

Analysis of Transformation Kinetics by Nonisothermal Dilatometry

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Nonisothermal dilatometry was shown to provide a powerful method for the analysis of solid-state transformation kinetics by measuring the shifts of the temperatures of inflection points on dilatometric curves as a function of heating rate. The method was applied to iron-nitrogen martensite specimens. To that end iron was nitrated in a NH_3/H_2 gas mixture and subsequently quenched. The experiments allowed the assessment of residual terms in the theoretical development. To demonstrate the high sensitivity of the method, the activation energy was determined for the initial stage of tempering iron-nitrogen martensite, involving a minute decrease of specific volume. The method developed is equally applicable to methods where other physical properties of the material under investigation (*e.g.*, electrical resistivity, magnetization) are measured on isochronal annealing.

I. INTRODUCTION

EVALUATION of kinetic reaction parameters, as activation energies, can be based on the analysis of measurements, taken as a function of time, t , and temperature, T , of a physical property (*e.g.*, specific volume/length, electrical resistivity, magnetization), p , of the material subject to investigation. The fraction transformed, f , can be defined as

$$f = \frac{p - p_0}{p_1 - p_0} \quad [1]$$

where p_0 and p_1 refer to start and finish of the transformation, respectively.

An obvious experimental approach implies the determination of f as a function of time for a series of fixed temperatures. Studying solid-state reactions the Johnson-Mehl-Avrami (JMA) description, originally developed for the analysis of *isothermal* behavior of f , can often be applied satisfactorily although the limitations of this theory are generally recognized.¹

However, experiments are frequently performed in a *non-isothermal* fashion. For example, application of a constant heating rate (isochronal annealing) may afford better experimental stability and reproducibility. It is tempting to adopt the JMA description also in the case of nonisothermal annealing, but its application is not straightforward (see Section II).^{1,2,3}

Isochronal annealing for the determination of kinetic parameters of transformations has mostly been performed in thermal analyses as differential scanning calorimetry (DSC). Then, the operating activation energy can be obtained according to the Kissinger analysis,⁴ or variants thereof (*e.g.*, Reference 5). To that end the temperature where the reaction rate is maximal, associated with the DSC peak signal, is investigated as a function of heating rate.

The analysis of length changes, dilatometry, provides a sensitive method to describe many solid-state transformations. Dilatometry is usually performed applying a constant heating rate. According to the present authors' opinion, in nonisothermal dilatometry a development of methods for

kinetic analysis, analogous to those applied for constant heating-rate experiments in thermal analyses, has been neglected until now. It is the purpose of this paper to demonstrate that such methods are possible. In particular it will be shown that a powerful method for the determination of the activation energy can be based on tracing the temperature where an inflection point occurs in the dilatometric curve, as a function of heating rate.

Relative length changes are proportional to relative volume changes if the system undergoing phase transformation can be conceived as (macroscopically) isotropic. In the case of anisotropy, that may occur in the case of specimens exhibiting preferred orientation for the constituent crystallites/grains, distinction should be made between length and volumetric changes. In principle this does not affect the treatment given in this paper; such anisotropy can be studied by the method presented.

First the theoretical background is indicated; special attention is devoted to the consequences of the temperature dependence of the reference (length) states, $l_0(T)[\triangleq p_0(T)]$ and $l_1(T)[\triangleq p_1(T)]$, as the specific volumes of virgin and product phases obviously depend on temperature and consequently change on (isochronal) annealing (Section II).

The analysis is applied to the initial stage of tempering iron-nitrogen martensite, which has been selected to serve as an example since (i) the high sensitivity of the method can be demonstrated because a minute length change is involved, and (ii) a thermal analysis has been made previously, thus allowing comparison^{6,7} (Sections III and IV).

II. KINETIC ANALYSIS BY ISOCHRONAL ANNEALING; EFFECT OF TEMPERATURE DEPENDENCE OF REFERENCE STATES

The JMA equation describing heterogeneous solid-state transformations under *isothermal* conditions reads^{8,9}

$$f = 1 - \exp(-\beta^n) \quad [2]$$

where

$$\beta = kt = k_0 t \exp(-E/RT) \quad [3]$$

The effective activation energy describing the overall process is designated by E ; n , k_0 , and R denote the JMA exponent, the preexponential factor, and the gas constant, respectively.

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In order to maintain the JMA description under *non-isothermal* conditions, the formalism of Eq. [3] is accepted for an infinitesimal lapse of time (see References 2 and 3):

$$d\beta = k dt = k_0 \exp(-E/RT) dt \quad [4]$$

Applying isochronal annealing, $\Phi = dT/dt = \text{constant}$, it follows from Eq. [4]

$$\begin{aligned} \beta(T) &= \frac{k_0}{\Phi} \int_{T_0}^T \exp(-E/RT) dT \\ &= \frac{k_0}{\Phi} \left\{ T \int_1^{\infty} \frac{\exp\left(-\frac{E}{RT}\right) z}{z^2} dz \right. \\ &\quad \left. - T_0 \int_1^{\infty} \frac{\exp\left(-\frac{E}{RT_0}\right) z}{z^2} dz \right\} \quad [5] \end{aligned}$$

where T_0 indicates the initial state; $\beta(T_0) = 0$. Several approximations exist for the exponential integral.¹⁰ In the sequel the following development will be used:

$$\beta(T) = \frac{T^2 R}{\Phi E} k(T) \left\{ 1 - 2\left(\frac{RT}{E}\right) + \dots \right\} \quad [6]$$

where it has been assumed that $T_0 \ll T$.

On the basis of Eqs. [1], [2], and [6] a relation between the physical property to be measured, p (Eq. [1]), and the kinetic parameters (E, n, k_0) can be obtained. An easily accessible and sensitive experimental quantity is the temperature, T_i , of the inflection point of the $p(T)$ curve. This implies the determination of the extremum of the dp/dT curve, that for example can be provided by standard software packets for data evaluation delivered with the equipment used for measurement of p (see Figure 2(a) and Sections III and IV). It should be noted here that the original Kissinger method for thermal analysis⁴ is based on *homogeneous* reactions (instead of *heterogeneous* reactions considered here) and analyzes the behavior of the extremum of df/dT , *not* dp/dT . Because of the temperature dependence of p_0 and p_1 , df/dT and dp/dT do not necessarily behave identically (*cf.* Eq. [1]).

A schematic picture of the dependence of p on T (or t) is shown in Figure 1. Recognizing the temperature dependence of the reference states, p_0 and p_1 , differentiation of Eq. [1] with respect to T yields

$$\begin{aligned} \frac{df}{dT} &= \frac{1}{p_1 - p_0} \left\{ \frac{dp}{dT} - \frac{dp_0}{dT} \right. \\ &\quad \left. - \frac{1}{p_1 - p_0} \left(\frac{dp_1}{dT} - \frac{dp_0}{dT} \right) (p - p_0) \right\} \quad [7] \end{aligned}$$

It will be assumed that p_0 and p_1 depend approximately linearly on temperature over the temperature range where the transformation occurs (Figure 1; for justification in dilatometry, see Section IV and Figure 2). Differentiation of Eq. [7] then leads to

$$\begin{aligned} \frac{d^2f}{dT^2} &= \frac{1}{p_1 - p_0} \left\{ \frac{d^2p}{dT^2} - \frac{2}{p_1 - p_0} \left(\frac{dp_1}{dT} - \frac{dp_0}{dT} \right) \left(\frac{dp}{dT} - \frac{dp_0}{dT} \right) \right. \\ &\quad \left. + \frac{2}{(p_1 - p_0)^2} \left(\frac{dp_1}{dT} - \frac{dp_0}{dT} \right)^2 (p - p_0) \right\} \quad [8] \end{aligned}$$

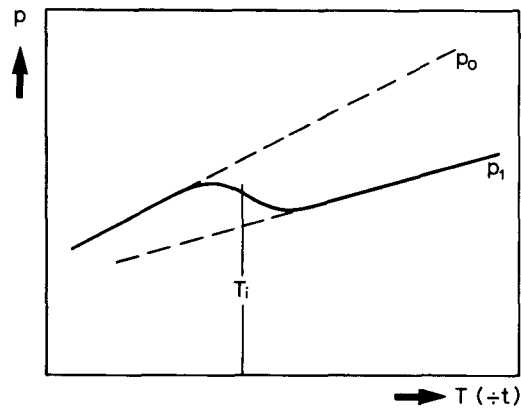
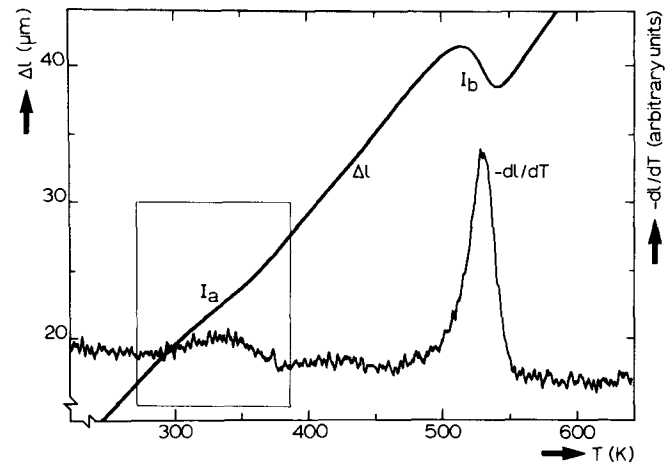
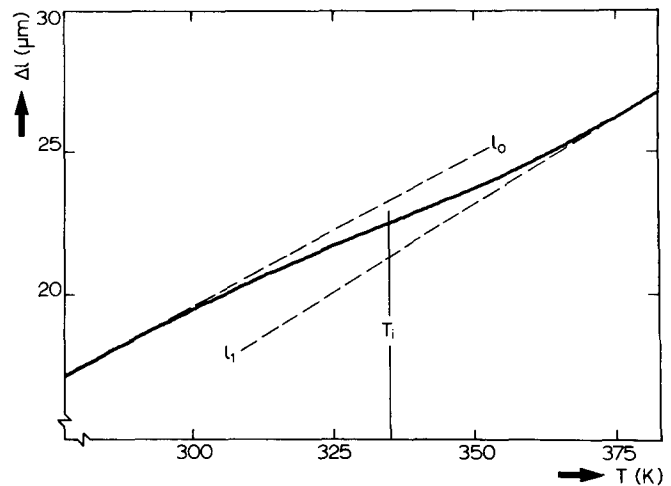


Fig. 1—Schematic picture showing the behavior of a physical property, p , of the specimen under investigation during isochronal annealing ($T = \text{temperature}$; $t = \text{time}$). The reference states p_0 and p_1 have been depicted too, as a function of temperature. In the temperature range where the transformation occurs the reference states are obtained by (linear) extrapolation. The temperature, T_i , corresponding to the inflection point on the curve has been indicated.



(a)



(b)

Fig. 2—(a) Dilatometric curve obtained on isochronal annealing ($\Phi = 5.0 \text{ K/min}$) of an iron-nitrogen martensite (1.0 wt pct N) specimen. The change of length, Δl , as well as the (negative) derivative of length with respect to temperature, $-dl/dT$, have been depicted. Tempering stages Ia and Ib have been indicated. (b) Enlargement of part of dilatometric curve shown in (a) corresponding to the initial stage, Ia, of tempering.

At $T = T_i$, $|dp/dT|$ is maximal and p is within the range $[p_0, p_1]$. Therefore,

$$\left| \left(\frac{dp_1}{dT} - \frac{dp_0}{dT} \right) \left(\frac{p - p_0}{p_1 - p_0} \right) \right|_{T_i} \ll \left| \left(\frac{dp}{dT} - \frac{dp_0}{dT} \right) \right|_{T_i}$$

Hence the last terms at the right-hand side of Eqs. [7] and [8] can be neglected. At $T = T_i$ where $d^2p/dT^2 = 0$ it is then obtained from Eqs. [7] and [8]

$$\frac{d^2f}{dT^2} \Big|_{T_i} = -C(T_i) \frac{df}{dT} \Big|_{T_i} \quad [9]$$

with

$$C = 2 \left(\frac{dp_1}{dT} - \frac{dp_0}{dT} \right) / (p_1 - p_0) \quad [10]$$

Noting that $df/dT = \Phi^{-1} \cdot df/dt$ and $d^2f/dT^2 = \Phi^{-2} \cdot d^2f/dt^2$ and using Eq. [2], Eq. [9] transforms into

$$\beta \frac{d^2\beta}{dT^2} \Big|_{T_i} - \{n(\beta^n - 1) + 1\} \left(\frac{d\beta}{dT} \Big|_{T_i} \right)^2 = -C\beta \frac{d\beta}{dT} \Big|_{T_i} \quad [11]$$

The JMA exponent, n , normally lies within the range [1, 4].¹ Then, in the temperature range where f significantly changes β is also of the order 1 (cf. Eq. [2]), thus allowing the approximation $\beta^n \approx 1 + n \ln \beta + n^2(\ln \beta)^2/2$. Further realizing that $RT_i/E \ll 1$ and applying Eq. [6], it is finally obtained from the above equation after rearrangement and omittance of terms of order higher than RT_i/E

$$\ln \frac{T_i^2}{\Phi} = \ln \frac{E}{Rk_0} + \frac{E}{RT_i} + \text{Res1} + \text{Res2} \quad [12]$$

with

$$\text{Res1} = \frac{C}{n^2} \frac{RT_i^2}{E} \quad \text{and}$$

$$\text{Res2} = 2 \left\{ 1 - \frac{1}{n^2} + n \ln \left[\frac{T_i^2}{\Phi} \frac{Rk(T_i)}{E} \right] \right\} \frac{RT_i}{E} \quad [13]$$

If it is allowed to neglect both residuals, Res1 and Res2, in Eq. [12], plotting of $\ln(T_i^2/\Phi)$ vs $1/T_i$ will result in a straight line; E can then be obtained from the slope.

It will practically always be justifiable to neglect Res2 (see also Section IV). However, no such general statement can be made for Res1 (note the presence of C in Res1). For any method of nonisothermal analysis where p is measured as a function of $T(\div t)$ (cf. Eq. [1]) it is advisable to verify the permissibility of the omittance of Res1 in each case. In Section IV such a calculation is made for dilatometry: in nonisothermal dilatometry it will normally be justifiable to neglect Res1 with respect to E/RT_i .

III. EXPERIMENTAL PROCEDURE

Specimens were made from iron with the composition 0.0042 at. pct Ni, 0.009 at. pct Cu, 0.0014 at. pct Mn, <0.01 at. pct Si, 0.011 at. pct C, 0.001 at. pct N, balance Fe. The specimens were of cylindrical shape with a wall thickness of about 0.2 mm, a height of about 10 mm, and an inner diameter of about 6.5 mm.

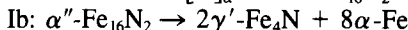
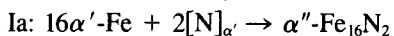
Nitriding was performed in a vertical furnace at a temperature of 1073 K (temperature control within ± 1 K) in a gas mixture of 96 vol pct H_2 (Hoek-Loos: 99.995 vol pct) and 4 vol pct NH_3 (Matheson: 99.96 vol pct). Both gases were purified by leading them through BTS catalyst and soda lime successively before entering the mixing bottle. The specimens thus obtained were nitrided homogeneously as was verified by microhardness and electron-microprobe measurements taken on cross-sections of the specimens. The nitrogen content was quantitatively determined employing the electron-microprobe method developed earlier by our group and reported elsewhere.¹¹ The measured nitrogen content was 1.0 (± 0.05) wt pct.

After nitriding the specimens were quenched in brine at room temperature and subsequently in liquid nitrogen. The latter quench was performed inside the dilatometer. By quenching, the nitrogen-austenite structure, developed from ferrite by nitriding above 863 K, was transformed into nitrogen martensite.^{6,7}

Dilatometric analysis was performed with a Du Pont thermal mechanical analyzer type 942. Data accumulation and evaluation (in this case comprising a differentiation of the specimen-length signal with respect to time) was achieved using a Du Pont thermal analyzer type 1090. Isochronal annealing experiments were performed in the temperature range (153 to 773) K employing calibrated heating rates in the range (5 to 40) K/min (cf. Table I). The dilatometer used in principle allows the imposition of larger heating rates. However, the results obtained, e.g., for $\Phi = 80$ K/min, showed a deviation from the linear dependence of $\ln(T_i^2/\Phi)$ on $1/T_i$ as expected and found for the lower heating rates (cf. Section IV). This aberration can be ascribed to the occurrence of significant temperature gradients in the specimen on heating. Therefore, no heating rates larger than 40 K/min were applied in the present experiments.

IV. RESULTS AND DISCUSSION

A survey of the tempering behavior of iron-nitrogen martensite is provided by References 6 and 7. Here the first stage of tempering, I, needs to be dealt with only. The main events occurring in stage I are the successive precipitations of $\alpha''(\text{Fe}_{16}\text{N}_2)$ - and $\gamma'(\text{Fe}_4\text{N})$ -nitrides:



where α' and α denote martensite and ferrite, respectively, and $[\text{N}]_{\alpha'}$ indicates nitrogen interstitially dissolved in α' .

In stage Ia ($T < 475$ K) the fine precipitation of α'' -nitride is accompanied with a significant heat effect, whereas in stage Ib ($475 \text{ K} < T < 560 \text{ K}$) the dissolution of α'' -nitride in favor of coarser γ' -nitride causes only a minor heat effect. As a consequence quantitative kinetic analysis by thermal methods was possible for stage Ia but not for stage Ib.

The change of length on isochronal annealing of iron-nitrogen martensite is shown in Figure 2(a) for the first stage of tempering. Two transformations can be discerned. The first transformation, associated with a very small decrease of specific volume (see enlargement of part of the figure: Figure 2(b)), is due to the precipitation of α'' -nitride (stage Ia) and the second transformation, associated with a

significant decrease of specific volume, is caused by the precipitation of γ' -nitride (stage Ib) (this structural interpretation is fully supported by transmission electron microscopy and X-ray and electron diffraction data^{6,7}).

Hence the thermal and dilatometric effects for α'' - and γ' -precipitations show antagonistic behavior. Stage Ia: large heat effect; minute volume effect. Stage Ib: minor heat effect; significant volume effect.

The derivative of specimen length with respect to temperature during isochronal annealing is also shown in Figure 2(a). Clearly, the position of the extremum of dl/dT ($\div dl/dt$), corresponding to an inflection point of the $l(T)$ curve, is more accurately determinable for stage Ib than for stage Ia. Yet, the activation-energy determination according to the method discussed in Section II is presented here for stage Ia to investigate the sensitivity of the method and because the energy value obtained can be compared with the one derived from the previous thermal analysis.

The inflection-point temperature, T_i , of the $l(T)$ curve for stage Ia was determined for a number of experiments at each of five heating rates employed (see Figure 3 and Table I). The significant rise, for increasing heating rate, of the average value of T_i , $\langle T_i \rangle$, at each heating rate, is shown in Figure 4. Finally, $\langle \ln(T_i^2/\Phi) \rangle$ is plotted vs $\langle 1/T_i \rangle$ in Figure 5. From the slope of the straight line obtained (least-squares fitting) the activation energy for the precipitation of α'' -nitride is obtained according to Eq. [12] (neglecting Res1 and Res2; see below):

$$E = 81.1 \text{ kJ/mole}$$

which agrees well with the result from thermal analysis: $E = 77.9 \text{ kJ/mole}$.⁶

The importance of both residuals, Res1 and Res2, can be estimated as follows for the case considered.

With $E \approx 80 \text{ kJ/mole}$ and $T_i \approx 350 \text{ K}$, Res2 equals maximally about 0.2 pct of E/RT_i . In practice nearly always Res2 can be neglected with respect to E/RT_i .

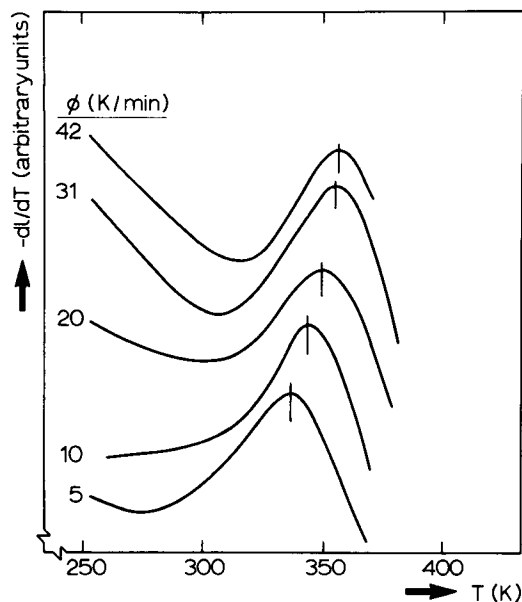


Fig. 3—Negative derivative of length with respect to temperature, $-dl/dT$, for the initial stage, Ia, of tempering iron-nitrogen martensite (1.0 wt pct N) specimens for various heating rates. The temperatures corresponding to the inflection points have been indicated by a vertical line on the curves.

Table I. Temperature, T_i , Corresponding to the Inflection Point on the Dilatometric Curve Obtained on Isochronal Annealing of Iron-Nitrogen Martensite (1.0 Wt Pct N), for the Initial Stage, Ia, of Tempering, as a Function of Heating Rate, Φ

Φ (K/min)	T_i (K)	$\langle T_i \rangle$ (K)
5.0	333.5	334.5
5.0	335.5	
9.9	344.0	343.2
9.9	341.0	
9.9	344.4	
9.9	343.4	
20.1	351.0	349.8
20.1	349.3	
20.1	349.0	
30.8	357.0	356.8
30.8	356.6	
42.2	358.0	358.4
42.2	358.7	

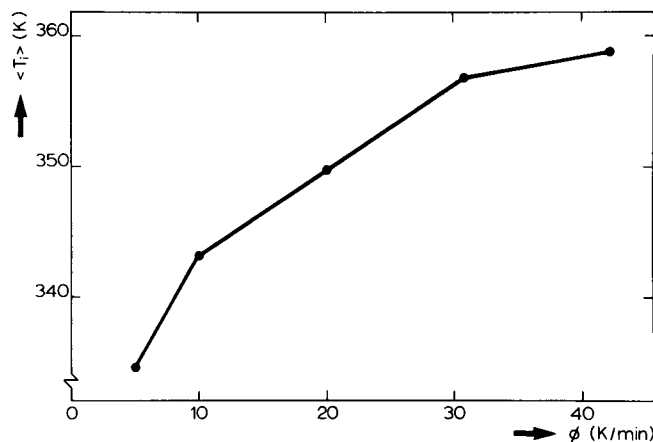


Fig. 4—The average inflection-point temperature, $\langle T_i \rangle$, as a function of heating rate, Φ , for the initial stage, Ia, of tempering iron-nitrogen martensite (1.0 wt pct N) specimens.

For dilatometry C can be given as (cf. Eq. [10])

$$C = 2 \frac{\alpha_1 l_1 - \alpha_0 l_0}{l_1 - l_0} \bigg|_{T_i} \approx 2 \frac{\Delta \alpha}{\Delta l/l} \bigg|_{T_i} \quad [14]$$

where α indicates the coefficient of linear expansion. For the example of Figure 2(b) it is obtained $C \approx 0.02$. With $E \approx 80 \text{ kJ/mole}$ and $T_i \approx 350 \text{ K}$, Res1 equals maximally about 1 pct of E/RT_i . It is noted that C , and thus Res1, is directly proportional to $\Delta \alpha$ (in the present case $\Delta \alpha \approx 1.8 \times 10^{-6} \text{ K}^{-1}$). On the other hand, this deliberately chosen example concerns a minute length change on transformation ($\Delta l/l \approx 0.02 \text{ pct}$). Many solid-state transformations bring about larger changes in length, and the difference in linear thermal expansion coefficient can be correspondingly larger (cf. Eq. [14]), while maintaining the right to ignore Res1 in Eq. [12]. Therefore, in nonisothermal dilatometry it is in general allowable to neglect Res1 with respect to E/RT_i .

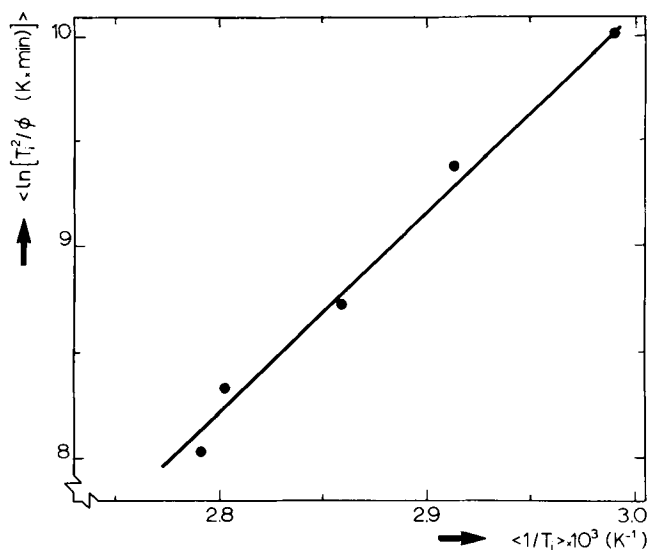


Fig. 5—Plot of $\langle \ln(T_i^2/\Phi) \rangle$ vs $1/T_i$ where T_i and Φ denote inflection point temperature and heating rate, respectively, for the initial stage, Ia, of tempering iron-nitrogen martensite (1.0 wt pct N) specimens.

The error made in the determination of T_i also affects the accuracy of the value obtained for E . The smaller the change of specific volume provoked by the transformation investigated, the larger the inaccuracy in the value obtained for T_i (cf. dl/dT for stage Ia and dl/dT for stage Ib in Figure 2(a)). For the example presented here the maximum error in T_i can be estimated from Table I. It appears that $|\Delta T_i| = (1 \text{ to } 1.5) \text{ K}$ corresponding to less than 1 pct of E/RT_i . Larger length changes than studied here occur normally and the error in T_i will be smaller. Hence, the already good results obtained in the case of α'' -nitride precipitation suggest a successful application of the proposed method for many other solid-state transformations. This holds in particular for transformations the kinetics of which are not well examinable by (standard) methods as thermal analysis (e.g., stage Ib of tempering iron-nitrogen martensite; discussion of the results obtained already is beyond the scope of the present paper).

V. CONCLUSIONS

1. Adopting a version of the Johnson-Mehl-Avrami theory suited for the description of nonisothermal solid-state transformations, for the case of isochronal annealing, a simple relation exists between the kinetic parameters and the (experimentally easily accessible) temperature of

the inflection point of the curve relating the physical property to be measured (e.g., specific volume/length; electrical resistivity, magnetization) and the temperature of the specimen.

2. In its most simple form the activation energy governing the transformation considered can be determined from the slope of the straight line obtained by plotting $\ln(T_i^2/\Phi)$ vs $1/T_i$, where T_i and Φ denote inflection-point temperature and heating rate, respectively.
3. Kinetic analysis by nonisothermal dilatometry requires the reference lengths, l_0 and l_1 , necessary for the calculation of the degree of transformation, to be taken temperature dependent. On the basis of experiments with iron-nitrogen martensite, analysis of residual terms in the final Eq. [12], incorporating this temperature dependence, indicates that activation-energy determination by nonisothermal dilatometry can normally be performed using the above procedure (conclusion 2).
4. As a test case, because of the minute length change involved, the activation energy of the initial stage of tempering iron-nitrogen martensite was determined by nonisothermal dilatometry. The result obtained agreed well with that from thermal analysis.

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