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The three activation energies with isothermal transformations: applications to metallic glasses

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In crystallization or precipitation, the activation energy for nucleation of particles, E_n, for growth of particles, E_g, and for the total process, E_c, can all be determined independently by experiment. Formulae relating these three values are developed. Cases of linear and parabolic growth are included for different nucleation rates and morphologies. The formulae are tested experimentally on amorphous alloys (metallic glasses) based on Fe–Ni. The agreement between the theory and the experiments is very satisfactory.

1. Introduction

There are many applications of nucleation and growth processes (e.g. crystallization, recrystallization, precipitation from solid solutions etc.) which follow the well-known Avrami kinetics [1]

$$x(t) = 1 - \exp\left(-\frac{t}{\tau}\right)^m \tag{1}$$

where $x(t)$ is the time-dependent volume fraction transformed, t is time, τ is the time constant and m is the Avrami exponent. τ is related to the activation energy of the whole process, E_c^*, by

$$\tau = \tau_0 \exp\left(\frac{E_c}{RT}\right) \tag{2}$$

provided E_c is a constant within a certain temperature range and the process follows an Arrhenius law. (R is the gas constant and T is temperature.)

Some authors, however, prefer the following representation of Avrami kinetics

$$x(t) = 1 - \exp(-Kt^m) \tag{3}$$

where k is a constant. In this case,

$$K = K_0 \exp\left(-\frac{\Delta H}{RT}\right) \tag{4}$$

in which ΔH is called "the activation energy of transformation" (e.g. Henderson [2]). Obviously, this is not the same as E_c, although in both cases the validity of an Arrhenius relationship for τ and K is presupposed. Rather, E_c and ΔH are connected by

$$\Delta H = m \cdot E_c, \tag{5}$$

simply because in one case m is included in the time term and in the other case it is not. For reasons which become clear later, we prefer to call E_c "the activation energy of the whole process", and not ΔH. If the nucleation rate is constant, it can be expressed as

$$\dot{n} = n_0 \exp\left(-\frac{E_n}{RT}\right) \tag{6}$$

where n is the number of nucleations with time, $\dot{n}$ is the nucleation rate and E_n is the (apparent) activation energy of nucleation. (The word "apparent" is intended to indicate that E_n itself is a sum of single contributions. Thus, in the case of a diffusion-controlled nucleation process it is the sum of the activation energy of diffusion E_d plus the energy required to form a critical nucleus

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[*] The subscript "c" refers to "combined process" or "crystallization".

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ΔG_c [3].) E_n can be determined from the slope of a plot of $\ln n$ against $1/T$. If the growth rate, u, is linear (as for interface-controlled growth, e.g. in ordinary recrystallization or pearlite growth), it can be written as

$$u = u_0 \exp\left(-\frac{E_g}{RT}\right) \tag{7}$$

where E_g is the activation energy of growth and can be determined from the slope of $\ln u$ against $1/T$. On the other hand, if growth is controlled entirely by diffusion (volume-controlled), it normally follows a parabolic law. The particle radius, r, is by

$$r = A\,(D \cdot t)^{1/2} \tag{8}$$

where A is a constant of the order of magnitude one and D is the diffusion coefficient. D is given by

$$D = D_0 \exp\left(-\frac{E_d}{RT}\right) \tag{9}$$

where D_0 is a constant and E_d is the activation energy of diffusion, which is determined from the slope of $\ln D$ against $1/T$.

We shall now consider the relationship between E_c and E_n, E_g and E_d. It is convenient to first consider four different cases with distinct control modes for nucleation and growth of particles.

2. Case 1: Linear growth, $r = u \cdot t$, nucleation rate $\dot{n} = 0$

(I.e. only a fixed number N of quenched-in nuclei with no further nucleation of particles.)

If particles are assumed to be *spherical*, the initial (total) volume, V, is $V = N \cdot 4/3\pi r^3$, and therefore

$$x(t) = 1 - \exp\left(-\frac{4}{3}\pi N u^3 t^3\right) \tag{10}$$

because for small V, $x = V \approx 1 - \exp(-V)$ is valid. For larger V (longer times) the Avrami approach and Equation 1 is a good mathematical description of the experimentally observed s-shaped reaction curves. Comparison of Equation 10 with Equations 3 and 4, and substitution by Equation 8 yields

$$K = K_0 \exp\left(-\frac{\Delta H}{RT}\right)$$
$$= -\frac{4}{3}\pi N u_0^3 \exp\left(-\frac{3E_g}{RT}\right). \tag{11}$$

Hence, because the pre-exponential values are constant, $\Delta H = 3 \cdot E_g$. The Avrami exponent, m, in Equation 10 is obviously equal to 3. In the case of two-dimensionally growing particles, i.e. discs with fixed thickness, the same analysis could be applied with $m = 2$, and in the case of one-dimensional growth (needles), $m = 1$. Hence,

$$\Delta H = m \cdot E_g \tag{12}$$

or, comparing Equation 12 with Equation 5 yields $E_g = E_c$.

3. Case 2: Linear growth, $r = u \cdot t$, constant nucleation rate $\dot{n} > 0$

In this case the initial total volume can be expressed as

$$V = \int_{t=0}^{t} \frac{4}{3}\pi u^3 t^3 \dot{n} \mathrm{d}t = \frac{\pi}{3} u^3 \dot{n} t^4 \tag{13}$$

for spherical particles.

$$x(t) = 1 - \exp\left(-\frac{\pi}{3} u^3 \dot{n} t^4\right) \tag{10a}$$

and from Equations 3, 4, 6 and 7

$$K = K_0 \exp\left(-\frac{\Delta H}{RT}\right)$$
$$= -\frac{\pi}{3} n_0 \exp\left(-\frac{E_n}{RT}\right) u_0^3 \exp\left(-\frac{3E_g}{RT}\right). \tag{14}$$

Therefore

$$\Delta H = E_n + 3E_g. \tag{15}$$

In this case the Avrami exponent, m, is equal to 4. For two-dimensional particles, similarly, $\Delta H = (E_n + 2E_g)$ and $m = 3$. In general, ΔH can be written as

$$\Delta H = E_n + (m - 1)E_g. \tag{16}$$

This case also includes the well-known primary recrystallization of metals after cold working.

4. Case 3: Parabolic growth, $r = A\ (\mathrm{Dt})^{1/2}$, nucleation rate $\dot{n} = 0$

$V = 4/3\,\pi A^3 D^{3/2} t^{3/2} \cdot N$ for spherical particles and A is a constant. Again, following a similar procedure to the one for Cases 1 and 2,

$$K = K_0 \exp\left(-\frac{\Delta H}{RT}\right)$$
$$= -\frac{4}{3}\pi N A^3 D_0^{3/2} \exp\left(-\frac{1.5E_d}{RT}\right), \tag{17}$$

where $m = 3/2$ for spherical (three-dimensional) particles. Since N, A and D_0 are all considered to be constants,

$$\Delta H = \frac{3}{2} E_d. \qquad (18)$$

For two-dimensionally growing particles, $m = 2/2$ and $\Delta H = E_d$. In the general case

$$\Delta H = m E_d. \qquad (19)$$

(In the case, from Equation 5, $E_c = E_d$, which is clear because no new nucleation is involved and the whole reaction is entirely diffusion controlled.)

5. Case 4: Parabolic growth, $r = A\ (Dt)^{1/2}$, constant nucleation rate $\dot{n} > 0$

$$V = \int_{t=0}^{t} \dot{n}\frac{4}{3}\pi A^3 D^{3/2} t^{3/2}\,dt$$

$$= \dot{n}\frac{4}{3}\pi A^3 D^{3/2} t^{5/2} \cdot \frac{2}{5} \qquad (20)$$

for three-dimensional particles. As before,

$$K = K_0 \exp\left(-\frac{\Delta H}{RT}\right)$$

$$= -\frac{8}{15} A^3 \pi n_0 \exp\left(-\frac{E_n}{RT}\right) D_0^{3/2} \exp\left(-\frac{1.5 E_d}{RT}\right) \qquad (21)$$

and an Avrami exponent of $m = 5/2$. Therefore,

$$\Delta H = E_n + \frac{3}{2} E_d \qquad (22)$$

or, as above including the two other cases of two- or one-dimensional particles, we obtain

$$\Delta H = E_n + (m-1) E_d. \qquad (23)$$

6. Discussion

After having developed these four cases, we can generalize for all cases, It is convenient to designate b, which is a morphology index, as

$b = 3$ for three-dimensionally growing particles,
$b = 2$ for two-dimensionally growing particles,
$b = 1$ for one-dimensionally growing particles.

Nucleation kinetics can be expressed by $n(t) = n' t^a$, with n' a constant and

$a = 0$ for nucleation rate zero,
$a = 1$ for constant nucleation rate,
$a > 1$ for increasing nucleation rate,
$0 < a < 1$ for decreasing nucleation rate,

Following the scheme developed above, we obtain for linear growth (from Equations 10 and 10a)

$$K \cdot t^m = -\text{constant}\ \dot{n}^a u^b t^{a+b},$$
$$a + b = m. \qquad (24)$$

For parabolic growth

$$K t^m = -\text{constant}\ \dot{n}^a u^{b/2} \cdot t^{a+b/2},$$
$$a + \frac{b}{2} = m. \qquad (25)$$

Now, combining Equations 5, 12, 16, 19 and 23 with information on the values of m for the four different cases discussed above and the defined meaning of a and b; the following general formulae can be written including all cases:
For linear growth

$$E_c = \frac{a E_n + b E_g}{a + b},$$
$$a + b = m \qquad (26)$$

and for parabolic growth

$$E_c = \frac{a E_n + \frac{b}{2} E_d}{a + \frac{b}{2}},$$
$$a + \frac{b}{2} = m. \qquad (27)$$

(In the latter case, as mentioned above, $E_d = E_g$.)

Of course it follows that if, by chance with regard to the special physical circumstances, E_n is *equal* to E_g or E_d, then $E_c = E_n = E_g$. This is expected from such a formula, and that is the reason why we prefer to call E_c "the activation of the total process" rather than ΔH, which is $m \cdot E_c$. If $E_n \neq E_g$, then the formulae give the desired E_c as a "weighted mean value" of E_n and E_g.

6.1. Applications

Out of the many cases in which E_n, E_g and E_c play a role and may be observed experimentally, we were interested in the crystallization of metallic glasses. In the following two commercially available alloys we were able to determine the three E values independently:

$Fe_{40}Ni_{40}P_{14}B_6$ ("Metglas® 2826") [4, 5]

and

$Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ ("Metglas® 2826A") [5, 6].

TABLE I Activation energies in amorphous alloys

Activation energy (kJ mol^{-1})	Alloy 2826 A	Alloy 2826
E_n	354	740
E_g	252	345
E_c (experiment)	270 [8] 286 [7]	440
E_c (formula)	293 with $a = 1$ and $b = 3$. Parabolic growth	444 with $a = 1$ and $b = 3$. Linear growth

Both are produced by Allied Chemical, USA. E_n and E_g were determined by quantitative transmission electron microscopy (TEM) (counting nuclei and measuring crystal sizes), E_c was determined by TEM volume fraction or by differential thermal analysis [7, 8]. Considering the fact that experimental accuracy is limited in the present cases to ~ 10%, the agreement between the experimentally obtained E_c and those from the formulae is very good in both examples.

The Avrami exponent m which has been taken in the above analysis as $a + b$ or $a + (b/2)$ has also been similarly used in the literature, e.g. p. 542 in Christian [3]. However, we would like to draw attention to the fact that Ilschner [9] as early as 1955 made a refined mathematical treatment of the relevant diffusion problem. His results for the Avrami exponents are different from just the sums of a and b. In the case of three-dimensional particles, parabolic growth and zero nucleation rate, his result is $1 < m < 1.2$ (and not 1.5). Even more striking is the difference for the case of constant nucleation rate: $m = 1.7$ (and not 2.5). Now, this latter value of 1.7 is in excellent agreement with the value observed experimentally of $m = 1.7$ [10]. Therefore, we believe that this is strong evidence for Ilschner's theory which obviously has somehow been overlooked in the literature of this field. Although in view of these facts the real Avrami exponent can no longer be expected to be $a + b$ or $a + b/2$,* we still think that all the derivations used in this paper to obtain the final Equations 26 and 27 are at least a good approximation. The reason is that a and b appear in both the numerator and the denominator. The general underlying analysis of putting the different activation energies of nucleation and growth into the Avrami kinetics is not strongly influenced by the refined mathematical treatments used by Ilschner [9].

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*This was also pointed out independently by Ham [11].