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INVESTIGATION OF KINETIC PROCESSES USING PEAK ANALYSIS

Z. Y. Cao*, H. U. Fritsch, H. W. Bergmann,
Institut für Werkstoffkunde und Werkstofftechnik, Technische Universität
Clausthal, Agricolastr. 2, D-3392 Clausthal-Zellerfeld, W. Germany
*Home address: Central South Institute for Mining an Metallurgy, Changsha,
The People's Republic of China

ABSTRACT

A method is presented which allows to determine the change of the reaction constant τ and the time exponent n during isothermal crystallization. This allows to prove the validity of the Johnson-Avrami-Mehl assumption and can show whether or not it is necessary to use sophisticated methods for the description of crystallisation kinetics.

INTRODUCTION

The analysis of thermodynamic data obtained eg by differential scanning calorimetry during a crystallization process is often carried out assuming an Avramian type of reaction (ref.1,2).

$$z(t) = 1 - \exp\left(-\left(\frac{t}{\tau}\right)^n\right) \qquad (1)$$

in which z represents the transformed volume fraction, t the time and n and τ are experimentally fitted parameters. It is furthermore assumed that in isothermal experiments n and τ are constant during the process, τ containing the temperature dependence:

$$\tau = \tau_o \cdot \exp(\Delta G_{tot}/RT) = \tau_o^* \exp(\Delta H_{tot}/RT) \qquad (2)$$

In equation (2) τ_o represents the preexponential factor and ΔG, ΔH the overall activation energy or enthalpy respectively.

For a series of isothermal crystallisation experiments n and ΔH can then be

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obtained using equations (1) and (2).

For many purposes it is convenient to carry out non isothermal rather than isothermal experiments. A recent paper of Uhlmann and coworkers (ref.2) gives a critical review of methods developed during the last 20 years. In non isothermal experiments one has to assume that still the Avrami relationship is valid, which is generally not true. With further assumptions it is then possible to evaluate one parameter n or ΔH respectively, (ref.3).

In general the assumption of constant n and ΔH values is critical even in isothermal experiments. Hence whenever a change in the physical process occurs one has to assume that variations in these values result.

DESCRIPTION OF THE METHOD

In Fig. 1 a schematic drawing of an isothermal crystallization process is shown. Determining the end of the crystallization process the peak is then either divided into eg. 30 equidistant time steps (case A) or 30 equiarea intervals (case B). Case A is the more straight forward approach while B has the advantage that high numerical errors due to the low experimental resolution at start and finish of the crystallization can be avoided. In the paper only the first approach is described but there is no difficulty in applying approach B. An equidistant time grid can be described by

$$t_i = t_o + \frac{i}{30} \Delta t \qquad i = 0,30 \qquad (3)$$

for isothermal treatments

The crystallized volume fraction at a certain time t_i is given by

$$z_i = (A_i/A_{tot}) \cdot f(z_i)/f(z_{tot}) \qquad i = 0,30 \qquad (4)$$

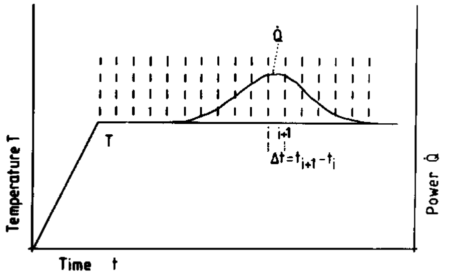


Fig. 1. Discretization of the crystallization peak.

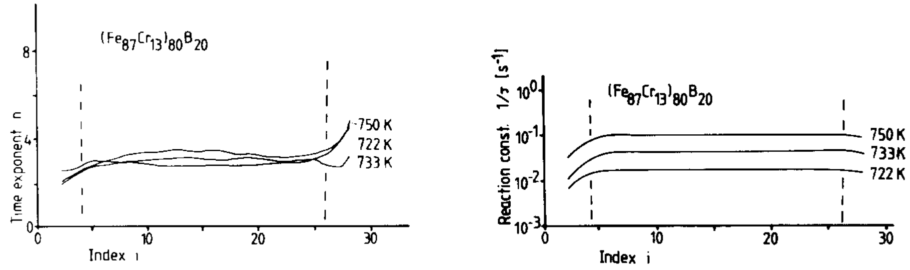
A_i and A_{tot} are the partial and total peak areas respectively and f(z) is a weighting function correlating the released heat to the crystallized volume fraction. Assuming that f(z) is constant z_i ist determined by the area ratio only. From equation (1) it follows that

$$\ln(-\ln(1 - z_i)) = n \ln t_i + n \ln \tau \qquad i = 1,30 \qquad (5)$$

Evaluating equation (5) an average reaction rate coefficient τ and time exponent n can be determined by means of linear regression. Choosing only a limited number eg 3 of the data points the change of n and τ with the crystallized volume fraction can be evaluated. For example one data point is obtained by z_i, z_{i+1} and z_{i+2} and the next one by z_{i+1}, z_{i+2} and z_{i+3}.

RESULTS AND DISCUSSION OF ISOTHERMAL PROCESSES

In Fig. 2 a - c the results of the crystallization experiments for $(Fe_{87}Cr_{13})_{80}B_{20}$ are shown.



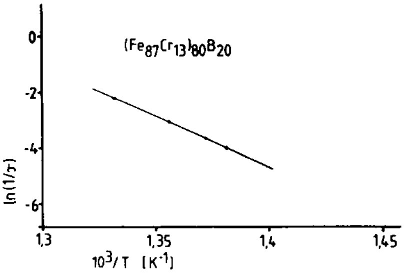


Fig. 2. Crystallization behaviour of $(Fe_{87}Cr_{13})_{80}B_{20}$, time exponent n (a) and reaction constant $1/\tau$ (b) as a function of the grid point number, (c) temperature dependence of the reaction constant.

The reaction order coefficient n is given in Fig. 2a showing that for the eutectic crystallization of α-(Fe, Cr) and $(Fe, Cr)_3B$ a reaction coefficient of approximately 2.5 is obtained which can be interpreted as resulting from 3-dimensional parabolic growth law and homogeneous nucleation (ref.4). The time constant τ as well is almost constant over the grid point number, see Fig. 2b, and ΔH can be evaluated using an Arrhenian plot (Fig. 2c). In another paper the crystallization behaviour of $Fe_{40}Ni_{40}B_{20}$ is reported to be consisting of several competiting processes (ref.5). It was found that apart from the eutectic crystallization of α- (Fe, Ni) + orthorombic $(Fe, Ni)_3B$ the $(Fe, Ni)_{23}B_6$ phase with cubic structure forms and in addition at higher temperatures even primary crystallization into γ-(Fe, Ni) occurs.

Using different analytical techniques the time temperature crystallization behaviour given in Fig. 3 shows three characteristic regions. The transitions of these correspond with jumps in the activation energy ΔH_{tot} obtained by temperature change experiments (ref.5). Such a transition is also found by TEM studies and Mössbauer experiments. The results obtained by the proposed discretization method are given in Fig. 4a - c.

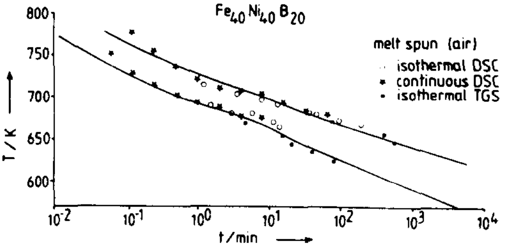
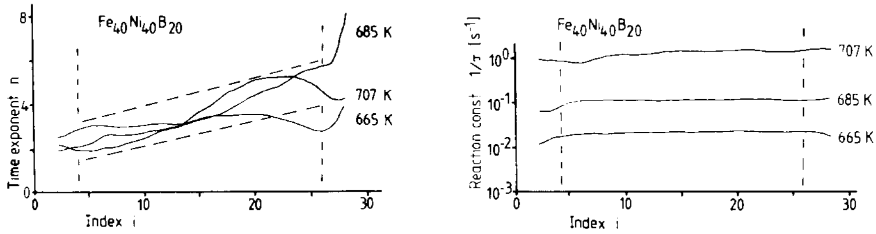


Fig. 3. Measured and calculated TTT diagramm for the crystallization of $Fe_{40}Ni_{40}B_{20}$ dots-experimental, line-calculated.

If the AJM relationship is valid, the time exponent n should not change neither with the crystallized volume fraction nor with the temperature. The reaction contsant τ should not change with the crystallized volume fraction and it should exhibit a temperature dependence of Arrhenian type as in equation (2). Consequently one expects a straight line by plotting ln 1/τ against 1/T with a slope of ΔH/R. The above assumptions are true for the crystallization process shown in Fig. 2.

Fig. 4a, however, shows a time exponent changing with both temperature and isothermal crystallized volume fraction. This temperature dependence can be explained by the different crystallization kinetics for the various phases involved. The variation over the crystallization peak results from a change in composition of the residual glass when primary phases form. The reaction parameter τ is almost constant over the crystallization peak, but its temperature dependence is by no means Arrhenian (see Fig. 4c). In such a case it is senseless to determine an activation energy e.g. by means of linear regression and plotting ln 1/τ against 1/T. This shall be shown by a classical example. In the system Al-Zn with 25 at% Al at 275 °C the Zn-rich Al crystal α' transforms into a phase with less Zn in solid solution and β-Zn

$$\alpha' \overset{275\ °C}{\rightleftarrows} \alpha + \beta \qquad (6)$$



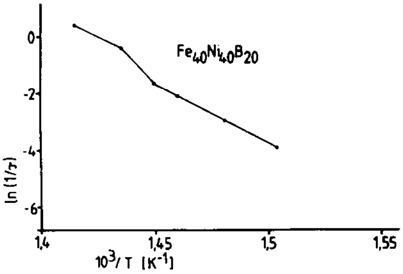


Fig. 4. as Figure 2 for $Fe_{40}Ni_{40}B_{20}$.

The kinetics of this transformation can be measured calorimetrically. The results are presented in form of a TTT diagram (see Fig. 5).

Close to the transformation temperature all methods to determine an activation energy are unsuccessful. For small undercoolings (overheating) with respect to the transformation temperature the driving force is strongly temperature dependent and the activation part can not be separated. Fig. 6 shows the difficulties in determining an activation energy, for reasons of simplicity the Kissinger method is used (ref.6). Obviously the figure demonstrates that any determination would be a misleading attempt.

For metastable transformations very often the situation is less transparent, because various TTT curves of different phases are superimposed. The experimental results, however, exhibit a single process behaviour (see Fig. 3 and 7). The proposed method could help to detect such difficult cases, which should then be investigated by more sophisticated methods.

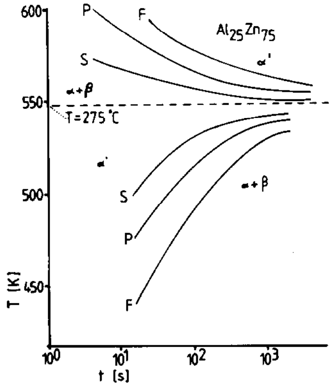


Fig. 5. TTT diagram for the α' → α + β and the inverse transformation for $Al_{25}Zn_{75}$

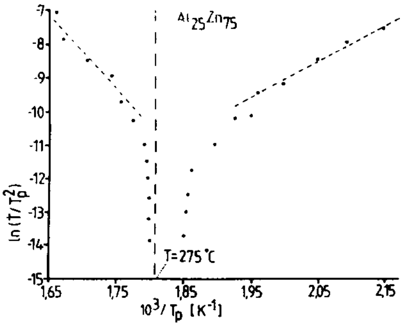


Fig. 6. Kissinger plot for the measurements in Fig. 5

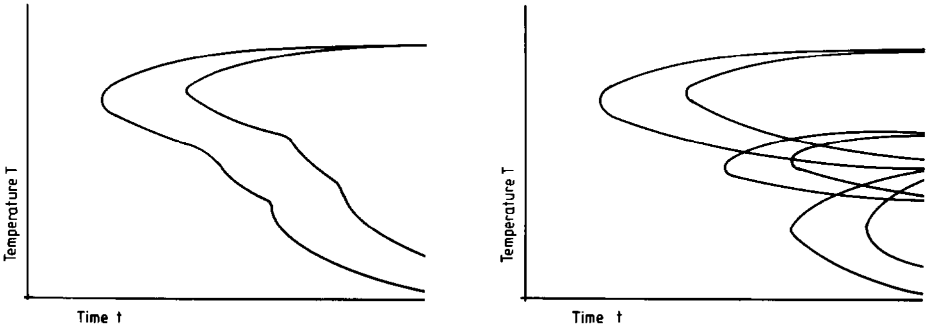


Fig. 7. Schematic drawing of a complex TTT diagram which forms as a superposition of three different processes.

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