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THE NON-EXISTENCE OF A GENERAL CORRECTION TERM IN CONTINUOUS HEATING EXPERIMENTS

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ABSTRACT

The simplest possible non-isothermal generalization of the phenomenological isothermal rate equation has been investigated. Its solution, the transformed fraction, C, is a functional of the temperature—time relation, $T(t)$. Previous works, based on the existence of a function-type solution, $C(T,t)$, suggest a way of generalization which is meaningless in the case of a functional solution. A difference is predicted by the function-type description between the kinetic parameters determined under isothermal and dynamic conditions which is in contradiction with our experimental results on the crystallization of $Fe_{75}B_{25}$ metallic glass.

It was suggested in a recent publication [1] that there is a general correction term in the equation expressing the transformation rate under non-isothermal conditions. As this type of correction is the result of a formal mathematical treatment and its physical significance is not clear [2], we intend to reconsider the subject. We will show that supposing the same transformation mechanism to be valid for isothermal and dynamic cases, there is no general correction term in the dynamic rate equation due to the changing temperature.

Most of the isothermal reactions can be described by the equation

$$\frac{dC}{dt} = f(C)\,k(T) \tag{1}$$

where C and T are the actual transformed fraction and the temperature, respectively, while the form of $f(C)$ depends on the type of transformation mechanism. Thermal activation is expressed by $k(T)$, which is usually approximated by an Arrhenius-type term. In order to determine the physical meaning of the suggested [1] non-isothermal generalization of eqn. (1) let us start from the trivial case: the same form of equation is valid under both isothermal and dynamic conditions, so the differential equation describing the non-isothermal process will be as follows

$$\frac{dC}{dt} = f(C)\,k(T(t)) \tag{2}$$

where $k(T(t))$ means a function of time. A solution can be obtained by the integration of the separated equation

$$\int_{C_0}^{C} \frac{1}{f(C')}\, dC' = \int_0^t k(T(t'))\, dt' \tag{3}$$

where C_0 is the initial transformed fraction. Denoting $\int f^{-1}$ by F and its inverse by F^{-1} we get

$$C\{T(t'), t\} = F^{-1}\left[\int_0^t k(T(t'))\, dt' + F(C_0)\right] \tag{4}$$

where different types of brackets in $C\{T(t'), t)$ show that the solution is a functional of the heating programme and the function of the upper limit of the integration (time), which is in good accordance with experiments where the actual transformed fraction is dependent on the whole T—t path of the dynamic measurement.

A different equation was suggested in ref. 1 where the transformed fraction is regarded as a function of time and the actual temperature only. It has a correction term in the non-isothermal rate equation, arguing that under isothermal conditions the

$$\left(\frac{\partial C}{\partial t}\right)_T = f(C)\, k(T) \tag{5}$$

partial derivative is measured only and the whole transformation rate must also contain the contribution due to the changing temperature

$$\frac{dC}{dt} = \left(\frac{\partial C}{\partial t}\right)_T + \left(\frac{\partial C}{\partial T}\right)_t \frac{dT}{dt} \tag{6}$$

which yields

$$\frac{dC}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right)\left[1 + \frac{E_a}{RT}\left(1 - \frac{T_0}{T}\right)\right] f(C) \tag{7}$$

when $T = T_0 + \dot{T}t$

using the $k(T) = k_0 \exp(-E_a/RT)$ Arrhenius equation, where k_0 is the frequency factor, E_a is the activation energy and R is the universal gas constant. It is a mathematically correct procedure as it is one of the possible dynamic generalizations of eqn. (1), but has no physical meaning in this case as it might be valid only if the transformed fraction were the *function* of time and the *actual temperature.* However, we have to emphasize that the actual transformed fraction is dependent on the *whole* T—t path, and a $C(T, t)$ *function* giving a fixed value for a T—t pair independently of the T—t curve cannot represent the thermal history of the material. The only mathematical object fit for this purpose is a functional. Appearance of the correction term in eqn. (6) comes from the false supposition that C is the function of time and the actual temperature. In the case of the functional solution the meaning of the expression

$$\left(\frac{\partial C}{\partial t}\right)_T = \mathrm{f}(C)\,k(T(t)) \qquad (8)$$

does not differ from that of eqn. (2) as the $C\{T(t'), t)$ functional has only one possible time derivative which can be obtained by its differentiation with respect to the upper limit of the integration.

Our calculations are based on the supposition that the reaction rate can be described by the same expression under both isothermal and dynamic conditions. The validity of this assumption was discussed by Henderson [3] who found that for transformations involving nucleation and growth it is correct in a limited number of special cases. One of them is the case of zero nucleation rate (saturation of point sites) which requires $n = 3$ in the Johnson—Mehl—Avrami equation [eqn. (9)] describing it under isothermal conditions [4]

$$C(t) = 1 - \exp\left\{-\left[k_0 \exp\left(-\frac{E_a}{RT}\right) t\right]^n\right\} \qquad (9)$$

where n is the Avrami exponent characteristic to the mechanism of the transformation. The crystallization of $Fe_{75}B_{25}$ metallic glass is a suitable experimental test of our generalization as it shows a single-step process, and the growth of a fixed number of nuclei is expected to be the mode of the transition.

A Perkin-Elmer type DSC-2 calorimeter was used for the investigation of both isothermal and dynamic kinetics. Isothermal kinetic parameters were determined following the method of Funakoshi et al. [5]. The samples were isothermally heat treated in the calorimeter, after which the remaining crystallization energy was measured with 10 K min^{-1} constant heating rate experiments. Results are shown in Fig. 1 [6], demonstrating that in the 670—690 K temperature range the process can be described with a constant exponent $n = 2.9 \pm 0.1$ which is very near to the expected value. The thermal

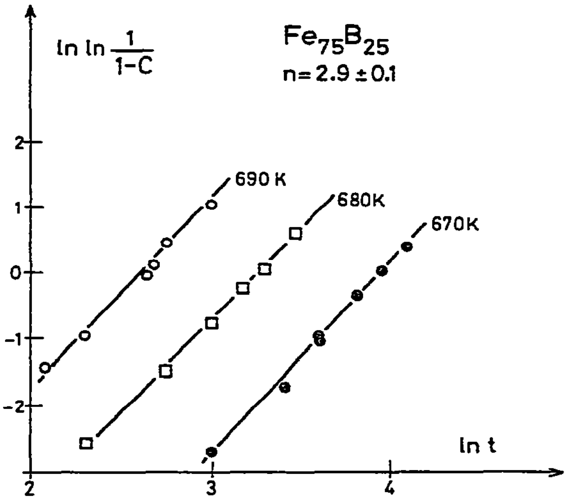

Fig. 1. Determination of the isothermal kinetic exponent.

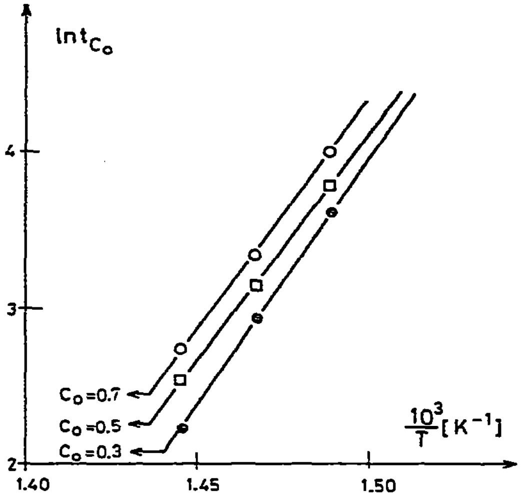

Fig. 2. Determination of the isothermal activation energy at different transformed fractions.

activation energy calculated from the slope of the $\ln t_{C_0}$ vs. $1/T_{C_0}$ plot (Fig. 2) is $E_a = 250 \pm 10$ kJ mole^{-1} K^{-1}.

The parameters of the non-isothermal kinetics were determined from a series of experiments made with different heating rates, 0.31—10 K min^{-1}. The activation energy was calculated with the method of Ozawa [7,8] based on eqn. (3), and the kinetic exponent was obtained by fitting the measurements to the differential form of the Johnson—Mehl—Avrami equation [2]

$$\frac{dC}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right)(1-C)[-\ln(1-C)]^{(n-1)/n} \qquad (10)$$

This fit is shown in Fig. 3.

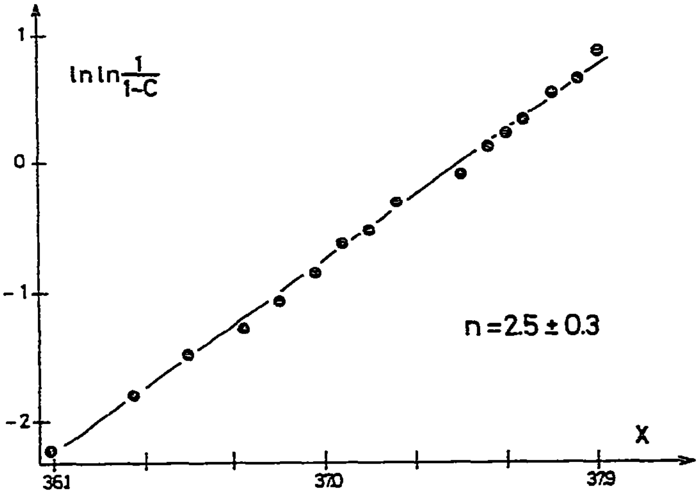

Fig. 3. Determination of the non-isothermal kinetic exponent by fitting the differential Johnson—Mehl—Avrami equation to a 10 K min^{-1} dynamic experiment. $X = \ln dC/dt + E_a/RT - \ln(1-C)$

TABLE 1

Activation energies obtained from the slope of the $[T_{C_0}(\dot{T})]^{-1}$ vs. ln $\dot{T}$ plot at different fixed transformed fractions

Transformed fraction (%)	E_a (kJ mole^{-1} K^{-1})
10	252 ± 5
15	251 ± 5
20	251 ± 4
25	250 ± 4
30	250 ± 4
35	249 ± 3
40	248 ± 3
45	248 ± 3
50	249 ± 3
55	249 ± 3
60	249 ± 3
65	248 ± 3
70	248 ± 3
75	248 ± 3
80	248 ± 3
85	248 ± 3
90	249 ± 3

The activation energies obtained from the slope of the $[T_{C_0}(\dot{T})]^{-1}$ vs. ln $\dot{T}$ plot at different fixed transformed fractions (C_0) are listed in Table 1, demonstrating that E_a is completely independent of the crystalline fraction, C_0. Their average value, $E_a = 249 \pm 5$ kJ mole^{-1} K^{-1}, is in good accordance with the isothermal one, while the characteristic exponent is somewhat lower than that of the isothermal case: $n = 2.5 \pm 0.3$, but the difference between them is near to the combined error of the two types of measurements.

These results suggest that in accordance with mathematical calculations there is no reason to suppose a general dynamic correction in the non-isothermal rate equation.

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