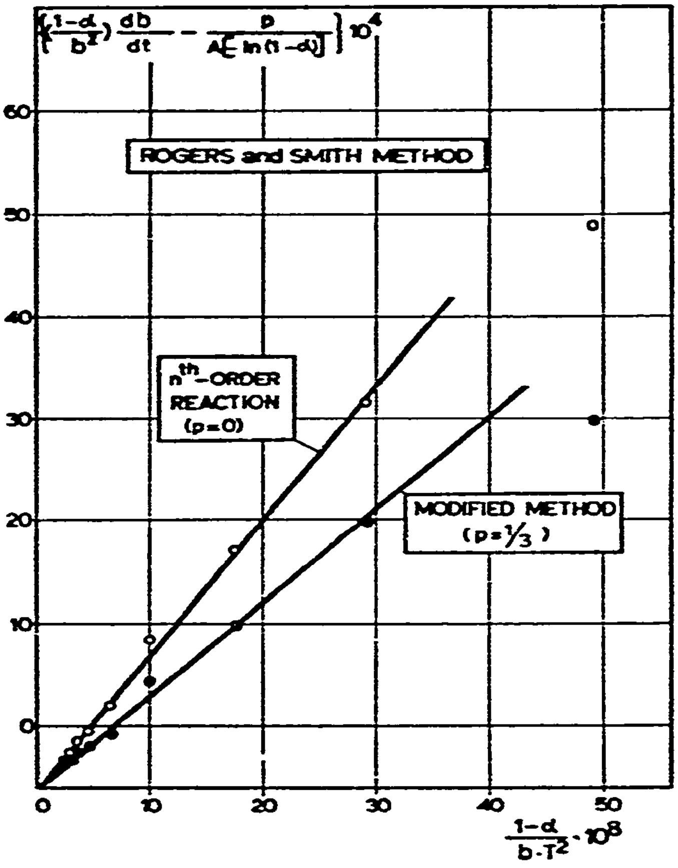

Fig. 5. Rogers and Smith plots according to the original method (upper curve) and to the generalized expression (9) adapted to Johnson–Mehl–Avrami's kinetics ($p = 1/3$, lower curve) for DSC curves of deformed copper heated at 30°C min^{-1}. b and t are measured in millimeters and seconds, respectively.

Borchardt and Daniels plot (unsuitable for a first order reaction, lower curve of Fig. 6a) is properly fitted if $n = 1.6$ (upper curve of Fig. 6a).

However, activation energy and frequency factor given by such diagrams strongly disagree with the other values of Table 1.

It is therefore worth pointing out that a linear fitting of the experimental data in Rogers and Smith's, and Borchardt and Daniels' plots may be obtained even in the presence of complex kinetics, which is obviously misleading if one expects to draw correct kinetic parameters.

A recent work on recrystallization of copper by Okada et al.[19] can be submitted to this kind of criticism, since a first order kinetics is assumed to calculate activation energy.

Rogers and Smith's method, however, is found suitable for detecting the very value of n that makes Borchardt and Daniels' plot become rectilinear (Fig. 6).

This fact brings one to surmise that $(1-\alpha)^n$ could be used as one of the two α-functions suitable for an empirical description of the recrystallization kinetics of copper.

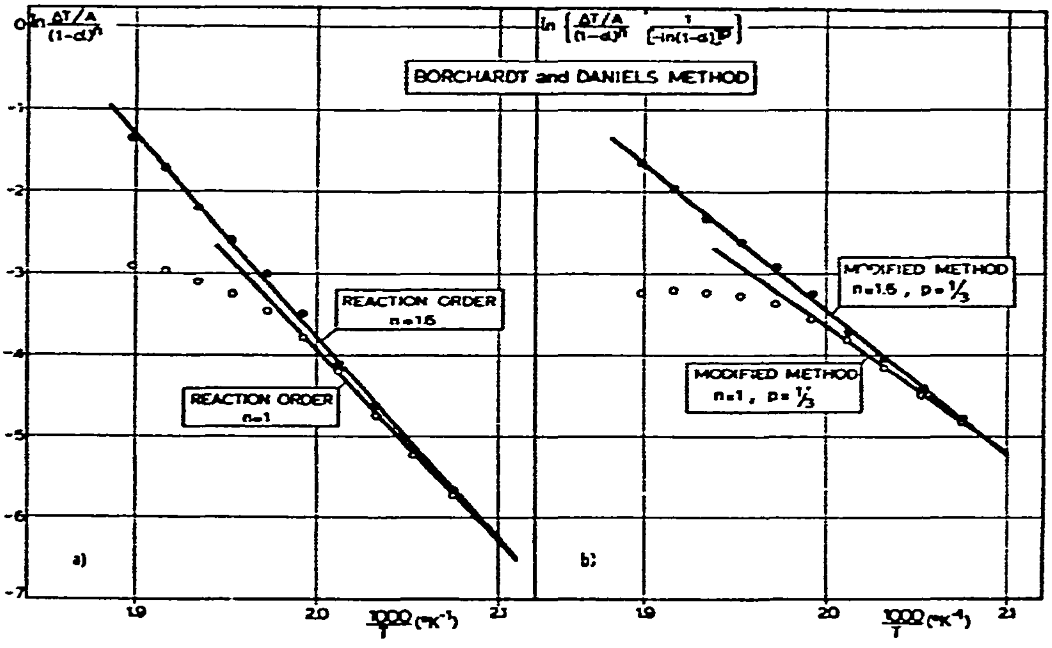

Fig. 6. Arrhenius plot of ln k vs. $1/T$ according to the Borchardt and Daniels method for DSC curves of deformed copper heated at 30 °C min^{-1}. (a) Original method for two different orders of reaction; (b) modified method in the simpler form (13) adapted to Johnson–Mehl–Avrami's kinetics ($n = 1$, $p = 1/3$; lower curve) and to the empirical expression $f(\alpha) = (1-\alpha)^{1.6}[-\ln(1-\alpha)]^{1/3}$ (upper curve).

The second function should be $[-\ln(1-\alpha)]^p$, which is contained in Johnson–Mehl–Avrami's equation. The appropriate choice of $p = 1/3$, in fact, leads to a plot of log $g(\alpha)$ vs. $1/T$ (Fig. 4) which is by 60% linear and has a correct slope.

The introduction of $p = 1/3$ and $m = 0$ values in Rogers and Smith's generalized expression (10) gives origin to the linear fitting of the present results reported in Fig. 5 (lower curve). While the intercept at the origin gives an n value similar to the one previously determined (1.6 instead of 1.7), it must be noted that both activation energy and frequency factor now become consistent with isothermal data, as reported in Table 1.

Modified Borchardt and Daniels' eqn (12) may be employed in its simpler form (13), in present experimental conditions of prestrained copper heated at 30°C min^{-1}. It may be seen (Arrhenius plot of Fig. 6b), that the introduction of the exponents $n = 1$ and $p = 1/3$ in expression (13), as suggested by Johnson–Mehl–Avrami's equation, can only account for the first half part of DSC peaks (lower curve), even though reasonable kinetic parameters may be deduced (see Table 1). A completely linear fitting of the Arrhenius plot is on the contrary obtained (Fig. 6b, upper curve) if one takes for the exponent n the 1.6 value furnished by the Rogers and Smith plot, corrected for the Johnson–Mehl–Avrami kinetics.

Both the generalized expressions by Borchardt and Daniels, and by Rogers and Smith lead to determine activation energy and frequency factor in good agreement with the isothermal method (see Table 1).

In the meantime both methods indicate that the rate of energy evolution during recrystallization of 85% cold-rolled copper depends on a function of the transformed fraction that may be expressed by:

$$f(\alpha) = (1-\alpha)^{1.6}[-\ln(1-\alpha)]^{1/3}$$

(*e*) *Kinetic parameters of recrystallization*

From a formal standpoint it is evident that the $n = 1.6$ exponent accounts for the symmetrical feature of the bell-shaped DSC curves, while the $p = 1/3$ exponent essentially fixes their width and the connected values of activation energy and frequency factor.

As for the E parameter, it has been shown that calibration tests by quenching strongly affects the results of Kissinger's and Ozawa's kinetic analysis and lead to calculate an activation energy higher than 31 kcal mol^{-1}. Such calibration, though less effective in the case of the single peak analysis, lowers the data of the generalized methods by Rogers and Smith and by Borchardt and Daniels down to 35 kcal mol^{-1}.

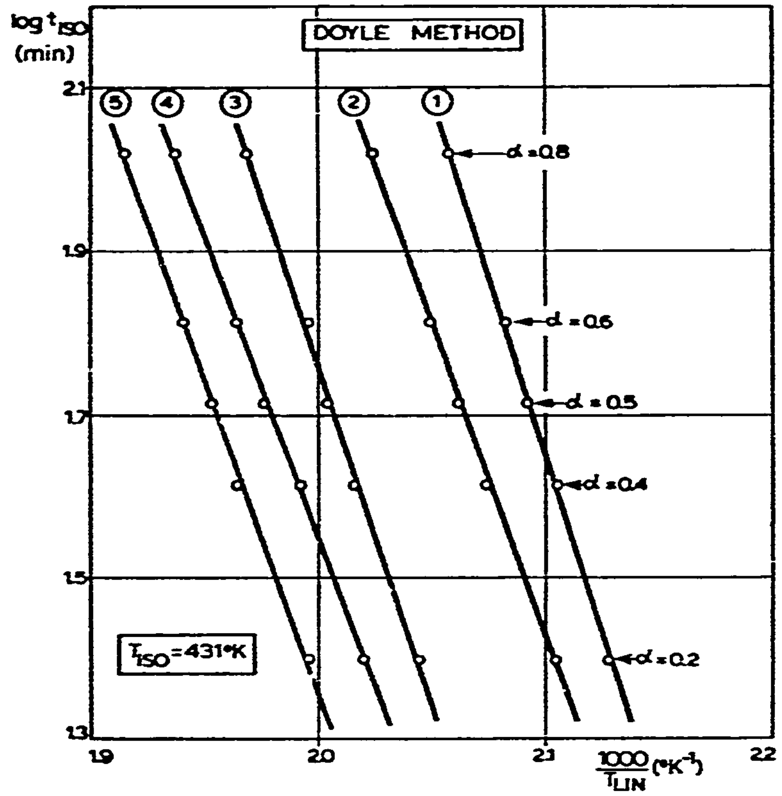

Fig. 7. Correlation between isothermal and non-isothermal heating, producing the same α transformed fraction in deformed copper: Doyle plot of the log time of isothermal heating at 431 K and the reciprocal of the absolute temperature at different constant heating rates. 1 = 5.5°C min^{-1}; 2 = 10°C min^{-1}; 3 = 20°C min^{-1}; 4 = 30°C min^{-1}; 5 = 50°C min^{-1}.

A further confirmation of this same field of possible values ranging between 31–35 kcal mol^{-1} is drawn from Doyle's method[20] which correlates the t_{ISO} times of isothermal treatment and the T_{LIN} temperatures reached at constant heating rate to produce the same α transformed fractions. Doyle's plot of log t_{ISO} at 431 K vs. $1/T_{LIN}$ for the present DSC results at various heating rates gives the straight lines of Fig. 7 and a consequent mean value of activation energy of 34.9 kcal mol^{-1} reported in Table 1.

The logarithmic values of Z frequency factor are also given in the same table. Their calculation has been performed on the basis of $g(\alpha) = [-\ln(1-\alpha)]^{1/3}$, as indicated by the Šatava method, or of $f(\alpha)$, when needed, with the exponents $n = 1.6$, $p = 1/3$. The $g(\alpha)$ contribution in the evaluation of Z is very small, when the isothermal and the Kissinger's and Ozawa's methods are employed, so that these data are practically independent of the kinetic model chosen. Taking a suitable $f(\alpha)$ is on the contrary of prime importance if Z is calculated from Rogers and Smith's or from Borchardt and Daniels' expressions.

As seen in Table 1, the relevance of a temperature calibration in the various cases examined is strictly parallel to the one discussed for activation energy results.

In any case the corrections adopted are able to reduce the spread in the values of Z by making them fall in the range 10^{10}–10^{14} sec^{-1}, typical for solid state reactions[12,13].

TABLE 1

KINETIC DATA FOR RECRYSTALLIZATION OF 99.999% COPPER DEFORMED BY ROLLING 85%

Method	*Activation energy, E (kcal mol^{-1})*			*Log of frequency factor, Z (Z in sec^{-1})*		
	(a)[a]	*(b)*	*(c)*	*(a)*	*(b)*	*(c)*
Kissinger[5]	22.4	27.9±1.8	31.1	7.64	10.31±0.79	13.62[b]
Ozawa[3]	23.2	28.4±1.7	31.4	8.12	10.60±0.78	12.02[b]
Šatava[11] ($n = 1, p = 1/3$)	30.8	29.8±0.6	29.0	11.48	11.27±0.27	11.12
Rogers and Smith[4]	—	52.4	—	—	21.37	—
Rogers and Smith modified ($p = 1/3$)	37.3	35.9±0.8	34.9	14.59	14.27±0.36	14.02
Borchardt and Daniels[17] ($n = 1$)	—	47.0	—	—	18.83	—
($n = 1.6$)	—	49.4	—	—	19.95	—
Borchardt and Daniels modified ($n = 1, p = 1/3$)	—	30.7	—	—	11.84	—
($n = 1.6, p = 1/3$)	36.4	35.3±0.4	34.3	14.15	13.92±0.19	13.70
Doyle[20]	—	34.9±2.5[c]	—	—	—	—
Isothermal		33.6±3.4			13.43±1.70[b]	

[a] The results are obtained: (a) from registered temperatures; and from temperatures calibrated (b) through melting tests, and (c) through quenching tests. [b] The frequency factor is evaluated on the basis of the Johnson–Mehl–Avrami equation $[-\ln(1-\alpha)]^{1/3} = k(T)\cdot t$. [c] Standard deviation calculated for straight lines of Fig. 7.

Among the various methods tested for a kinetic study of recrystallization, the isothermal technique, the non-isothermal analyses by Kissinger and Ozawa, and Doyle's correlation between isothermal and non-isothermal parameters do not require any initial assumption as regards the acting mechanisms to determine the activation energy of the process investigated. All of them have been found sufficiently in agreement, as to the value obtained for activation energy, to lead one to discard all kinetic formulations for solid state processes except the Johnson–Mehl–Avrami equation for linear growth of random nuclei ($p = 1/3$), which is also supported by the corresponding value of frequency factor, as mentioned above.

A mono-dimensional growth of recrystallized particles could actually prevail in the deformed matrix of copper before grain growth after recrystallization, because of the strong tendency of this metal to produce textures of isooriented crystals.

It should be of some interest, as far as the comprehension of the recrystallization process is concerned, to assess the theoretical significance of a change from 1 to 1.6 in the n exponent of the Johnson–Mehl–Avrami theory, which only foresees possible variations of the p exponent, according to the dimension of the process.

CONCLUSIONS

General aspects of non-isothermal kinetic analysis applied to the DSC technique have been considered in the present work, together with topics more specifically related to the recrystallization process investigated on copper.

Two orders of considerations have then been drawn, and those of the former type may be summed up as follows:

(1) Temperature calibration of DSC thermograms is mandatory when kinetic parameters are deduced from peak temperature dependence on heating rate. Kissinger's and Ozawa's methods would otherwise make one underestimate activation energy and frequency factor.

(2) When $f(\alpha)$ and $g(\alpha)$ functions of known reaction mechanisms cannot fully account for the experimental results of a given process according to Šatava's method, this latter could loose its efficacy as a means for detecting the more suitable kinetic model. The knowledge of activation energy deduced otherwise can, however, favour such a choice, thus giving information about the functions to be used for an empirical description of the phenomenon, as suggested by Šesták and Berggren.

(3) A linear fitting of the plots by Borchardt and Daniels and by Rogers and Smith is not probatory in establishing that the reaction or transformation is of nth-order, but rather indicates that $(1-\alpha)^n$ is one of the two suitable functions for an empirical evaluation of $f(\alpha)$. Both above-mentioned methods have been modified to widen the field of their application to more complex kinetics, which could not be described in terms of nth-order reactions.

As regards recrystallization of pure copper, prestrained to an 85% reduction in thickness, the following conclusions have been reached:

(1) Stored energy released during linear temperature rise gives a symmetrical DSC peak, the maximum rate of heat evolution always occurring at the half-transformation point $\alpha = 0.5$, independent of which heating rate has been adopted.

(2) Kinetic parameters of recrystallization derived from analytical methods of non-isothermal kinetics have been found consistent with the results of the isothermal method. Six different ways of evaluation indicate that the activation energy lies in the range 31–35 kcal mol^{-1} and the frequency factor between 10^{12} and 10^{14} sec^{-1}.

(3) In spite of the complex nature of the recrystallization process, the activation energy remains practically constant along the whole temperature range of stored energy release.

(4) The Johnson–Mehl–Avrami theory for phase transformation in metals can account for recrystallization progress in copper up to 60% of the transformed fraction, through its expressions for $f(\alpha) = (1-\alpha)\cdot[-\ln(1-\alpha)]^{1/3}$ and $g(\alpha) = [-\ln(1-\alpha)]^{2/3}$.

A description of energy evolution rate comprehensive of the later stages beyond $\alpha = 0.6$ is obtained if the dependence on the transformed fraction is expressed by $f(\alpha) = (1-\alpha)^{1.6}[-\ln(1-\alpha)]^{1/3}$.

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