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Determination and interpretation of isothermal and non-isothermal transformation kinetics; the effective activation energies in terms of nucleation and growth

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A general model for the kinetics of solid state phase transformations has been discussed. The model is valid for both isothermal as well as non-isothermal transformations. In certain specific cases, the model can be simplified such that it reduces to so-called Johnson-Mehl-Avrami (JMA) kinetics. The model kinetic parameters are independent of the time-temperature program. In addition, it has been shown that in certain cases where the presented model does not pertain to JMA exactly, the JMA description still holds within practical accuracy. This holds for example, for nucleation of mixed nature. In this case, it is possible to obtain the activation energies for growth and for nucleation, separately, from measurements, if it is possible to vary the nucleation mode, for example by pre-annealing. This determination of the separate activation energies has been tested on a virtual and a real phase transformation: crystallisation of glassy $Pd_{40}Cu_{30}P_{20}Ni_{10}$.

1. Introduction

Solid state phase transformations play an important role in the production of very many materials. Therefore, a great interest exists for a (potentially) general description of the kinetics, i.e. the time-temperature behaviour of phase transformations. Solid state phase transformations are generally the outcomes, for both isothermally and non-isothermally conducted annealings, of two, often simultaneously operating, mechanisms: nucleation and growth. For special cases of nucleation and growth, it is possible to derive the well-known analytical description of transformation kinetics according to Johnson, Mehl and Avrami (JMA) [1–4]. However, the JMA kinetics description is often applied generally, whereas it can be shown that, e.g. in the case of a non-isothermal transformation, such an analytical description does not hold without more ado (cf. Section 4). Therefore, fitting of JMA kinetics to some phase transformation in general only yields a phenomenological description, and the obtained kinetic parameters do not necessarily have a physical meaning.

In the present work, a general kinetic, numerical model is described that combines nucleation and growth models. The model is applicable to both isothermal and non-isothermal transformations. This allows correction of erroneous application to non-isothermal transformation of certain concepts that in fact are only valid for isothermal transformations (see Section 2). Depending on the type of nucleation and growth models adopted and approximations applied, it is possible to derive analytical expressions for the transformation kinetics, such as the JMA equation, as will be shown here.

The general model will be used (i) to assess the limits to which JMA can be applied in practice, (ii) to provide a physical interpretation of the values of the JMA parameters and (iii) to derive an expression for the overall activation energy of the transformation in terms of the separate activation energies for the nucleation and growth processes, that can be utilised in experimental analysis of transformation kinetics (Section 6).

2. The path variable for isothermal and non-isothermal transformations

By measuring a suitable material parameter during a phase transformation, it is possible to trace the progress of this phase transformation as a function of the time (t)-temperature (T) program to which the material is subjected. The degree of transformation f $(0 \leq f \leq 1)$ can be calculated from such data. The transformed fraction does not depend on t or $T(t)$ in a direct way: the thermal history of the material determines the degree of transformation. Therefore a path variable β is introduced which fully determines the degree of transformation, and depends on the thermal history. The transformed fraction can then be given as [5]:

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$$f = F(\beta). \tag{1}$$

The dependence of the path variable β on the thermal history (i.e. the path in the time-temperature diagram) can be described as the integral over time of a rate constant $k(T(t))$, not conceived to be dependent on t other than through T:

$$\beta = \int k(T(t))\,\mathrm{d}t. \tag{2}$$

This equation is compatible with the additivity rule [5], which supposes that throughout the temperature/time range of interest the transformation mechanism is the same. A change of transformation mechanism in the course of the transformation, as might be caused by a rate constant $k(T(t))$ that is not solely dependent on $T(t)$, would cause a breakdown of the additivity rule and the applicability of Equation 2 for the path variable. The rate constant $k(T(t))$ can be given by an Arrhenius equation:

$$k(T(t)) = k_0 \exp\left(-\frac{Q}{RT(t)}\right), \tag{3}$$

with k_0 as the pre-exponential factor, Q as the overall, effective activation energy (cf. Section 4), and R as the gas constant.

It follows from Equation 2 for isothermal annealing:

$$\beta = k(T)t. \tag{4}$$

In the literature, kinetic theories for non-isothermal transformations have usually been derived starting with formulations for isothermal transformations [6–9]. If a non-isothermal experiment is described as a series of subsequent isothermal anneals, each of infinitesimal length of time, and Equation 4 is applied to each time step (as done in refs. [7, 9] for isochronal (i.e. constant heating rate) experiments), then, obviously, the outcome is in accordance with the postulate Equation 2. However, in the literature, the straightaway application of an equation equivalent to Equation 4 to isochronal annealing is often made (see, e.g. ref. [8]). This leads to different values of kinetic parameters for different type of annealings. This different values of kinetic parameters are solely caused by the different formulation of the kinetic model for different type of annealings, not by the non-isokinetic transformation behaviour. The main advantage of using the path variable according to Equation 2, is that the values of the kinetic parameters found are not influenced by the type of annealing as long as the mechanism of the transformation is also not influenced by the type of annealing.

3. General kinetic theory

It is supposed that the overall transformation is the result of, more or less, simultaneously occurring nucleation and growth processes. One strives for determination of the kinetic parameters of these processes from the overall kinetics. First, different nucleation and growth models are considered.

3.1. Nucleation models

Various possible models are illustrated in Fig. 1, for the case of isothermal annealing.

3.1.1. Continuous nucleation

Upon a phase transformation interfaces develop between the old and the new phases, and (possibly) misfit strain is introduced in the system. Whereas the production of the new phase releases chemical Gibbs energy, the creation of the interfaces and the introduction of misfit strain costs Gibbs energy. According to the classical nucleation theory [10], a critical particle size of the new phase can be defined such that if the particle (nucleus) is of sub-critical size, it costs energy to increase the size of the particle, whereas if the particle (nucleus) is of super-critical size, energy is released if the particle grows. The formation of particles of super-critical size from particles of sub-critical size is called nucleation.

The nucleation rate is determined by the number of nuclei of critical size and the rate of the jumping of atoms through the interface between the nucleus of critical size and the parent phase. The frequency of jumping through the interface is given by an Arrhenius term. The number of nuclei of critical size depends on an activation energy ΔG^*, which, according to the above

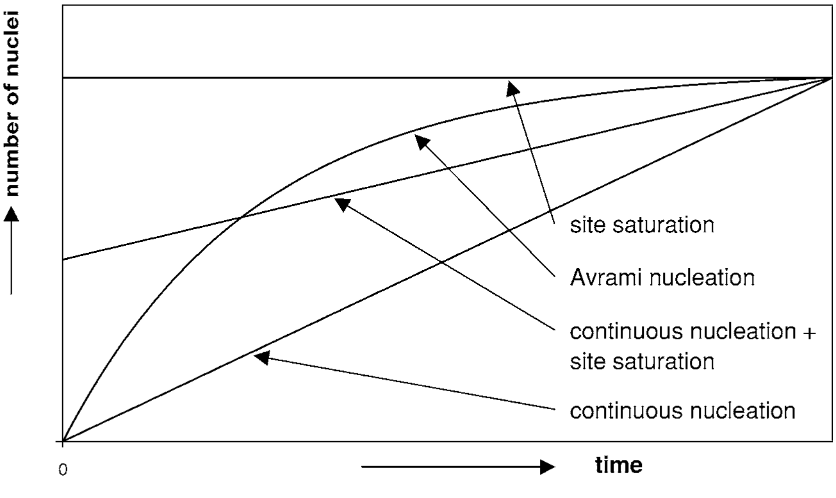


Figure 1 Schematic diagram of the number of nuclei as a function of time at constant temperature for four different nucleation models.

description depends on the decrease of the chemical Gibbs free energy per unit volume, the interface energy per unit area interface and the misfit strain energy per unit volume. ΔG^* can be approximated as $\frac{A}{\Delta T^2}$ [11], where A is a constant, and ΔT is the undercooling or overheating with respect to the temperature at which the two phases are in equilibrium. If the undercooling or the overheating is very large, ΔG^* can be considered to be very small. This is the case for a frozen-in metastable state, which transforms to the stable state upon heating. The nucleation rate per unit volume $\dot{N}(T)$ (i.e. the rate of formation of particles (nuclei) of supercritical size) is then only determined by the atomic mobility for transport through the interface, which can be given by an Arrhenius term:

$$\dot{N}(T) = N_0 \exp\left(-\frac{Q_N}{RT}\right), \tag{5a}$$

where N_0 is a temperature independent rate, and Q_N is the temperature independent activation energy for nucleation. The definition of continuous nucleation implies that the number of particles (nuclei) N of supercritical size equals 0 at $t = 0$.

3.1.2. Site saturation

The term site saturation is used in those cases where the number of (supercritical) nuclei does not change during the transformation: all nuclei, of number N^*, are present at $t = 0$ already:

$$\dot{N}(T) = N^* \delta(t - 0), \tag{5b}$$

with $\delta(t - 0)$ denoting the Dirac function.

3.1.2.1. Mixture of site saturation and continuous nucleation. In practice, intermediate types of nucleation occur often: a significant amount of nuclei is present before the transformation starts and other nuclei are formed during the transformation. Two explicit models for this type of nucleation are given.

(a) Summation of site saturation and continuous nucleation.

The first model involves that the nucleation rate at a certain stage is equal to some weighted sum of the nucleation rates according to the given continuous nucleation and site saturation models. By variation of the contribution of the two nucleation models, the mode of nucleation can be varied from pure site saturation to pure continuous nucleation:

$$\dot{N}(T) = N^* \delta(t - 0) + N_0 \exp\left(-\frac{Q_N}{RT}\right). \tag{5c}$$

where N^* and N_0 express the relative contributions of the separate modes of nucleation.

(b) Avrami nucleation.

The second model is due to Avrami [2–4]. The nuclei of supercritical size are formed from the nuclei of subcritical size N_{sub} ($\dot{N} = -\dot{N}_{\text{sub}}$), such that the total number of nuclei, of sub- and supercritical size, N', is constant. The change of the number of nuclei of supercritical size is thus equal to the product of the number of nuclei of subcritical size, N_{sub}, and the rate, λ, at which an individual subcritical nucleus becomes supercritical:

$$\dot{N} = -\dot{N}_{\text{sub}} = \lambda N_{\text{sub}} \tag{6}$$

It is supposed that λ obeys Arrhenius-type temperature dependence:

$$\lambda = \lambda_0 \exp\left(-\frac{Q_N}{RT}\right). \tag{7}$$

with λ_0 as a temperature independent rate.

Upon integration of Equation 6, after separation of variables, using Equation 7 and the boundary condition that the number of subcritical nuclei equals N' at $t = 0$, it is obtained for the rate of formation of supercritical nuclei at $t = \tau$:

$$\dot{N}(T) = -\dot{N}_{\text{sub}} = \lambda N' \exp\left(-\int_0^\tau \lambda \, \mathrm{d}t\right). \tag{5d}$$

By variation of λ_0 the mode of nucleation can be varied from site saturation (λ_0 infinitely large) to continuous nucleation (λ_0 infinitely small).

3.2. Growth models

Two (extreme) growth models are considered; one for volume diffusion controlled growth and one for interface controlled growth. Volume diffusion controlled growth can occur upon phase transformations where long range compositional changes take place. The case of interface controlled growth can occur in the absence of compositional changes, e.g. in cases of allotropic phase transformations.

3.2.1. Diffusion controlled growth

In this case, long distance diffusion in the matrix governs the growth of the new phase particles. A characteristic diffusion length, L, is in the isothermal case given by

$$L = (Dt)^{1/2}, \tag{8a}$$

where D is the diffusion coefficient. The squared diffusion length is proportional to the time. This leads to so-called parabolic growth laws for phase transformations. For non-isothermal annealing the characteristic diffusion length is accordingly given by (e.g. see ref. [12]):

$$L = \left(\int D(T(t)) \, \mathrm{d}t\right)^{1/2}. \tag{8b}$$

The diffusion coefficient depends on temperature according to:

$$D(T(t)) = D_0 \exp\left(-\frac{Q_D}{RT}\right), \tag{9}$$

with D_0 as the pre-exponential factor and Q_D as the activation energy for diffusion.

Growth laws corresponding to Equations 8a and b are only valid for growth of a second phase particle into an infinitely large parent phase matrix, and thereby application of such growth laws is strictly valid only for initial stages of transformation (see also ref. [13]).

If Equations 8a and b hold, the volume of the growing particle, Y, is given by:

$$Y = gL^d, \tag{10}$$

with d as the number of dimensions in which the particle grows and g as a particle-geometry factor.

3.2.2. Interface controlled growth

In this case, processes at the particle/matrix interface govern the growth of the new phase particle. The velocity of the particle/matrix interface is determined by the net number of atoms that jump through the interface from the matrix to the new phase particle per unit of time. The Gibbs energy of an atom in the new phase differs an amount ΔG with the Gibbs energy in the parent phase (ΔG is the driving force for the phase transformation; i.e. $\Delta G < 0$). The transfer of this atom is however frustrated by the interface, which forms an energy barrier. The Gibbs energy of an atom in the interface differs an amount ΔG^a with the Gibbs energy in the matrix (i.e. $\Delta G^a > 0$).

The net flux of atoms from the parent phase to the new phase particle is the difference between the flux of atoms from the matrix to the particle and the flux of atoms from the particle to the matrix. The flux of atoms in one direction can be given by an Arrhenius equation with the corresponding Gibbs energy barrier as the activation energy. If the pre-exponential factors for both fluxes are equal, the net flux for growth, J, can be given as [10]:

$$\begin{aligned} J &\propto \exp\left(-\frac{\Delta G^a}{RT}\right) - \exp\left(-\frac{\Delta G^a + \Delta G}{RT}\right) \\ &= \exp\left(-\frac{\Delta G^a}{RT}\right)\left(1 - \exp\left(-\frac{\Delta G}{RT}\right)\right). \end{aligned} \tag{11}$$

If the driving force ΔG is large as compared to RT, as for large undercooling or overheating, then it follows for the net flux:

$$J \propto \exp\left(-\frac{\Delta G^a}{RT}\right) \tag{12}$$

The flux, J, is proportional to the interface velocity, j, and therefore the volume of a growing particle, Y, is given by:

$$\begin{aligned} Y &= g\left(\int j \,\mathrm{d}t\right)^d \\ j &= j_0 \exp\left(-\frac{\Delta G^a}{RT}\right), \end{aligned} \tag{13}$$

where j_0 is a temperature independent interface velocity.

3.2.3. Diffusion controlled growth and interface controlled growth

Both growth models, diffusion controlled growth and interface controlled growth, represented by Equations 10 and 13, can be given in a compact form. At time t_e, the volume, Y, of a particle nucleated at time τ is given by:

$$\begin{aligned} Y &= g\left(\int_\tau^{t_e} v \,\mathrm{d}t\right)^{\frac{d}{m}} \\ v &= v_0 \exp\left(-\frac{Q_g}{RT}\right), \end{aligned} \tag{14}$$

with v_0 as the a temperature independent growth velocity, Q_g the activation energy for growth, and m as the growth mode parameter. For the case of diffusion controlled growth, $m = 2$, Q_g equals Q_D (activation energy for diffusion) and v_0 equals D_0. For the case of interface controlled growth $m = 1$, Q_g equals ΔG^a (interface energy barrier) and v_0 equals j_0.

3.3. Impingement of growing particles; the total degree of transformation

The number of (supercritical) nuclei formed in a unit volume, at time τ during a time lapse $\mathrm{d}\tau$ is given by $\dot{N}(T(\tau))\,\mathrm{d}\tau$ with $\dot{N}(T(\tau))$ according to Equation 5. The volume of each of these nuclei grows from τ until t according to Equation 14, where it is supposed that every particle grows into an infinitely large parent phase, in the absence of other growing particles (see discussion below Equation 9). The volume of all particles at time t, according to this treatment is then given by:

$$V_e = \int_0^t V\dot{N}Y \,\mathrm{d}\tau, \tag{15}$$

with V as the total volume of the system, which is supposed to be constant throughout the transformation. This result, V_e, is called the extended volume. Clearly, in reality, the particles are not growing into an infinitely large parent phase: V_e does not account for the overlap of particles (hard impingement) and their possibly surrounding diffusion fields (soft impingement). Therefore, the relationship between the extended volume V_e and the actual volume V^t of transformed phase is required.

It is supposed that the nuclei are dispersed randomly throughout the volume. Suppose that at time t the actually transformed volume is V^t. If the time is increased by $\mathrm{d}t$, the extended and the actual transformed volumes will increase by $\mathrm{d}V_e$ and $\mathrm{d}V^t$. From the change of the extended volume $\mathrm{d}V_e$, only a part will contribute to the change of the actually transformed volume $\mathrm{d}V^t$, namely a part as large as the untransformed volume fraction $(V - V^t)/V$. Hence,

$$\mathrm{d}V^t = \left(\frac{V - V^t}{V}\right)\mathrm{d}V_e. \tag{16}$$

This equation can be integrated, giving the degree of transformation, f, as:

$$f \equiv \frac{V^t}{V} = 1 - \exp\left(-\frac{V_e}{V}\right). \tag{17}$$

3.4. Summary of main assumptions

For the above treated nucleation and growth models, some assumptions have been made.

It has been assumed, (i) in both the continuous nucleation model (Section 3.1.1) and in the interface controlled growth model (Section 3.2.2) that the undercooling, or the overheating is large, in order to obtain an Arrhenius temperature dependence for the continuous nucleation and growth rates. In the literature the use of an Arrhenius-like temperature dependence for both the nucleation rate, and for the growth rate has been assumed several times, without motivation (e.g. see refs. [6, 8, 9, 14]). It should be recognised that such a description of the growth rate and especially the nucleation rate is problematic if the undercooling is small [15, 16]. Experimental proof of Arrhenius temperature dependence of both the nucleation rate and the growth rate has been obtained for the crystallisation of metallic glasses [17].

In the impingement treatment, it has been assumed that (ii) the nuclei are dispersed randomly in space and (iii) that the specific volume is constant throughout the transformation. The assumption of randomly dispersed nuclei is justified in the case of homogeneous nucleation, and in the case of heterogeneous nucleation if the nucleation takes place on randomly dispersed nucleation sites, as with clustering of solute atoms or crystallisation of a glass. The assumption of constant specific volume is an approximation for almost all transformations, which is justified as long as the change of the specific volume is small.

4. Validity of Johnson-Mehl-Avrami description

The general recipe for deriving an explicit analytical formulation for the degree of transformation in terms of the nucleation and growth mechanisms is as follows. The extended volume is calculated according to Equation 15, using the appropriate nucleation (Equation 5) and growth models (Equation 14). The expression for the extended volume is then substituted into Equation 17 to give the degree of transformation.

4.1. Isothermal annealing

If the above recipe is applied to isothermal transformations using for nucleation, either the continuous nucleation model or the site saturation model and for growth the general model (Equation 14), pertaining to either volume diffusion controlled growth or interface controlled growth, it is straightforwardly obtained:

$$f = 1 - \exp(-(k(T)t)^n), \tag{18}$$

with $k(T)$ as the rate constant given in Equation 3 with constant T, and n as a constant. Note that this equation cannot be derived for a mixture of the nucleation models (cf. Section 3.1.2.1). Equation 18 has first been derived by Johnson and Mehl (for the case of isothermal transformations with continuous nucleation [1] and by Avrami (for isothermal transformations with continuous nucleation and site saturation) [2–4] and therefore it is called the JMA equation with JMA exponent n.

The above formulation of JMA kinetics is compatible with the identification of the variable β as described by Equation 4: function F from Equation 1 in this case becomes:

$$F(\beta) = 1 - \exp(-\beta^n). \tag{19}$$

The prescription of Equation 1 implies that the equations describing the degree of transformation are identical for the cases of isothermal annealing and non-isothermal annealing *if they are expressed in terms of* β (see Equations 2 and 4).

4.2. Isothermal annealing versus non-isothermal annealing

It has been shown above that for isothermal annealing definition of β according to Equation 4 leads to the recognition that the JMA equation satisfies Equation 1. Now the question arises if for non-isothermal annealing, on the basis of the considered nucleation and growth models, (i) an equation for V_e can be derived (from Equation 15) that after substitution into Equation 17 leads to a JMA-like equation that (ii) fulfils the prescription of Equation 1 with β defined according to Equation 2. Additionally, if a JMA-like equation can be obtained, the associated kinetic parameters n, Q and k_0 can be given in terms of the various nucleation and growth models for the case of non-isothermal annealing too. In the following, it will be shown that this is possible for, at least, the case of isochronal annealing as long as the nucleation process involved is either site saturation or continuous nucleation.

4.3. Isochronal annealing

The recipe for deriving an equation for the degree of transformation given in the beginning of Section 4 can be used in general. Now this recipe is applied to the case of isochronal annealing characterised by:

$$T(t) = T_0 + \Phi t, \tag{20}$$

where T_0 is the start temperature (i.e. at $t = 0$) of the experiment and Φ is the constant heating rate. Although the treatment is analogous to that for isothermal transformations, some mathematical problems now occur. The integrals in Equations 14 and 15 cannot be evaluated analytically in general, and also not for cases of only site saturation or only continuous nucleation. An Arrhenius term, as for example obtained by substitution of Equations 3 and 20 into Equation 2, has to be integrated over time as follows:

$$\beta = k_0 \int_0^{t_e} \exp\left(-\frac{Q}{R(T_0 + \Phi t)}\right) \mathrm{d}t, \tag{21}$$

The integral in Equation 21 is also called the temperature integral [5] if it is integrated over the temperature, with the time dependent on temperature (i.e. $t = (T - T_0)/\Phi$). Here, the integration is performed over a new time parameter $t' = t + T_0/\Phi$, involving $\mathrm{d}t = \mathrm{d}t'$ and $T_0 + \Phi t = \Phi t' = T(t')$. The boundaries for the integration then become T_0/Φ and t'_e. If on heating T_0 is chosen small, such that $\beta(T < T_0) \approx 0$, the start of the new time scale (i.e. $t' = T_0/\Phi$) can be shifted to $t' = 0$ without changing the value of the integral [18]:

$$\beta = k_0 \int_{\frac{T_0}{\Phi}}^{t'_e} \exp\left(-\frac{Q}{R\Phi t'}\right) \mathrm{d}t' \approx k_0 \int_{0}^{t'_e} \exp\left(-\frac{Q}{R\Phi t'}\right) \mathrm{d}t'. \tag{22}$$

Thus, an analytical approximation of the integral becomes possible, using a series expansion of the following type [19]:

$$\int_{1}^{\infty} \frac{\mathrm{e}^{-xt}}{t^n} \mathrm{d}t = \frac{\mathrm{e}^{-x}}{x}\left[1 - \frac{n}{x} + \frac{n(n+1)}{x^2} + \cdots\right]. \tag{23}$$

Application of Equation 23 requires variable substitution as described in [5]. An example of the result of this approximation is given here for β as expressed by Equation 22:

$$\beta \approx k_0 \int_{0}^{t'_e} \exp\left(-\frac{Q}{R\Phi t'}\right) \mathrm{d}t' \approx \frac{k_0 \Phi R t'^2}{Q} \exp\left(-\frac{Q}{R\Phi t'}\right)$$
$$\times \left[1 - 2\frac{R\Phi t'}{Q} + 6\left(\frac{R\Phi t'}{Q}\right)^2 - \cdots\right]_0^{t'_e} \tag{24}$$

For practical use (see below Equation 27), the back substitution $t' = T(t')/\Phi$ is made, and thus none of the time parameters (t or t') is involved anymore. On basis of Equation 24, explicit analytical equations can be derived for the degree of transformation in the case of isochronal annealing, and for specific nucleation and growth models following the recipe indicated at the beginning of Section 4: see Appendix A. In general, (e.g. for a mixture of nucleation mechanisms (cf. Section 3.1.2.1)) the derivations do *not* lead to JMA-like equations for the degree of transformation. However, for pure site saturation (Section 3.1.2) and for pure continuous nucleation (Section 3.1.1), both in combination with growth according to Equation 14, JMA-like equations are obtained that are compatible with Equation 1 with β as given by Equation 2 and k as given by Equation 3.

The case of a mixture of nucleation mechanisms (cf. Section 3.1.2.1)), in combination with growth, is considered separately: see Section 6.

The above treatment leads to explicit expressions for n, Q and k_0 in terms of the operating nucleation and growth mechanisms: see Table I.

It is striking to observe that, for the nucleation and growth cases considered, the JMA parameters pertaining to isothermal annealing and to isochronal annealing are equal (except for the correction factor s). Two related treatments regarding this type of kinetic analysis have been published before. The oldest work is incomplete (ref. [6]: no expression for s (cf. Table I) is given, and diffusional growth is not considered), whereas the more extended, recent work [8] is erroneous. In ref. [8] equations for β^n have been interpreted according to $\beta^n = kt^n$ for both isothermal and isochronal annealing, whereas Equation 2 and Equation 3 should have been used for non-isothermal (isochronal) annealing. Then, the conclusion in ref. [8] that the kinetic parameters for isochronal and isothermal annealing are not equal is obvious in view of the assumption made, but unjustified. If the kinetic descriptions used for isothermal and non-isothermal transformations are compatible, as in this work, then the kinetic parameters for isothermal and for non-isothermal annealing are equal, as is shown in Table I, for the cases considered.

TABLE I Expressions for n, Q, and k_0 in terms of nucleation and growth mechanisms. The nucleation model parameters given are the temperature independent rate N_0, activation energy Q_N (continuous nucleation, cf. Equation 5a) or the number of nuclei $N^\star$ (site saturation cf. Equation 5b). The growth model parameters are the temperature independent growth velocity v_0 and the activation energy Q_g for growth, dimensionality of growth d, a geometrical factor g and the growth mode parameter m (cf. Equation 14). The parameter s is a correction factor for the difference between the activation energies of nucleation and growth, specified by Equation A.17

Continuous nucleation	Isothermal	Isochronal
n	$\frac{d}{m} + 1$	$\frac{d}{m} + 1^{\mathrm{a}}$
Q	$\frac{(n-1)Q_g + Q_N}{n}$	$\frac{(n-1)Q_g + Q_N^{\mathrm{a}}}{n}$
k_0	$\sqrt[n]{\frac{gN_0v_0^{n-1}}{n}}$	$\sqrt[n]{\frac{gN_0v_0^{n-1}s^{\mathrm{a}}}{n}}$
Site saturation		
n	$\frac{d}{m}$	$\frac{d}{m}$
Q	Q_g	Q_g
k_0	$\sqrt[n]{gN^{\mathrm{a}}v_0^n}$	$\sqrt[n]{gN^{\mathrm{a}}v_0^n}$

[a] Only possible to proof analytically for *d/m* having an integer value.

4.4. General representation of the overall activation energy; mixture of nucleation mechanisms

The expressions for the overall, effective activation energy, Q, given in Table I can be represented by a single equation, incorporating the exponent n, the ratio of the number of growth dimensions and the growth mode, *d/m*, and the separate activation energies for nucleation, Q_N, and for growth, Q_g, as follows:

$$Q = \frac{\frac{d}{m}Q_g + \left(n - \frac{d}{m}\right)Q_N}{n}, \tag{25}$$

where n has the value $\frac{d}{m}$ in the case of site saturation and $\frac{d}{m} + 1$ in the case of continuous nucleation. Equation 25 pertains to both isothermal and non-isothermal annealing. For the case of isothermal annealing an equation similar to Equation 25 has been given in refs. [9, 14]. Equation 25 demonstrates that, for the cases considered, the effective activation energy Q can be conceived as a weighted sum of the activation energies for nucleation and growth, with $\frac{d}{nm}$ and $(n - \frac{d}{m})/n$ as weighing factors. It is suggested here (and this will be verified: Section 6) that this equation has a more general validity, and thus it may be applied to cases where a mixture of nucleation mechanisms occurs. No JMA-like equations can be derived for such cases (see Section 6), and thus exact explicit analytical expressions for Q cannot be given.

5. Determination of kinetic parameters

In order to evaluate the kinetics of a transformation, measurements have to be performed from which the transformed fraction as a function of time and temperature can be obtained. By adopting a certain function $f = F(\beta)$ (Equation 1), which describes the relation between the path variable β and the transformed fraction, f, it is possible to calculate β as a function of time/temperature from the measurement.

If JMA kinetics occurs, the function F is given by Equation 19. Then, if values for the transformed fraction are known from measurements, the corresponding values of β^n are also known. The kinetic parameters n, Q and k_0, can then be determined from the β^n data as follows.

For isothermal annealing it holds (cf. Equation 4):

$$\beta^n = (k(T)t)^n. \qquad (26)$$

Both parameters $k(T)$ and n can be determined from one isothermal experiment (i.e. measuring the progress of the transformation as a function of time at a constant temperature) comprising at least two data points $(t,\ \beta^n)$. Determination of Q and k_0, incorporated in $k(T)$ according to Equation 3, requires at least two such isothermal experiments, each at a different temperature.

For isochronal annealing it holds (cf. Equation 24):

$$\beta^n \approx \left(\frac{k_0 \Phi R t'^2}{Q} \mathrm{e}^{\left(-\frac{Q}{R\Phi t'}\right)}\right)^n. \qquad (27)$$

In practical cases, β^n is measured as a function of temperature T. In order to obtain an equation compatible with this measurement, back substitution of t'_e by T/Φ in the right hand side of Equation 27 is often performed (see below Equation 21).

In principle, values of n, Q and k_0 can be obtained from one isochronal experiment (i.e. measuring the progress of the transformation as a function of time/temperature at a constant heating rate) comprising at least three data points $(t'_e,\ \beta^n)$. Substituting these three $(t'_e,\ \beta^n)$ pairs in Equation 27, leads to a system of three equations with the three unknowns, k_0, Q and n. A unique analytical solution for this system of equations does exist, but, upon testing this method in practice, it was observed that the values thus obtained for the kinetic parameters appeared to be extremely sensitive to small changes in the values of the measured data $(t'_e,\ \beta^n)$, rendering the results obtained in this way practically meaningless. Therefore, in practice, at least two isochronal heating experiments, with different heating rates Φ, are required.

It should be noted that (only) the value for the overall, effective activation energy can be determined without recourse to a specific kinetic model; see discussion in ref. [5].

The accuracy of the determination of the kinetic parameters can be increased by choosing the temperature-time program parameters (Φ (isochronal experiments) or T (isothermal experiments)) far apart, but this is bound to practical limits.

6. Determination and interpretation of kinetic parameters; practical limits in the use of the JMA description

If one attempts to describe the kinetics as observed in practice with JMA-like equations, one very often obtains values for the JMA exponent which cannot be interpreted directly on the basis of Table I: the value of the JMA exponent appears to be between the JMA exponent expected for site saturation and the JMA exponent expected for continuous nucleation. In these cases, it may be deduced that the actual nucleation is of ‘intermediate’ nature. However, a JMA description is in principle not applicable to cases where a mixture of nucleation mechanisms operates (see Section 4.3). This has not always been realised, for example see refs. [20, 21]. Nevertheless, it is worthwhile to investigate the (extent of) applicability of JMA for cases of intermediate nucleation too. Further, knowledge about the validity of Equation 25, suggested to be of general applicability in Section 4.4, is desired.

6.1. Exact vs. JMA kinetics; the effective activation energy

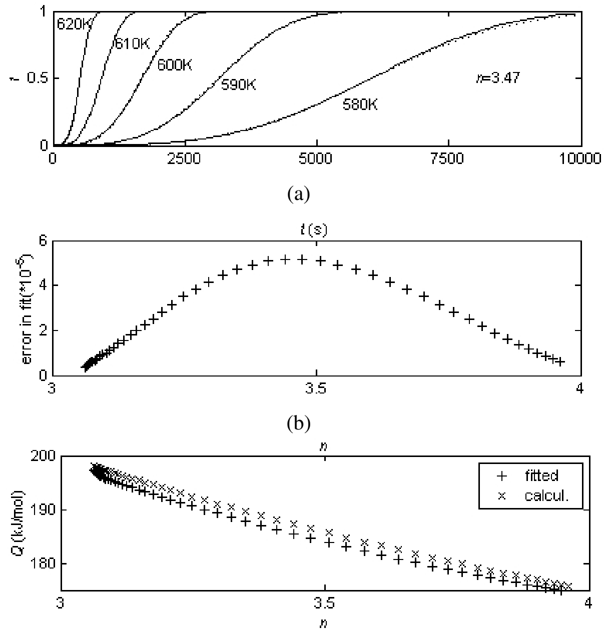
As explained before (Section 4.3), analytical results cannot be derived for an arbitrary combination of the nucleation and growth models and therefore the recipe at the beginning of Section 4 is used for *numerical* calculation of the transformed fraction. Then JMA kinetics is fitted to this transformed fraction as function of time/temperature. Thereby the following steps are performed successively.

1. Values are chosen for the model parameters Q_g, v_0 and d/m (Equation 14) and Q_N (Equations 5d and c), and N_0 and N^* (Equation 5c) or λ_0 and N' (Equation 5d); i.e. a mixture of nucleation mechanisms is adopted.
2. Rigorous numerical application of the recipe given in the beginning of Section 4 provides the transformed fraction f as a function of time/temperature. This calculation is performed for five different temperatures (isothermal annealing) or five different heating rates (isochronal annealing).
3. JMA kinetics, (i.e. Equation 2 or 4, in combination with Equations 3 and 19) is fitted to the transformed fraction as obtained in step 2 *simultaneously* for the five different temperatures (isothermal annealing) or the five different heating rates (isochronal annealing). Fitting is performed by minimisation of the sum of the squares of the residuals, employing a simplex fitting procedure [22]. Thus, values for the (JMA) kinetic parameters n, Q, and k_0 are obtained.

The above procedure has been performed for a range of values of N_0 and N^* (Equation 5c) or λ_0 (Equation 5d). Thus, the mode of transformation varies from pure site saturation to pure continuous nucleation. The values of the preset kinetic parameters have been gathered in Table II. The applicability of JMA kinetics for the cases of intermediate nucleation can be judged from the goodness of the fits. The exponent n should vary

TABLE II Values of the kinetic parameters as used in the model calculations for isothermal and isochronal annealings for a case of mixture of nucleation mechanisms, Avrami nucleation according to Equation 5d and site saturation + continuous nucleation according to Equation 5c, and the growth mechanisms pertaining to both (volume) diffusion and interface controlled growth, according to Equation 14

Avrami nucleation				Site saturation + continuous nucleation			
Q_g	(kJ/mol)	200		Q_g	(kJ/mol)	200	
v_0	(s^{-1})	1×10^9		v_0	(s^{-1})	1×10^9	
d/m		3		d/m		3	
Q_N	(kJ/mol)	100		Q_N	(kJ/mol)	100	
λ_0^{start} (s^{-1})	1×10^5	λ_0^{end} (s^{-1})	1×10^8	N_0^{start} (s^{-1})	5×10^{15}	N_0^{end} (s^{-1})	5×10^{13}
N'		5×10^{15}		$N^{*\text{start}}$	5×10^8	$N^{*\text{end}}$	5×10^{10}

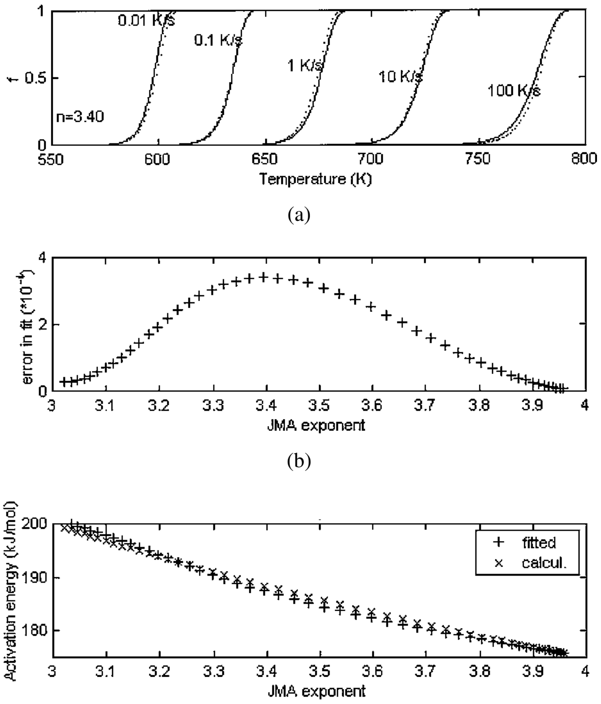


(a)

(b)

(c)

Figure 2 (a) Transformed fraction, f, versus time, for five isothermal holding temperatures. The model calculations (·) using Avrami nucleation and the JMA fit (—), for the maximum least squares difference between the transformed fraction according to the model calculations and the JMA fit, are shown. λ_0 has a value of 1.46×10^6 s^{-1}. (b) Least squares difference of the transformed fraction according to the model calculations and the fitted JMA kinetics, as a function of JMA exponent as determined in the fits. (c) Activation energy as a function of fitted JMA exponent both according to Equation 25 (x), using the parameter prescriptions as given in Table II, and according to the fits (+).



(a)

(b)

(c)

Figure 3 (a) Transformed fraction, f, versus temperature, for five heating rates. The model calculations (·) using Avrami nucleation and the JMA fit (—), for the maximum least squares difference between the transformed fraction according to the model calculations and the JMA fit, are shown. λ_0 has a value of 5.18×10^6 s^{-1}. (b) Least squares difference of the transformed fraction according to the model calculations and the fitted JMA kinetics, as a function of JMA exponent as determined in the fits. (c) Activation energy as a function of fitted JMA exponent, both according to Equation 25 (x), using the parameter prescriptions as given in Table II and according to the fits (+).

from d/m (site saturation) to $d/m + 1$ (continuous nucleation). The values obtained for the activation energy Q as a function of exponent n can be considered to see if Equation 25 holds for the cases of intermediate nucleation.

The results of the exact numerical calculations of the kinetics and the fits of JMA kinetics are shown in Figs 2–5. In the upper part of the figures the transformed fraction as a function of time/temperature is shown for the case of the worst fit (the maximum in the middle part of the figures). The error in the fit is given in the middle part of the figures as a function of the fitted JMA exponent, i.e. the least squares difference between the exact calculated transformed fraction, $f(t)$, and the JMA fitted $f(t)$.

Clearly, the JMA description provides a reasonable fit, also in the cases where it does not hold in principle. Note that the calculations have been performed for a broad ‘experimental’ window in relation to the kinetic parameters. A temperature range of 50 K has been used for the isothermal transformations, in which the transformation time varies over two decades. Five decades in heating rate have been used for isochronal annealing, in which the transformation temperature varies over a temperature range of 250 K.

The activation energy obtained by fitting has been plotted vs. the JMA exponent as obtained by fitting in Figs 2c–5c. In these figures, the predicted values of the activation energy *according to Equation* 25 have also been shown. It can be concluded that Equation 25 provides a very good description of the operating, effective activation energy (difference within 3%)

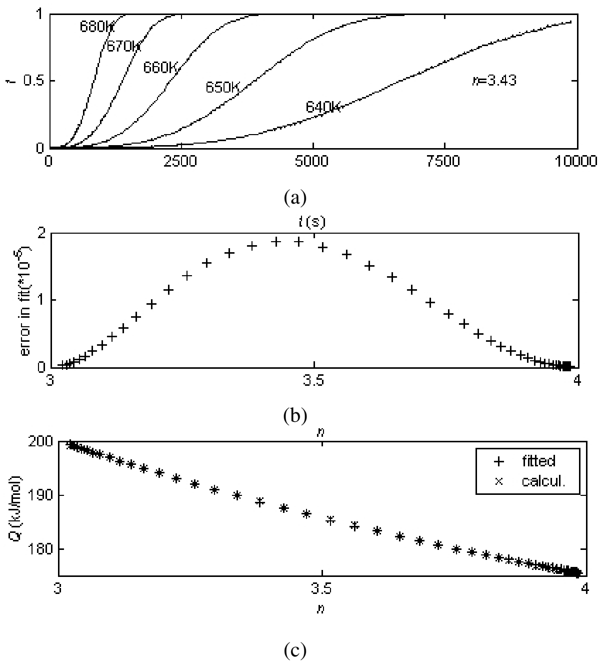


Figure 4 (a) Transformed fraction, f, versus time, for five isothermal holding temperatures. The model calculations ($\cdot$) using the summation nucleation model and the JMA fit (—), for the maximum least squares difference between the transformed fraction according to the model calculations and the JMA fit, are shown. The mixing parameters from the nucleation model have the following values: $N^{\star} = 1.0 \cdot 10^{10}$ m^{-3} and $N_0 = 2.5 \cdot 10^{14}$ s^{-1} m^{-3}. (b) Least squares difference of the transformed fraction according to the model calculations and the fitted JMA kinetics, as a function of JMA exponent as determined in the fits. (c) Activation energy as a function of fitted JMA exponent, both according to Equation 25 (x), using the parameter prescriptions as given in Table II and according to the fits (+).

6.2. Determination of separate activation energies for nucleation and growth

The effective activation energy as a function of the JMA exponent can experimentally be determined if it is possible to vary the mode of the nucleation for the observed phase transformation. From these data the separate activation energies for nucleation and growth can be determined using Equation 25.

This case can be illustrated using several data points from the simulations dealt with in Section 6.1. From Figs 2c–5c, the (n, Q) data points pertaining to the end points of the n range and the (n, Q) data point corresponding to Figs 2a–5a (i.e. the maximum in 2b–5b) have been used. Fitting of Equation 25 to the three (n, Q) data points leads to values for the activation energies for nucleation and growth, given in Table III together with to corresponding exact values:

TABLE III The Activation energy for nucleation Q_N and the activation energy for growth Q_g as put in the model and determined by fitting Equation 25 to three (n, Q) data points from the calculated cases considered in Section 6.1. The value of *d/m* is taken 3

	Q_N (kJ/mol)	Q_g (kJ/mol)
Input (see Table II)	100	200
Isothermal Avrami nucleation	97.7	198.9
Isochronal Avrami nucleation	97.1	200.4
Isothermal summation (see 3.1.2.1(a))	100.9	199.9
Isochronal summation (see 3.1.2.1(a))	103.9	199.5

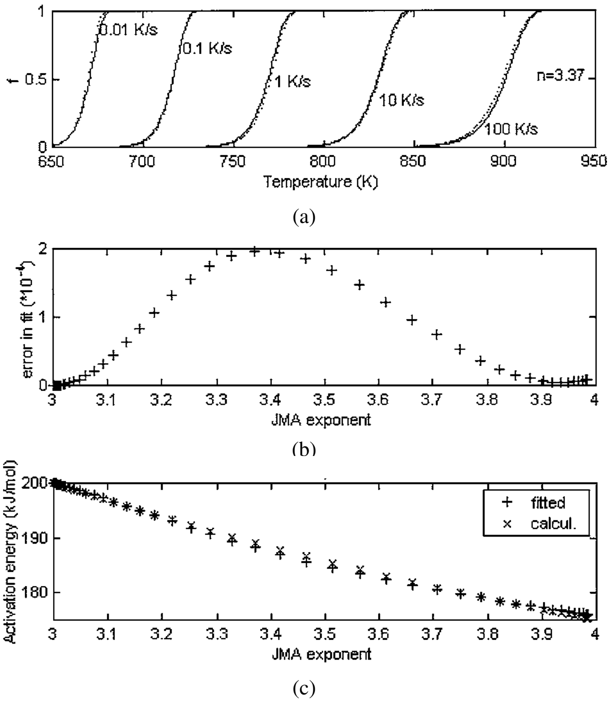


Figure 5 (a) Transformed fraction, f, versus temperature, for five heating rates. The model calculations ($\cdot$) using the summation nucleation model and the JMA fit (—), for the maximum least squares difference between the transformed fraction according to the model calculations and the JMA fit, are shown. The mixing parameters for the nucleation model have the following values: $N^{\star} = 1.4 \cdot 10^{9}$ m^{-3} and $N_0 = 3.5 \cdot 10^{14}$ s^{-1} m^{-3}. (b) Least squares difference of the transformed fraction according to the model calculations and the fitted JMA kinetics, as a function of JMA exponent as determined in the fits. (c) Activation energy as a function of fitted JMA exponent, both according to Equation 25 (x), using the parameter prescriptions as given in Table II and according to the fits (+).

Clearly, adoption of Equation 25 leads to practically correct values of the activation energies for nucleation and growth for both isothermal and isochronal transformations.

6.3. Experimental example: crystallisation of bulk amorphous $Pd_{40}Cu_{30}P_{20}Ni_{10}$

The kinetics of the crystallisation of bulk amorphous $Pd_{40}Cu_{30}P_{20}Ni_{10}$ can be investigated on the basis of measurements performed in this project and as presented in ref. [23]. Isothermal pre-annealing in the supercooled liquid temperature range has significant influence on the kinetics of the transformation (see Fig. 6). Experimental details regarding specimen preparation and DSC analysis have been described in ref. [23].

The JMA kinetic parameters have been determined by fitting a JMA model to the measurements for 5 heating rates simultaneously. The values obtained for the kinetic parameters of the transformation have been given in Table IV.

This transformation involves three-dimensional diffusional growth and the pre-annealing has no influence on the growth mechanism [23]. Thus *d/m* has the constant value 3/2. According to the theoretical treatment (see Section 4.4), the value of n can vary between *d/m* (3/2) in the case of site saturation and *d/m* + 1 (5/2) in the case of continuous nucleation.

TABLE IV The JMA exponent n and the effective activation energy Q for isochronal crystallisation of amorphous $Pd_{40}Cu_{30}P_{20}Ni_{10}$ as determined by fitting

Pre annealing temperature (K)	n	Q (kJ mol^{-1})
623	2.44	292
625	2.04	304
626	2.01	300
628	1.71	307
629	1.55	317

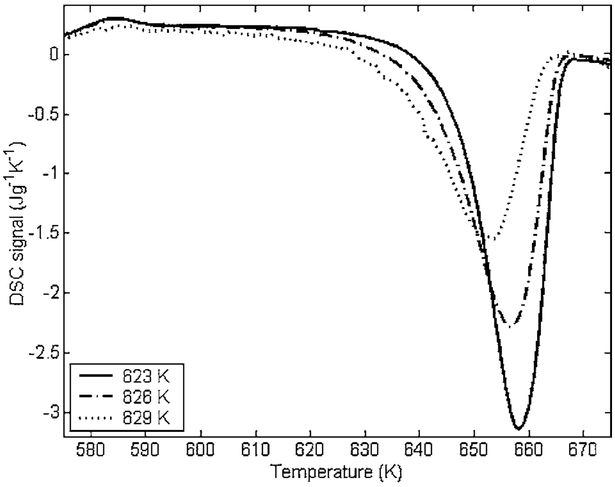


Figure 6 DSC scans for heating rate 20 K/min showing crystallisation behaviour of initially amorphous $Pd_{40}Cu_{30}P_{20}Ni_{10}$. Results are shown as obtained after different pre-annealing heat treatments of 600 s at the temperatures 623, 626 and 629 K.

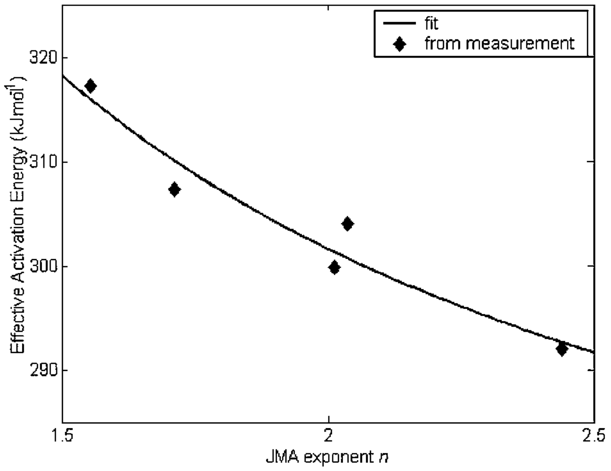


Figure 7 The effective activation energy, Q, as a function of JMA exponent, n, as measured (◆) and as fitted according to Equation 25 (full line) using $d/m = 3/2$.

Equation 25 can be fitted to the 5 data points gathered in Table IV, corresponding to the 5 different pre-anneals, leading to determination of values for the separate activation energies for nucleation and growth (Section 6.2). The activation energy for nucleation is found to be 252 kJ/mol and the activation energy for growth is found to be 318 kJ/mol; see also Fig. 7. The value of the activation energy for nucleation as determined here is within the range of activation energies for nucleation for metal-metalloid glasses ($Co_{70}B_{30}$: 191 kJ/mol, $Fe_{65}Ni_{10}B_{25}$: 300 kJ/mol [24]). The value of the activation energy for diffusion as determined here (318 kJ/mol) is low in comparison to the activation energy for Au diffusion in amorphous $Pd_{40}Ni_{40}P_{20}$ (420 kJ/mol) [25] and is high in comparison to the values for self diffusion in the crystalline constituents: Pd 266 kJ/mol, Cu 209 kJ/mol and Ni 285 kJ/mol [26], which is reasonable.

7. Conclusions

(i) Both for isothermal and non-isothermal transformations the degree of transformation is uniquely described by the path variable β (Equation 1), which is given, independent of the time-temperature program, by Equations 2 and 3. The Johnson–Mehl–Avrami (JMA) equation is compatible with this concept: there is one JMA equation for both isothermal and non-isothermal transformations only if expressed in terms of β (Equation 19).

(ii) The JMA equation (transformed fraction, f, as function of β) holds only for specific, extreme cases of nucleation: pure site saturation or pure continuous nucleation. For general phase transformations, in particular if a mixture of nucleation mechanisms, in association with diffusion or interface controlled growth mechanisms, occurs, JMA kinetics does not hold in principle. However, the JMA equation can provide a good description of the reaction kinetics also in such cases as demonstrated by the model simulations.

(iii) The values for the JMA kinetics parameters are equal for isothermally and isochronally conducted phase transformations, in contrast with earlier published results.

(iv) The effective activation energy can be given for very many transformations as a weighted sum of the separate activation energies for nucleation and growth, with the weights d/mn for growth and $1\text{-}d/mn$ for nucleation, where d is the dimensionality of the growth, n is the JMA exponent and m depends on the growth mode: $m = 1$ for interface controlled growth, and $m = 2$ for diffusion controlled growth (Equation 25). This result allows determination of the separate activation energies for nucleation and growth by varying the mode of nucleation for a phase transformation, e.g. by pre-annealing.

Appendix A: Calculating the kinetic parameters analytically

A.1. Site saturation

The extended volume of N^* particles growing from time 0 until time t is given by:

$$V^e = VN^*g\left(\int_0^{t_e} v_0 \exp\left(-\frac{Q_g}{RT(t)}\right)\mathrm{d}t\right)^{\frac{d}{m}}, \qquad (A.1)$$

with the parameters as given under Equations 14 and 15. This Equation A.1 is in the same form as JMA kinetics (see Equations 2, 3 and 19):

$$V^e = V\left(\int_0^{t_e} k_0 \exp\left(-\frac{Q}{RT(t)}\right)\mathrm{d}t\right)^n. \qquad \text{(A.2)}$$

If it now is considered that k_0 and n from Equation A.2 and v_0, N^*, g, d and m from Equation A.1 are independent of time, it can be shown that:

$$\begin{aligned} V^e &= V k_{_0}^n \left(\int_0^{t_e} \exp\left(-\frac{Q}{RT(t)}\right)\mathrm{d}t\right)^n \\ &= V N^* g v_{_0}^{\frac{d}{m}} \left(\int_0^{t_e} \exp\left(-\frac{Q_g}{RT(t)}\right)\mathrm{d}t\right)^{\frac{d}{m}}, \end{aligned} \qquad \text{(A.3)}$$

and, from Equation A.3, the JMA parameters can be given in terms of nucleation and growth:

$$\begin{aligned} n &= \frac{d}{m} \\ Q &= Q_g. \\ k_0 &= \left(N^* v_{_0}^n g\right)^{\frac{1}{n}} \end{aligned} \qquad \text{(A.4)}$$

These values for the JMA parameters do not depend on the time temperature program and, as shown, can be derived without any mathematical assumptions.

A.2. Continuous nucleation during isothermal annealing

The extended volume from a 'Continuous Nucleation' process as described can be given by:

$$\begin{aligned} V^e = V &\int_0^{t_e} g N_0 \exp\left(-\frac{Q_N}{RT}\right) \\ &\times \left(\int_\tau^{t_e} v_0 \exp\left(-\frac{Q_g}{RT}\right)\mathrm{d}t\right)^{\frac{d}{m}} \mathrm{d}\tau, \end{aligned} \qquad \text{(A.5)}$$

with the same parameters as in Equation A.1, apart from N_0 which is the temperature independent nucleation rate, and Q_N is the activation energy for nucleation.

If the isothermal case is considered, it can be shown that:

$$\begin{aligned} V^e = V &\int_0^{t_e} g N_0 v_0^{\frac{d}{m}} \exp\left(-\frac{Q_N}{RT}\right) \exp\left(-\frac{\frac{d}{m}Q_g}{RT}\right) \\ &\times (t_e - \tau)^{\frac{d}{m}} \mathrm{d}\tau, \end{aligned} \qquad \text{(A.6)}$$

which in turn can be integrated, and equated to the integrated version of Equation A.2 to give:

$$\begin{aligned} V^e = V k_0^n \exp\left(-\frac{nQ}{RT}\right) t^n &= V g \frac{1}{\frac{d}{m}+1} N_0 v_0^{\frac{d}{m}} \\ &\times \exp\left(-\frac{\frac{d}{m}Q_g + Q_N}{RT}\right) t^{\left(\frac{d}{m}+1\right)}, \end{aligned} \qquad \text{(A.7)}$$

and thus, the JMA parameters can be given by:

$$\begin{aligned} n &= \frac{d}{m} + 1 \\ Q &= \frac{(n-1)Q_g + Q_N}{n}. \\ k_0 &= \left(N_0 v_0^{n-1} \frac{g}{n}\right)^{\frac{1}{n}} \end{aligned} \qquad \text{(A.8)}$$

A.3. Continuous nucleation during isochronal annealing

During isochronal annealing, the temperature depends on time as is shown in Equation 20. If this equation is combined with Equation A.2, it is impossible to integrate the resulting equations without any mathematical assumptions.

By using the mathematical assumption (Equation 24) twice, once for the inner integral in Equation A.5, and once for the outer integral in Equation A.5, it is possible to perform the integration. The inner integral can be written as:

$$\int_\tau^{t_e'} v_0 \exp\left(-\frac{Q_g}{R\Phi t'}\right)\mathrm{d}t' = v_0\left(f\left(\frac{R\Phi t_e'}{Q_g}\right) - f\left(\frac{R\Phi\tau}{Q_g}\right)\right) \qquad \text{(A.9)}$$

$$f\left(\frac{R\Phi t_e'}{Q_g}\right) = \frac{R\Phi t_e'^2}{Q_g} \exp\left(-\frac{Q_g}{R\Phi t_e'}\right)\left[1 - 2\frac{R\Phi t_e'}{Q_g}\right].$$

Now filling this out in Equation A.5 it follows:

$$\begin{aligned} \frac{V_e}{V} &= \int_0^{t_e'} g N_0 \exp\left(-\frac{Q_N}{R\Phi t_e'}\right) \\ &\times \left(\int_\tau^{t_e'} v_0 \exp\left(-\frac{Q_g}{R\Phi t_e'}\right)\mathrm{d}t'\right)^{\frac{d}{m}} \mathrm{d}\tau = \int_0^{t_e'} g N_0 v_0^{\frac{d}{m}} \\ &\times \exp\left(-\frac{Q_N}{R\Phi t_e'}\right)\left(f\left(\frac{R\Phi t_e'}{Q_g}\right) - f\left(\frac{R\Phi\tau}{Q_g}\right)\right)^{\frac{d}{m}} \mathrm{d}\tau \end{aligned} \qquad \text{(A.10)}$$

This integration can be made using the same analytical approximation of the exponential in two terms, giving for the case of $d/m = 1$:

$$\begin{aligned} \frac{V^e}{V} &\approx \frac{g}{2} v_0 N_0 C (R\Phi)^3 \exp\left(-\frac{Q_N + Q_g}{R\Phi t_e'}\right) t_e'^4 \\ C &= 2\frac{Q_N^2 Q_g^2 + Q_N Q_g^3 - 6R\Phi t_e' Q_N Q_g^2 - 2R\Phi t_e' Q_g^3 - 6(R\Phi t_e')^2 Q_N^2 + 8(R\Phi t_e')^2 Q_N Q_g + 4(R\Phi t_e')^2 Q_g^2}{Q_g^2 Q_N^2 (Q_N + Q_g)^2} \\ &\approx \frac{2}{Q_N(Q_N + Q_g)} \end{aligned} \qquad \text{(A.11)}$$

This latter approximation is based on $R\Phi t'_e \ll Q$, which is also the assumption needed for the termination of the approximation series is used twice in Equation A.10 in only the first order, the results obtained then are:

$$\frac{V^e}{V} \approx \frac{g}{2} v_0 N_0 C (R\Phi)^3 \exp\left(- \frac{Q_N + Q_g}{R\Phi t'_e} \right) t'^4_e$$
$$C = \frac{2}{Q_N (Q_N + Q_g)}. \qquad \text{(A.12)}$$

It is seen that C is a constant, defined by the activation energies of nucleation and growth. It is also seen that the second order approximation is not needed in the integration, as the both assumptions will give the same result. Nevertheless, it is checked for the cases of $d/m = 2$ and $d/m = 3$ that the first and the second order approximation give the same result. It is seen, that the second order approximation is not needed in the calculation, and therefore, the first order approximation results are shown here.

For the cases of $d/m = 2$ and $d/m = 3$, first the case of $d/m = 2$:

$$\frac{V^e}{V} = \frac{g}{3} N_0 v_0^2 C (R\Phi)^3 \exp\left(- \frac{Q_N + 2Q_g}{R\Phi t'} \right) t'^6$$
$$C = \frac{6}{Q_N (Q_N + Q_g)(Q_N + 2Q_g)} \qquad \text{(A.13)}$$

And the case of $d/m = 3$:

$$\frac{V^e}{V} = \frac{g}{4} N_0 v_0^3 C (R\Phi)^4 \exp\left(- \frac{Q_N + 3Q_g}{R\Phi t'_e} \right) t'^8_e$$
$$C = \frac{24}{Q_N (Q_N + Q_g)(Q_N + 2Q_g)(Q_N + 3Q_g)} \qquad \text{(A.14)}$$

In order to obtain the JMA kinetic parameters, Equations A.12–A.14 are supposed to be identical to the JMA expression for V_e/V (Equation A.2). For the comparison however, the same mathematical approximation is used for Equation A.2, also only developed in the first order:

$$\left(\int_0^{t_{e'}} k_0 \exp\left(- \frac{Q}{R\Phi t'} \right) \mathrm{d}t' \right)^n \approx k_0^n \left(\frac{\Phi R}{Q} \right)^n \exp\left(- \frac{nQ}{R\Phi t'_e} \right) t'^{2n}_e. \qquad \text{(A.15)}$$

If it is now supposed that Equation A.15 equals Equations A.12–A.14 respectively, then the values for the JMA kinetic parameters are given by:

$$n = \frac{d}{m} + 1$$
$$Q = \frac{(n-1)Q_g + Q_\mathrm{N}}{n}. \qquad \text{(A.16)}$$
$$k_0 = \left(N_0 v_0^{n-1} \frac{g}{n} C Q^n \right)^{\frac{1}{n}}$$

Now, in this equation, the value of CQ^n can be given in a more general form, which is proven to be correct for $n = 2$, 3 and 4:

$$s = CQ^n = \frac{(n-1)!}{n^{(n-1)}} \frac{(Q_N + (n-1)Q_g)^n}{\prod_{j=0}^{j=n-1} (Q_N + jQ_g)}. \qquad \text{(A.17)}$$

This factor corrects for a difference in activation energy for nucleation and growth.

To conclude, one can calculate analytically the JMA parameters from Arrhenius nucleation and Arrhenius growth. The mathematical approximation to be made is used several times in the case of continuous nucleation on isochronal heating. The development of the exponential integral is used only in the first order approximation. This is correct in the case that $RT \ll Q$ for the used temperature and activation energy of interest. Usually, for solid-state phase transformations, this is the case.

The kinetic parameters n and Q obtained are exactly the same for the isochronal and isothermal annealing. The value of the pre-exponential factor k_0 however is not exactly the same in all cases.

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