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KINETICS OF NUCLEATION AND GROWTH REACTIONS INVESTIGATED BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

A method of evaluating non-isothermal calorimetric measurements is presented, which enables a kinetic study of the kinetics of nucleation and growth reactions. It is not necessary to assume a relationship such as the Johnson–Mehl–Avrami. All reactions can be investigated which are described by a single activation energy. A discussion is presented of the particularities and boundary conditions of calorimetry as well as the mathematical treatments of the results. The method is demonstrated by using the kinetics of the recrystallization of deformed silver.

INTRODUCTION

Empirically the course of a reaction can always be investigated by means of experiments. If, in addition, conclusions are to be drawn regarding kinetic laws then a model expression is required which applies to the reaction under consideration. Parameters can then be determined, such as activation energy, order of reaction and frequency terms. An elegant experimental method for following the course of a reaction is calorimetry. It is universally applicable, since each reaction is associated with a heat of reaction.

Modern calorimeters [1] measure the rate of heat production, i.e., the energy released per unit time, $\dot{E}(t)$. This is a measure of the instantaneous reaction rate. The specimen is subjected to a defined heating programme during which the reaction proceeds to completion. In the most common heating programme the specimen is heated in the calorimeter at a linear rate. The experimental parameter is the heating rate $\phi = \mathrm{d}T/\mathrm{d}t$, which can be varied over a certain range limited by the specifications of the calorimeters in use. Such calorimeters are termed "scanning" or "differential scanning calorimeters" (DSC). The $\dot{E}(t)$ curves often have the form of a peak, i.e., they are more or less bell-shaped. In the above-mentioned programme the temperature also changes during the reaction, which makes evaluation of the kinetic parameters more difficult, because the reaction is not only controlled by the kinetic mechanisms but also by the increased thermal activation. The

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temperature effect must be eliminated from the data before a quantitative analysis is possible.

This problem does not arise in the second, more frequently used method, namely, isothermal annealing. In this method the specimen is heated from a low temperature to the test temperature as quickly as possible and then maintained at this temperature. An abrupt change in temperature is not possible experimentally, hence the reaction starts before the test temperature is reached. The starting point of the reaction is thus not exactly defined. In addition, the temperature profile in the calorimeter is disturbed by the rapid heating and therefore the instrument is not capable of providing reliable results during heating and for some time after. Consequently the start of the reaction in isothermal heating is not known exactly. These problems, however, do not arise in non-isothermal heat treatment with a constant heating rate. The settling down of the control system at the start of the programme is long completed before the reaction starts and hence the complete reaction is recorded. The definition of a starting point is irrelevant in non-isothermal reactions. To evaluate the results (see below) the signal $\dot{E}$ is required not as a function of the time but of the temperature $\dot{E}(T)$. The time is thus only a process parameter, which is used during measurement but eliminated before the evaluation.

A further disadvantage of isothermal measurements is that the appropriate temperature must be previously determined. At too high a temperature, the reaction proceeds too quickly and occurs during the initial "perturbed" period. If the temperature is too low the heat flow is insufficient and the noise level is such that the accuracy is reduced. In non-isothermal experiments the possible temperature interval is passed until the reaction is complete. Thus the reaction temperature is found automatically, without special experiments.

The comparison of isothermal and non-isothermal experiments can be summarized as follows: the isothermal method is easier to evaluate, there are, however, some important disadvantages concerning the course of the measurements. The non-isothermal method is experimentally superior but requires specific evaluation procedures due to the change in temperature during the reaction. The advantages of the non-isothermal method are sufficiently marked that an effort should be made to develop appropriate procedures for evaluation, particularly since with modern computers increased calculation time is no longer a handicap.

For chemical reactions of order n there are various methods with which non-isothermal measurements can be evaluated. They assume a kinetic differential equation of the form

$$\dot{X} = \frac{\mathrm{d}X}{\mathrm{d}t} = A(1 - X)^n \exp(-Q/RT) \tag{1}$$

where X is the fraction of reactants which at time t have already reacted, n

is the order of reaction, A a frequency factor and Q the activation energy of the reaction. The reaction rate $\dot{X}(t)$ is directly proportional to the calorimetric signal $\dot{E}(t)$. $X(t)$ is thus proportional to the released energy up to time t.

$$E(t) = \int_0^t \dot{E}(t')\mathrm{d}t'.$$

The often cited method of Borchardt and Daniels [2] and that of Rogers and Smith [3] enable a determination of the kinetic parameters in eqn. (1) from a single non-isothermal calorimetric curve. Kissinger [4,5] and Ozawa [6] describe procedures to calculate the activation energy, Q, from the dependence of the peak maximum temperature upon the heating rate. Several measurements on like specimens are necessary at different heating rates. A high resolution is not required as the curve itself is not evaluated: the only requirement being that the maximum can be clearly recognised. The procedures cannot be adopted for reactions for which the kinetic differential equation (1) does not apply, e.g., reactions involving nucleation. Reactions which follow eqn. (1) exhibit for isothermal conditions the highest rate, $\dot{X}$, at the start which then decreases as the reactants are consumed. Nucleation-controlled reactions show, on the other hand, initially an incubation period, i.e., a period of very low reaction rate, followed by an acceleration of the reaction towards a maximum and a final decrease to zero.

Such principal differences in the shape of the data curves for reactions with and without nucleation are not to be found for non-isothermal measuring conditions: In both types of reaction the chart curve passes through a maximum. By this, one can be misled into applying one of the above evaluation procedures to reactions for which the basic differential equation (1) is not valid. The results of such incorrect procedures are computer-optimized parameters, which cannot be reasonably interpreted (see, e.g., refs. 7 and 8). In the case of reactions involving nucleation and growth there are phenomenological models which apply to the isothermal case only (Johnson and Mehl [9], Avrami [10], Cahn [11]). The use of these assumptions in non-isothermal experiments is possible under some circumstances [6,12].

In this work a procedure for evaluating non-isothermal measurements is presented, which is based on a more general kinetic differential equation than eqn. (1). It permits the study of nucleation and growth processes without using the prerequisites of a specific model like that of Johnson–Mehl–Avrami. The technique is discussed for the case of primary recrystallization of plastically deformed silver. To this end the primary recrystallization process is first characterized, then the experimental details are presented. This is followed by a description of the model used and a discussion of the evaluation and interpretation. Finally the possibilities and limitations of the technique are discussed.

PRIMARY RECRYSTALLIZATION, PHYSICAL CHANGES AND KINETIC DESCRIPTION

When a metal is plastically deformed, lattice defects and, in particular, dislocations are produced. The enthalpy of the metal is increased predominantly as a result of the energy of the elastic strain fields of these defects. The increase is called "stored energy". At sufficiently high temperatures this thermodynamically metastable, deformed state is replaced by an almost defect-free state, the defects becoming mobile and annealing out by thermal activation. The stored energy is released. Primary recrystallization is such a process (e.g., see ref. 13) with a specific reaction mechanism: after an incubation period small regions of low dislocation density form in the metal, which are bounded by large angle boundaries. These nuclei grow into the high dislocation density region by grain boundaries moving until they touch those of other growing nuclei. During movement, atoms are absorbed by the boundary from the dislocation-dense regions and then deposited in the correct crystallographic orientation on growing nuclei. Thus the material is swept out from the dislocations by the moving grain boundaries. The energy of disorder caused by dislocations is released as heat of recrystallization. On completion of primary recrystallization the metal consists of completely new grains.

Primary recrystallization is thus an inhomogeneous process. During recrystallization, regions of deformed material lie next to recrystallized regions. The course of recrystallization is described in kinetic studies by the degree of recrystallization, X, which represents the fraction of recrystallized volume, V_R, of the total volume, V_T

$$X = \frac{V_R}{V_T} (X = 0\text{–}100\%) \tag{2}$$

The degree of recrystallization is determined using stereology, i.e., by quantitative measurement of metallographic sections. Even if great care is taken, a large degree of uncertainty is unavoidable, particularly for small and large degrees of recrystallization. To determine the time dependence of recrystallization a whole series of specimens must be prepared, which is very time consuming.

Kinetics can be studied very elegantly using calorimetry. In calorimetry the release of stored energy is recorded continuously. Thus the degree of recrystallization, $X(t)$, can be simply determined from the energy, $E(t)$,, which is released up to time t and the total energy released, E_f (f = final). The unrecrystallized specimen volume contains the same energy density as was present before recrystallization in the whole specimen. In the recrystallized volume, on the other hand, an undeformed state exists with a defect energy density effectively zero. Hence

$$\frac{E(t)}{V_R(t)} = \frac{E_f}{V_T}$$

or, with eqn. (2)

$$X(t) = \frac{V_R(t)}{V_T} = \frac{E(t)}{E_f} \tag{3}$$

A condition for these equations is that there are no competing processes which reduce the disorder-energy. In the case of metals which show a marked tendency for recovery, e.g., aluminium, an evaluation based on calorimetric measurements cannot be applied, without taking specific precautions.

The reaction rate from eqn. (3) is

$$\dot{X}(t) = \dot{E}(t)/E_f \tag{4}$$

The calorimeter measures, therefore, apart from the normalising factor, E_f, the reaction rate directly. The reaction coordinate, $X(t)$, can be obtained by integration. In other experimental techniques, as, for example, stereological measurements, the degree of recrystallization itself is the primary experimental quantity. Since a calorimetric signal, $\dot{E}(t)$, can be measured accurately and easily resolved the uncertainty in $X(t)$ in calorimetric measurements is much smaller than in other experimental techniques suitable for studying recrystallization kinetics.

EXPERIMENTAL DETAILS

Cylindrical silver specimens, purity 99.999% (Degussa, Hanau), with a uniform grain structure and a mean grain size of 0.03 mm were plastically deformed in torsion up to a shear strain of $\gamma = 4.8$ at the surface. A specimen of 8 mm diameter and length 30 mm must thus be twisted through six revolutions. Torsion leads to a radially inhomogeneous deformation. Thus for the calorimetric measurements thin-walled tubes, which can be considered as homogeneously deformed, were cut from the rods.

The calorimetric measurements were carried out in a differential heat flux calorimeter, type MCB (Thermanalyse, Grenoble). Specimens with the same deformation were annealed at six different heating rates between 0.09 and 4.4 K min^{-1}.

In all calorimetric measurements it must be borne in mind that the signal is a delayed and distorted reproduction of the course of the heat flux at the site of the specimen. This is unavoidable due to the thermal resistance and capacity of parts in the calorimeter. The distortion changes the shape of the peak and also displaces it to higher temperatures. Characteristic points in the peak, e.g., the time of and temperature of the peak maximum at the specimen itself and in the recorded signal, are not the same. This distortion

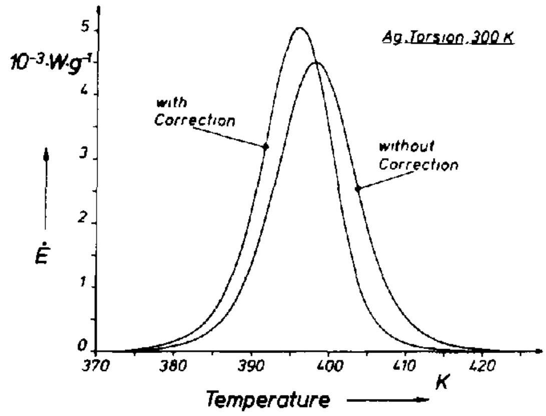

Fig. 1. A typical recrystallization peak and the curve corrected for distortion. Twisted silver, $\dot{E}$ = rate of heat release, heating rate $\phi = 4.4$ K min^{-1}.

can be largely eliminated [15] by suitable correction, so that the result is the undelayed heat rate with respect to the specimen mass, $\dot{E}(t)$ (see example, Fig. 1). The total released energy, E_f, is obtained from this by integration. This is independent of the heating rate, 770 mJ g^{-1} ± 5%.

The procedure to determine the recrystallization rate and degree of recrystallization is as follows: the time in the abscissa for the heating rate $\dot{E}(t)$ and the heat released $E(t)$ is replaced by the absolute temperature according to the programme used: $T = T_0 + \phi t$. After division by the total energy, E_f, the rate of recrystallization, $\dot{X}(T, \phi)$, and the degree of recrystallization, $X(T, \phi)$, are calculated (eqns. 3 and 4). Figure 2 shows the curves of $X(T, \phi)$ for different heating rates. The shift of the recrystallization to higher temperatures with increasing heating rate can be clearly seen.

The course of $\dot{X}(T, \phi)$ and $X(T, \phi)$ presents the kinetic data in a form appropriate for evaluation. Further processing requires some rather general relationships which are presented and confirmed below.

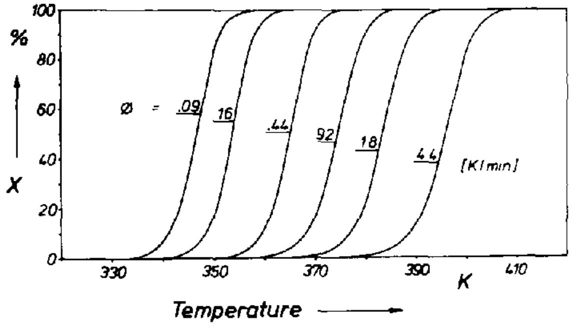

Fig. 2. Degree of recrystallization, X, versus temperature for non-isothermal measurements with different heating rates. Specimens: twisted silver.

KINETIC DIFFERENTIAL EQUATION AND MODEL DESCRIPTION

An adequate mathematical description of anisothermal calorimetric quantities is obviously not without problems (see, for example, ref. 16). This will therefore be discussed here in some detail.

Since recrystallization is an irreversible process, the degree of recrystallization is not a state parameter but depends on the history of the specimen. In a thermally activated process, therefore, this depends on the temperature programme, $T(t)$, that the specimen has experienced. For an individual specimen subjected to particular heating programme, X is determined initially as a function of the variable time, i.e., $X(t)$. In the case of results from non-isothermal measurements the results are transformed using the known $T(t)$ to a dependence on T, i.e., $X(T)$. If several measurements with different temperature programmes are available for similar specimens, X can be expressed as a function of a continuous variable and a discontinuous test parameter. It must be clear in each case which type of experimental programme is being used. A general formulation, e.g., $X = X(T, t)$, is not possible.

Hence for isothermal experiments

$$X = X(t, T)$$

where t = time, continuous; T = test temperature, discrete values. For non-isothermal experiments

$$X = X(T, \phi)$$

where T = temperature, continuous; ϕ = heating rate, discrete values.

The correlation of these expressions with the measured recrystallization rate, $\dot{X}$, may easily be given, bearing in mind that $\dot{E}$ as a measured physical quantity and, in consequence, $\dot{X}$ are total differentials: $\dot{X} = \mathrm{d}X/\mathrm{d}t$. Therefore the following relations hold. In the isothermal case

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \left.\frac{\partial X}{\partial t}\right|_T + \left.\frac{\partial X}{\partial T}\right|_t \frac{\mathrm{d}T}{\mathrm{d}t} = \left.\frac{\partial X}{\partial t}\right|_T \quad (T = \text{const.})$$

in the non-isothermal case

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \left.\frac{\partial X}{\partial T}\right|_\phi \frac{\mathrm{d}T}{\mathrm{d}t} + \left.\frac{\partial X}{\partial \phi}\right|_T \frac{\mathrm{d}\phi}{\mathrm{d}t} = \left.\frac{\partial X}{\partial T}\right|_\phi \phi \quad (\phi = \text{const.})$$

A disadvantage of the previous representations is that they depend on the temperature programme and hence cannot be directly compared. This problem can be eliminated if one variable from the corresponding values for the reaction rate and degree of recrystallization is eliminated. For isothermal measurements, the time

$$\left.\begin{matrix} \dot{X}(t, T) \\ X(t, T) \end{matrix}\right\} \rightarrow \dot{X}(X, T)$$

for non-isothermal measurements, the heating rate

$$\left.\begin{matrix}\dot{X}(T, \phi) \\ X(T, \phi)\end{matrix}\right\} \rightarrow \dot{X}(X, T)$$

This formal mathematical transformation can be carried out in any case in a similar manner, even for different types of temperature programme.

It cannot, however, be concluded that the functions $\dot{X}(X, T)$ found do not depend on the type of temperature programme! Such programme-independent kinetic equations can only be expected under a special physical condition: it is necessary that for a particular value of X, the same internal state always exists within the specimen, independent of the way in which this state was achieved. Only then can a programme-independent description $\dot{X}(X, T)$ be found. This description corresponds to a simple general idea about the course of the observed process: the instantaneous change of the reaction, described by $\dot{X}$ depends only on the actual temperature and the actual condition of the specimen, described by X. Carrying out a series of measurements on identical specimens under various conditions (isothermal: change in temperature of measurement; non-isothermal: variation of heating rate) $\dot{X}(X, T)$ may be evaluated over a wide range of values without further assumptions being necessary. In order to obtain sufficient accuracy, however, very many measurements would be necessary. In addition, in an experimentally determined variation of this function the information on the reaction mechanisms is contained in a concealed form.

In order to reduce the volume of experimental work and to interpret the results it is necessary to make further assumptions regarding $\dot{X}(X, T)$ which must subsequently be verified. In many cases a separating of the variables has proved useful in which the influence of temperature is described by an Arrhenius equation

$$\dot{X}(X, T) = \mathrm{f}(X) \exp(-Q/RT) \tag{6}$$

The following evaluation is based on this kinetic differential equation. No assumption is made regarding the transformation function $\mathrm{f}(X)$. The aim of the following method of evaluation of the "complete analysis" is

(1) to prove that the observed reaction can be described by a differential equation of the form (6),

(2) to determine the activation energy, Q, and the transformation function, $\mathrm{f}(X)$.

This evaluation also includes, as a special case, reactions of the nth degree according to eqn. (1).

COMPLETE KINETIC EVALUATION

The complete kinetic evaluation requires that the results must be in a form that enables a comparison with the differential equation (6). To this end the

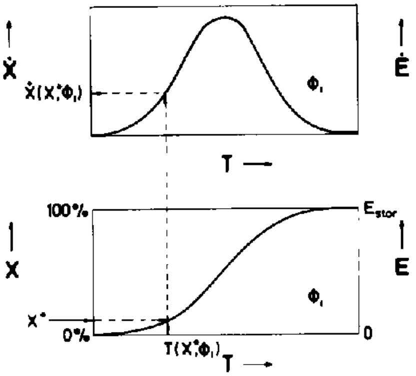

Fig. 3. Scheme of the evaluation of the temperature, T^+, and the rate of recrystallization, $\dot{X}^+$, for a given degree of recrystallization, X^+, and a fixed heating rate, ϕ_i.

heating rate, ϕ, is eliminated from the corresponding experimental curves for the recrystallization rate, $\dot{X}(T, \phi)$, and degree of recrystallization, $X(T, \phi)$. If a fixed degree of recrystallization, X^+, is considered (e.g., $X^+ = 15\%$) then this is attained at different temperatures depending on the heating rate. As shown in Fig. 3 the corresponding recrystallization rates, $\dot{X}_i^+$, may be determined simply, so that for each heating rate a pair $(\dot{X}_i^+, T_i^+)$ can be found which satisfies the differential equation when the degree of recrystallization in question is substituted

$$\dot{X}_i^+ = f(X^+) \exp(-Q/RT_i^+) \tag{7}$$

If ln $\dot{X}_i^+$ is plotted against $(1/T_i^+)$ then the points should lie on a straight line with slope $(-Q/R)$. The intercept with the abscissa $(1/T = 0)$ gives ln f(X^+). Since Q is assumed to be constant it should be independent of the special value of X^+. Figure 4 shows corresponding plots for various degrees

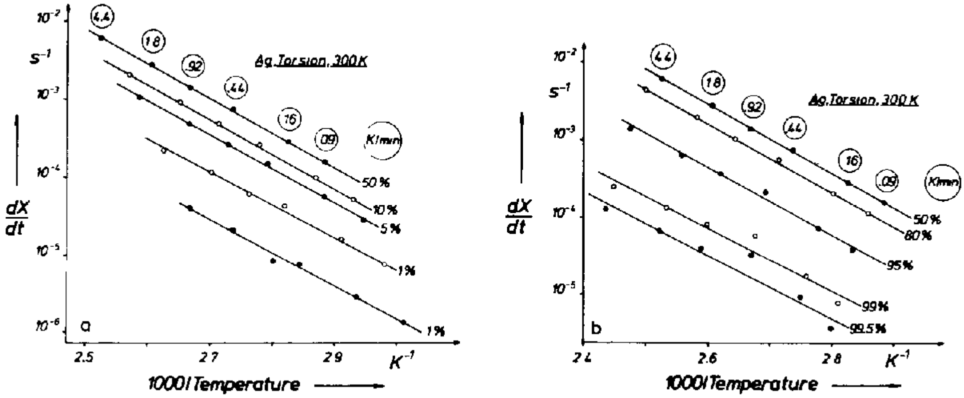

Fig. 4. Logarithmic representation of the rate of recrystallization, $\dot{X}$, versus the reciprocal absolute temperature. Points belonging to the same degree of recrystallization, X, are approximated by straight lines.

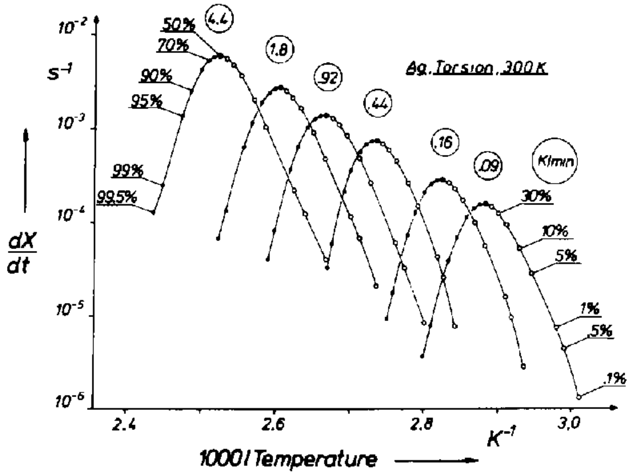

Fig. 5. All data points used for evaluation. Points belonging to the same measuring-run (i.e., the same heating rate) are connected. For the coordinates see Fig. 4.

of recrystallization, X^+. As can be seen the points for the same degree of recrystallization lie on a straight line. The agreement is poorer for low and high degrees of recrystallization, as the heat flux is too low to obtain a very high accuracy. The slopes of the straight lines agree well, which demonstrates that they involve the same activation energy. Not all points are plotted in Fig. 4 for reasons of clarity. These are shown in Fig. 5.

The activation energies obtained are plotted in Fig. 6, also showing the appropriate standard deviation (see, for example, ref. 17) against the degree

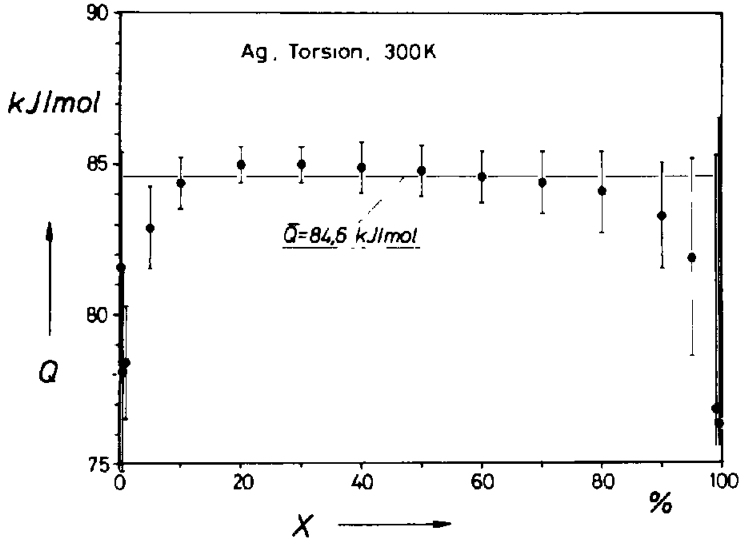

Fig. 6. Apparent energy of activation, Q, evaluated for different degrees of recrystallization, X. Mean value $\bar{Q} = 84.6$ kJ mol^{-1}.

of recrystallization. The scatter at low and high degrees of recrystallization are, as expected, much larger than for intermediate values, due to the above-mentioned uncertainty. A value of $Q = 84.6$ kJ mol^{-1} lies within the scatter band of almost all experimental points. The decision whether the deviations from this value are caused by experimental error or represent a physical reality cannot be made on the basis of mathematical considerations alone. Physical considerations must also play a role. The different processes which take place during recrystallization must be considered (see Interpretation of Results Section). If, for the present, one assumes that a single activation energy exists, then a completion of the evaluation is possible. The transformation function $f(X)$ can be calculated from the mean activation energy and from the experimental points for $\dot{X}$ using eqn. (6). Equation (6) is transformed to give $f(X)$ when the values for $\dot{X}$, T and the mean value for Q are substituted. One value $f(X)$ is obtained for each X and each heating rate. Figure 7 shows the transformation function. Each point is the mean of six values. The function is almost parabolic with zero values at $X = 0$ and 100%.

The numerical part of the kinetic evaluation is thus complete. The various steps in the evaluation procedure are collated in the following diagram.

Scheme of complete kinetic evaluation

(1) Measurement of heat flux at various heating rates ϕ_t on identical specimens.

(2) Correction of the "distortion", i.e., determination of the true heat flux, $\dot{E}(t, \phi_t)$.

(3) Elimination of time scale using the known temperature programme $T = T_0 + \phi_t t$: $\dot{E}(T, \phi_t)$.

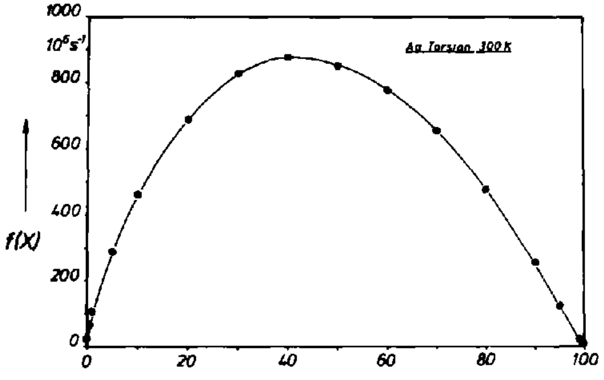

Fig. 7. Transformation function, $f(X)$, for the recrystallization of twisted silver. $f(X)$ was calculated using an activation energy of 84.6 kJ mol^{-1}.

(4) Calculation of released energy, $E(T, \phi_t)$, and the total released energy, E_f

$$E(T, \phi_0) = (1/\phi_t)T_0 \int_0^T \dot{E}(T', \phi_t)\mathrm{d}T'$$

$E_f = E(T_f, \phi_t)$ should be independent of the heating rate, T_f = final temperature.

(5) Calculation of the recrystallization rates, $\dot{X}$, and degree of recrystallization, X

$\dot{X}(T, \phi_t) = \dot{E}(T, \phi_t)/E_f; \quad X(T, \phi_t) = E(T, \phi_t)/E_f$

(6) Calculation of the temperatures, T_t^+, and the recrystallization rates, $\dot{X}_t^+$, which exist for a particular heating rate on attaining a chosen degree of recrystallization, X^+.

(7) Check, whether the plot of ln $\dot{X}_t^+$ against $1/T_t^+$ is linear. If yes determine the activation energy from the slope.

(8) Carry out steps (6) and (7) for various values of the degree of recrystallization, X^+. The result is the dependence of $Q(X)$.

(9) Decide whether deviations of $Q(X)$ from the mean value are the result of experimental error or physical effects. Only if a single value of Q is confirmed the evaluation of the kinetics is valid.

(10) The transformation function, f(X), is calculated from the experimental data to 7, 8 ($\dot{X}_t^+$, T_t^+, X^+) and the single value of activation energy in the kinetic differential equation.

INTERPRETATION OF RESULTS

The physical arguments are first discussed as to whether the deviation of the measured activation energy from the mean value is an actual effect or simply experimental error. To this end the recrystallization process will be recapitulated. Recrystallization consists of nucleation and growth. It is generally assumed that each process has its own activation energy (see, e.g., ref. 18). The activation energy for nucleation has the largest influence in the initial stages and that of growth in the latter stages of recrystallization. Thus it is to be expected that the effective activation energy increases monotonically, if the activation energy of nucleation is less than that of growth. In the reverse case $Q(X)$ should decrease monotonically. An effective activation energy first increasing and then decreasing, as would appear to be the case in Fig. 6, is not to be expected. Thus it is reasonable to interpret those small deviations in the measured activation energy in Fig. 6 as experimental scatter. The condition for a complete kinetic evaluation is thus fulfilled.

The models of theories on the kinetics of nucleation and growth are based on the works of Johnson/Mehl [9], Avrami [10] and Cahn [11]. The isothermal recrystallization is described by

$$X(t, T) = 1 - \exp\left[-\left(\frac{t}{t_0}\right)^r\right] \tag{8}$$

whereby r, depending on the details of the model used, lies between 1 and 4. The quantity t_0 contains, besides other parameters, the influence of temperature on the course of the reaction. Following the procedure given above, the kinetic differential equation for an Avrami-reaction can be derived if it is assumed that only one activated process is involved

$$t_0 = \tau_0 \exp(+Q/RT) \tag{9}$$

τ_0 = constant for fixed specimen parameters.

First, the reaction rate is calculated by derivation of the Avrami equation with respect to time, t. Then the time is eliminated from the resulting equation using relations (8) and (9).

One obtains

$$\dot{X} = A \exp\left(-\frac{Q}{RT}\right)(1 - X)\left[\ln\left(\frac{1}{1 - X}\right)\right]^p; \quad p = 1 - \frac{1}{r}, \quad A = \frac{r}{\tau_0} \tag{10}$$

The transformation function for the Avrami relation is obtained by comparison with relationship (6)

$$\mathrm{f}(X) = A(1 - X)\left[\ln\left(\frac{1}{1 - X}\right)\right]^p \tag{11}$$

The quantities $f_{\text{ext}}(X) \equiv \mathrm{f}(X)/(1 - X)$ and $X_{\text{ext}} \equiv -\ln(1 - \mathrm{X})$ are plotted double logarithmically to test whether the transformation function established for twisted silver satisfies eqn. (11). In the case that eqn. (11) is valid the experimental points should lie on the straight line

$$\log f_{\text{ext}}(X) = A + p \log X_{\text{ext}}(X) \tag{12}$$

The corresponding plot for silver (Fig. 8) confirms a linear relationship only for low X values up to 50%. The exponent, p, determined from the slope, was 0.666. Hence the Avrami exponent, $r = 1/(1 - p) = 3$. The Avrami relationship is thus only satisfied up to $X = 50\%$. Thereafter, recrystallization proceeds much more slowly. This effect cannot be attributed to recovery as Vandermeer and Gordon [19] did in the case of aluminium. Silver, with its lower stacking-fault energy, does not tend to recovery. Additional experiments on other metals have shown that such a deviation from a straight line is common at high degrees of recrystallization. This is discussed, together with the metal physical interpretation for r and Q, in a separate publication [20].

Šesták [21] in a review article listed a series of parametric assumptions for the transformation function f(X). The only one which may be applied for recrystallization is the following expression since it is the only one with zero values at $X = 0$ and $X = 1$

$$\mathrm{f}(X) = AX^n(1 - X)^m \tag{13}$$

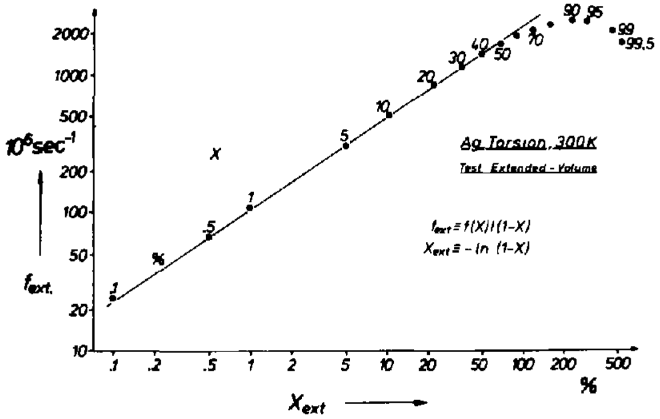

Fig. 8. Plot used for testing the non-isothermal measuring data for fitting the Avrami-theory. See text, especially (11) and (12).

The parameters A, n and m were fitted to the experimentally determined transformation function for silver by using a computer. It could be observed that the transformation function could be well described by eqn. (13). Over the range $X = 5$–80% the optimised function deviated from the experimental points by not more than 2% (Fig. 9). A similarly accurate matching is not to be expected at lower and higher degrees of recrystallization due to experimental uncertainty. For a physical discussion of these results, see also ref. 20. This possible representation of results is presented here simply to show

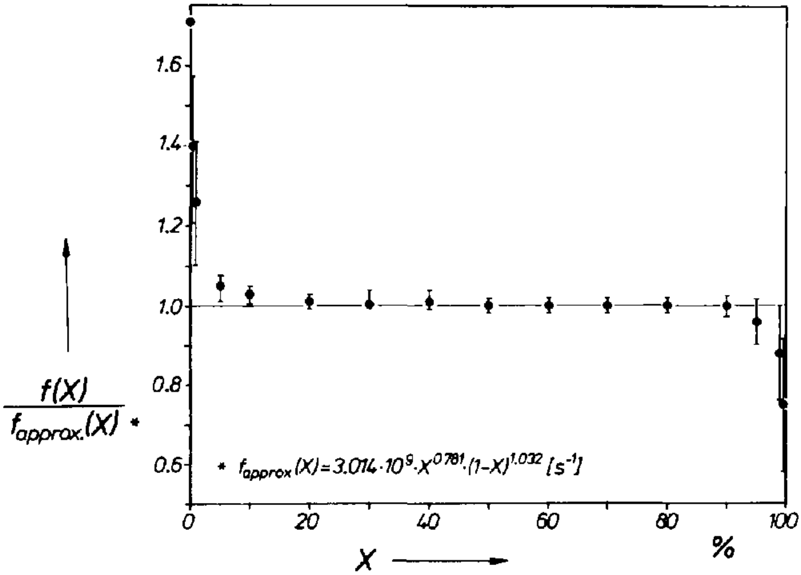

Fig. 9. Optimized approximation of the transformation function, f(X), by an equation of the type f(X) = $AX^n(1-X)^m$. The fraction of measured and optimized values is plotted.

that in an evaluation of measurements of kinetics of nucleation and growth reactions, it cannot be generally assumed that a description of the process by a generalized Johnson–Mehl–Avrami equation (10) is valid. This must first be established!

In conclusion, it should be pointed out that in other methods of studying recrystallization, e.g., metallographic methods, it is most probably not possible to detect the above-mentioned deviations. It seems most likely that a false, apparent Avrami exponent is obtained. There are two explanations for this. Metallographic measurements cannot be carried out at such low and high degrees of recrystallization as is the case in calorimetry. The range in which the Avrami plot can be checked is thus markedly limited. On the other hand the plot shown in Fig. 8 is particularly "sensitive" as the recrystallization rate and not only the degree of recrystallization is used.

ASSESSMENT OF CALORIMETRY AS AN EXPERIMENTAL METHOD AND OF THE PRESENTED PROCEDURE FOR THE EVALUATION

Calorimetry as an experimental method offers a series of clear advantages over other techniques.

The calorimeter provides a continuous signal which is proportional to the rate of reaction, $\dot{X}$, and is measured under defined thermal boundary conditions. The resolution and accuracy which can be obtained with modern instruments is excellent. The measurement does not interfere with the reaction and provides a volume-average signal for the specimen.

In a calorimetric measurement the specimen is subjected to a predetermined temperature programme. Common programmes are linear rates of heating and measurements at constant temperatures. Both have specific advantages and disadvantages. The isothermal experiments are more easily evaluated and the non-isothermal easier to carry out. In our opinion, with a suitable evaluation procedure, non-isothermal experiments are superior.

Some common evaluation procedures are either limited to reactions which satisfy the kinetic differential equation of the form $\dot{X} = A(1 - X)^n \exp(-Q/RT)$ or assume a generalised Avrami equation without further examination, or use only isothermal measurements. In all these equations X is a dimensionless quantity, which represents the fraction of transformed material.

The evaluation procedure presented here enables non-isothermal calorimetric data to be used to investigate reactions which do not satisfy the above kinetic differential equation, for instance nucleation and growth reactions. The only condition for a satisfactory evaluation is that the thermal activation process can be described by one single activation energy. The procedure presented here enables (1) a check to be made whether $X = f(X) \exp(-Q/RT)$ is satisfied and (2) to determine the parameter Q and the transformation function f(X) to within a few percent. No assumptions must be made regarding the form of f(X). In particular, the high degree of accuracy should be noted. The activation energy as well as the transformation function show a scatter of only a few percent.

It remains a problem in a particular case to find a suitable physical model to interprete the results. A decrease in the experimental error naturally leads to deviations from the available theories being detected, thus the theories must either be extended or modified.

The computer effort required for the evaluation is not a significant disadvantage. If the calorimeter is connected directly to the computer, the calculations are easily carried out.

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