An analytical model for isothermal and isochronal transformation kinetics

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An analytical model for the kinetics of phase transformations has been discussed that combines three overlapping processes: nucleation, growth, and impingement. Two kinds of nucleation have been considered in particular: a mixture of site saturation and continuous nucleation and Avrami nucleation. In combination with either interface-controlled growth or volume diffusion controlled growth, and incorporating the effect of impingement of the growing particles, a general analytical description of the transformation kinetics has been given for both isothermally and isochronally conducted transformations. The corresponding kinetic parameters are time and temperature dependent. In specific, limiting cases, the model reduces to the so-called Johnson-Mehl-Avrami description of transformation kinetics. The analytical model has been verified by exact results obtained from numerical calculations. The influences of the different nucleation and growth modes on the time and temperature dependencies of the transformation rate and the kinetic parameters have been demonstrated. © *2004 Kluwer Academic Publishers*

1. Introduction

Solid-state phase transformations play an important role in the production of very many materials. Therefore, a great interest exists for a comprehensive 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 three, often simultaneously operating, mechanisms: nucleation, growth and impingement.

For special cases of nucleation, growth and impingement the well-known analytical description of transformation kinetics according to Johnson, Mehl and Avrami (JMA) [1–6] holds. Recently a more general modular, numerical kinetic model [7–9] has been proposed that recognizes the three mechanisms, nucleation, growth, and impingement of growing new phase particles, as entities that can be modeled separately. The model is applicable to both isothermally conducted (time dependent) and isochronally conducted (temperature dependent) transformations. The kinetic model parameters of the JMA description and the modular model, the growth (Avrami) exponent, n, the overall effective activation energy, Q, and the rate constant, K_0, depend on the operating nucleation and growth modes. Applying such a model to a phase transformation, it is assumed that throughout the temperature/time range of interest the transformation mechanism is the same (which is called "iso-kinetic") and the kinetic parameters are assumed to be constant with respect to time and temperature [7–10].

Many experimental results of phase transformation kinetics have been reported and fitted with a JMA (-like) model. Often the measured kinetics cannot be described with constant values for n and Q within a JMA-like model (e.g., [11–13]): the fitted parameters, n and Q, are different for different stages of the transformation. This has been explained by corresponding changes in the nucleation and growth mechanisms [11–13], i.e., the transformation process is not iso-kinetic. Fitting of JMA kinetics to such phase transformations therefore only yields a phenomenological description.

In the recently proposed modular kinetic model, an expression for the overall effective activation energy, Q, was given, incorporating the activation energies for nucleation, Q_N, and for growth, Q_G, as follows [10]:

$$Q = \frac{\frac{d}{m}Q_G + \left(n - \frac{d}{m}\right)Q_N}{n} \quad (1)$$

where the value of n is equal to d/m for site saturation and equal to $d/m + 1$ for continuous nucleation, with m as growth mode parameter ($m = 1$ for interface-controlled growth; $m = 2$ for volume diffusion controlled growth) and d as the dimensionality of the growth ($d = 1, 2, 3$).

In principle, JMA kinetics is not applicable, if a mixture of nucleation mechanisms prevails. Equation 1 has been verified analytically only for the extreme conditions, i.e., for pure continuous nucleation or pure site saturation as nucleation mechanisms [10]. However, it has been shown numerically that a JMA-like

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description provides a reasonable fit for intermediate cases, i.e., transformation controlled by mixed nucleation or Avrami nucleation [8]. Against this background, in the present work an analytical model for the solid-state phase transformation has been developed that incorporates the three mechanisms: nucleation, growth and impingement. The model is applicable to both isothermally and isochronally conducted transformations, with time or temperature dependent kinetic parameters. On this basis Equation 1 has been analytically and generally validated. Only for special cases, the model reduces to the well-known JMA description of transformation kinetics.

2. Theoretical basis
2.1. The path variable for isothermal and isochronal transformations

It appears appropriate to introduce a path variable, β, which depends on the thermal history, i.e., the path followed in the temperature-time diagram: $T(t)$ prescribes β [7]. The transformed fraction, f, depends on the path variable β through:

$$f = F(\beta) \tag{2}$$

The dependence of the path variable β on the thermal history 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:

$$\beta = \int K(T(t))\,dt \tag{3a}$$

with K as the rate constant. It follows from Equation 3 for isothermal annealing:

$$\beta = K(T)t \tag{3b}$$

For many applications, $K(T)$ can be given by an Arrhenius-type equation

$$K(T(t)) = K_0 \exp\left(-\frac{Q}{RT(t)}\right) \tag{4}$$

with Q as the overall, effective activation energy, K_0 as the temperature and time-independent rate and R as the gas constant.

2.2. Modes of nucleation, growth, and impingement

In the following a brief description of the applied nucleation, growth and impingement modes is given.

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^* per unit volume, are present at $t = 0$ already:

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

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

The *continuous nucleation* rate per unit volume (i.e., the rate of formation of particles (nuclei) of supercritical size) is at large undercooling only determined by the rate of the jumping of atoms through the interface between the nucleus of critical size and the parent phase, which can be given by an Arrhenius term:

$$\dot{N}(T(t)) = N_0 \exp\left(-\frac{Q_N}{RT(t)}\right) \tag{6}$$

where N_0 is a temperature-independent nucleation rate, and Q_N is the temperature-independent activation energy for nucleation. The number of nuclei equals 0 at $t = 0$.

The *mixed nucleation* mode involves that the nucleation rate is equal to some weighted sum of the nucleation rates according to continuous nucleation and site saturation:

$$\dot{N}(T(t)) = N^*\delta(t - 0) + N_0 \exp\left(-\frac{Q_N}{RT(t)}\right) \tag{7}$$

where N^* and N_0 represent the relative contributions of the two modes of nucleation.

So-called *Avrami nucleation* involves that the rate of formation of supercritical nuclei at time t is given by [1–4, 8],

$$\dot{N}(T(t)) = N'\lambda \exp\left(-\int_0^t \lambda\,d\tau\right) \tag{8a}$$

where λ is the rate at which an individual subcritical nucleus becomes supercritical: $\lambda(t = \tau) = \lambda_0 \exp(-\frac{Q_N}{RT(\tau)})$, with λ_0 as a temperature-independent rate and N' as the total number of subcritical nuclei at $t = 0$. For isothermal annealing, λ is constant, and Equation 8a becomes,

$$\dot{N}(T) = N'\lambda \exp(-\lambda t) \tag{8b}$$

and in these cases Avrami nucleation reduces to pure continuous nucleation for $\lambda t \to 0$, and to pure site saturation for $\lambda t \to \infty$. The isochronal case will be treated in Section 3.4.

The *diffusion controlled and the interface-controlled growth* can be given in a compact form [8]. At time t, the volume Y, of a particle nucleated at time τ is given by,

$$Y = g\left[\int_\tau^t v\,dt\right]^{\frac{d}{m}} \tag{9a}$$

with g as a particle-geometry factor and $v = v_0 \exp(-\frac{Q_G}{RT})$ (for d and m see below Equation 1).

For *interface-controlled growth*, v_0 is a temperature-independent interface velocity and Q_G represents the interface energy barrier. For *volume diffusion controlled growth*, v_0 equals the pre-exponential factor for diffusion D_0 and Q_G represents the activation energy for diffusion, Q_D.

Isochronal annealing is characterized by $T(t) = T_0 + \Phi t$ with T_0 as the starting temperature of the

experiment and Φ as the constant heating rate (i.e., $\Phi = \mathrm{d}T/\mathrm{d}t$). For isochronal annealing, Equation 9a can then be given as,

$$Y = g\left[\int_{T(\tau)}^{T(t)} \frac{1}{\Phi}\nu\,\mathrm{d}T\right]^{\frac{\mathrm{d}}{\mathrm{m}}} \qquad (9b)$$

The number of supercritical nuclei formed in a unit volume, at time τ during a time lapse $\mathrm{d}\tau$, is given by $\dot{N}(T(\tau))\,\mathrm{d}\tau$ according to Equations 5–8. The volume of each of these nuclei grows from τ until t according to Equation 9 where it is supposed that every particle grows into an infinitely large parent phase, in absence of the other growing particles. In this hypothetical case, the volume of all particles at time t, called *the extended volume*, is given by,

$$V^{\mathrm{e}} = \int_0^t V\dot{N}(T(\tau))Y(T(t))\,\mathrm{d}\tau \qquad (10)$$

with V as the sample volume, which is supposed to be constant throughout the transformation.

In reality, the particles do not grow individually into an infinitely large parent phase: V^{e} does not account for the overlap of particles (hard impingement) and their possible surrounding diffusion fields (soft impingement). It is supposed here that the nuclei are dispersed randomly throughout the total 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 $\mathrm{d}V^{\mathrm{e}}$ and $\mathrm{d}V^{\mathrm{t}}$. From the change of the extended volume $\mathrm{d}V^e$, only a part will contribute to the change of the actually transformed volume $\mathrm{d}V^{\mathrm{t}}$, namely a part as large as the untransformed volume fraction [1–3, 6]. Hence,

$$\mathrm{d}V^{\mathrm{t}} = \left(\frac{V-V^t}{V}\right)\mathrm{d}V^{\mathrm{e}} \qquad (11)$$

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

$$f = V^{\mathrm{t}}/V = 1 - \exp\left(-\frac{V^{\mathrm{e}}}{V}\right) \qquad (12)$$

For other impingement models, see [7, 8].

3. Analytical models for transformation involving interface-controlled growth

The strategy adopted in the sequel can be described as follows. It is strived for to arrive in all cases considered at an analytical formulation for the degree of transformation that can be given a structure like the JMA equation [1–6]:

$$f = 1 - \exp\left(-K_0^{\mathrm{n}}\exp\left(-\frac{nQ}{RT}\right)\alpha^{\mathrm{n}}\right) \qquad (13)$$

where α is a function of time and/or temperature, yet to be specified. However, unlike the extreme cases for which the JMA equation holds strictly, in general n, Q, and K_0 will then be time or temperature dependent. Corresponding, analytical formulae for n, Q, and K_0 will be obtained here after an appropriate (re)formulation of the extended volume has been carried out.

3.1. Isothermal transformation: mixed nucleation and interface-controlled growth

The extended volume, for the case of isothermal transformation subject to mixed nucleation and interface-controlled growth, can be described as (see Equations 7, 9a, and 10):

$$V^e = V\int_0^t \left(N_1^*\delta(\tau-0) + N_{01}\exp\left(-\frac{Q_{\mathrm{N}}}{RT}\right)\right)g$$
$$\times \left(\int_\tau^t \nu_0\exp\left(-\frac{Q_{\mathrm{G}}}{RT}\right)\mathrm{d}t\right)^{\frac{\mathrm{d}}{\mathrm{m}}}\mathrm{d}\tau \qquad (14)$$

where N_1^* and N_{01} represent the relative contributions of the two modes of nucleation considered. Integration of the Dirac function can be expressed as $\int f(x)\delta(x-a)\,\mathrm{d}x = f(a)$ for an arbitrary function $f(x)$, and thus Equation 14 can be rewritten as:

$$V^e = VN_1^*gv_0^{\frac{\mathrm{d}}{\mathrm{m}}}\exp\left(-\frac{\frac{d}{m}Q_{\mathrm{G}}}{RT}\right)t^{\frac{\mathrm{d}}{\mathrm{m}}}$$
$$+ \left(\frac{1}{\frac{d}{m}} + 1\right)VN_{01}gv_0^{\frac{\mathrm{d}}{\mathrm{m}}}$$
$$\times \exp\left(-\frac{\frac{d}{m}Q_{\mathrm{G}} + Q_{\mathrm{N}}}{RT}\right)t^{\frac{\mathrm{d}}{\mathrm{m}}+1} \qquad (15)$$

Hence, the overall extended volume is composed of two parts: $V_{\mathrm{s}}^{\mathrm{e}}$ due to pure site saturation and $V_{\mathrm{c}}^{\mathrm{e}}$ due to pure continuous nucleation, such that

$$V_{\mathrm{s}}^{\mathrm{e}} = VN_1^*gv_0^{\frac{\mathrm{d}}{\mathrm{m}}}\exp\left(-\frac{\frac{d}{m}Q_{\mathrm{G}}}{RT}\right)t^{\frac{\mathrm{d}}{\mathrm{m}}} \qquad (16a)$$

$$V_{\mathrm{c}}^{\mathrm{e}} = \left(\frac{1}{\frac{d}{m}+1}\right)VN_{01}gv_0^{\frac{\mathrm{d}}{\mathrm{m}}}\exp\left(-\frac{\frac{d}{m}Q_{\mathrm{G}} + Q_{\mathrm{N}}}{RT}\right)t^{\frac{\mathrm{d}}{\mathrm{m}}+1}$$
$$(16b)$$

The ratio of $V_{\mathrm{c}}^{\mathrm{e}}$ and $V_{\mathrm{s}}^{\mathrm{e}}$ is given by,

$$\frac{V_{\mathrm{c}}^{\mathrm{e}}}{V_{\mathrm{s}}^{\mathrm{e}}} = \frac{\left(1/\left(\frac{d}{m}+1\right)\right) + 1N_{01}t\exp\left(-\frac{Q_{\mathrm{N}}}{RT}\right)}{N_1^*} = \frac{r_2}{r_1} \qquad (17)$$

Now, in order to arrive at explicit, analytical expressions for the growth exponent n, the effective activation energy Q, and the rate constant K_0, the extended volume is reformulated proceeding as follows. For the values N_1^* and N_{01} in Equations 16a and b, different values N_2^* and N_{02} can be chosen in such a way that V^{e} is due

to only site saturation

$$V_{s'}^e = V N_2^* g v_0^{\frac{d}{m}} \exp\left(-\frac{\frac{d}{m}Q_G}{RT}\right) t^{\frac{d}{m}} \qquad (18a)$$

or that V^e is due to only continuous nucleation

$$V_{c'}^e = \left(\frac{1}{\frac{d}{m}+1}\right) V N_{02} g v_0^{\frac{d}{m}} \exp\left(-\frac{\frac{d}{m}Q_G + Q_N}{RT}\right) t^{\frac{d}{m}+1}$$

$$(18b)$$

with $V_{s'}^e = V_{c'}^e = V^e$. Then, the total extended volume can be written as

$$V^e = \frac{1}{r_1 + r_2}\left(r_1 V_{s'}^e + r_2 V_{c'}^e\right) \qquad (19)$$

and

$$N_2^* = N_1^*\left(1 + \frac{r_2}{r_1}\right) \quad \text{and} \quad N_{02} = N_{01}\left(1 + \left(\frac{r_2}{r_1}\right)^{-1}\right)$$

$$(20)$$

For any set of V_s^e and V_c^e describing a phase transformation (c.f., Equation 16) both V_s^e and V_c^e are positive and smaller than V^e. Always two integers r_1 and r_2 can be found to satisfy $\frac{V_c^e}{V_s^e} = \frac{r_2}{r_1}$ (c.f., Equation 17) with $r_1 + r_2 = 10^k$, $k = 1, 2, \ldots$. Further, for integers r_1 and r_2, it holds that $r_1 V_{s'}^e = \sum_{i=1}^{r_1} V_s^e(i)$ if $V_s^e(1) = V_s^e(2) = \cdots = V_s^e(r_1) = V_{s'}^e$; and that $r_2 V_{c'}^e = \sum_{i=1}^{r_2} V_c^e(i)$ if $V_c^e(1) = V_c^e(2) = \cdots = V_c^e(r_2) = V_{c'}^e$. Then, taking both $V_s^e(i)$ and $V_c^e(i)$ equal to V^e, Equation 19 can be rewritten as,

$$V^e = \frac{1}{r_1 + r_2}\left(\sum_{i=1}^{r_1} V_s^e(i) + \sum_{i=1}^{r_2} V_c^e(i)\right) \qquad (21)$$

Note that all volume terms in Equation 21 are equal. Substituting all $V_s^e(i)$ and $V_c^e(i)$ according to Equations 18a, b and 20, Equation 21 becomes,

$$V^e = \frac{V g v_0^{\frac{d}{m}}}{\left(\frac{d}{m}+1\right)^{\frac{1}{1+(r_2/r_1)^{-1}}}}\left[\left(N_1^*\left(1 + \frac{r_2}{r_1}\right)\right)^{\frac{1}{1+r_2/r_1}}\right.$$

$$\times \left(N_{01}\left(1 + \left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+(r_2/r_1)^{-1}}}\left.\right]$$

$$\times \exp\left(-\frac{\frac{d}{m}Q_G + \frac{1}{1+(r_2/r_1)^{-1}}Q_N}{RT}\right) t^{\left(\frac{d}{m}\right) + \frac{1}{1+(r_2/r_1)^{-1}}}$$

$$(22)$$

Now, Equation 12, after substitution of Equation 22, can be rewritten as,

$$\ln(-\ln(1-f))$$

$$= \ln\left[\frac{g v_0^{\frac{d}{m}}}{\left(\frac{d}{m}+1\right)^{\frac{1}{1+(r_2/r_1)^{-1}}}}\left(N_1^*\left(1 + \frac{r_2}{r_1}\right)\right)^{\frac{1}{1+r_2/r_1}}\right.$$

$$\left.\left(N_{01}\left(1 + \left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+(r_2/r_1)^{-1}}}\right]$$

$$- \left(\frac{\frac{d}{m}Q_G + \frac{1}{1+(r_2/r_1)^{-1}}Q_N}{RT}\right)$$

$$+ \left(\frac{d}{m} + \frac{1}{1 + \left(\frac{r_2}{r_1}\right)^{-1}}\right)\ln t \qquad (23)$$

where, r_2/r_1 depends on the transformation time, t (cf., Equation 17). This result can be compared with the correspondingly rewritten Equation 13,

$$\ln(-\ln(1-f)) = n \ln(K_0) - \frac{nQ}{RT} + n \ln\alpha \qquad (24)$$

By comparing Equations 24 and 23 time dependent expressions for n, Q, and K_0^n result, which have been gathered in Table I. Apparently, in this case of isothermal annealing, α can be identified with the annealing time t.

It is concluded that the degree of transformation in this case of isothermal annealing can be represented by

$$f = 1 - \exp\left(K_0(t)^{n(t)} \exp\left(-\frac{n(t)Q(t)}{RT}\right)t^{n(t)}\right) \quad (25)$$

where the kinetic parameters, n, Q, and K_0^n are time dependent. Only if pure site saturation or pure continuous nucleation prevails, Equation 25 reduces to the classical JMA equation with constant values for n, Q, and K_0^n.

3.2. Isochronal transformation: mixed nucleation and interface-controlled growth

In isochronal annealing with a constant heating rate, Φ, the nucleation rate at $t = \tau$ can be written as (c.f., Equation 7)

$$\dot{N}(T(\tau)) = N_1^* \delta\left(\frac{T(\tau) - T_0}{\Phi}\right) + N_{01} \exp\left(-\frac{Q_G}{RT(\tau)}\right)$$

$$(26)$$

where, $T_0 = T(t = 0)$ and $T(\tau) = T_0 + \Phi\tau$ with $\Phi = dT(\tau)/d\tau = dT(t)/dt$; (c.f., Equation 9b). Using Equations 26, 9b and 10, the extended volume at time t can then be written as,

$$V^e = V\left[\int_{T_0}^{T(t)}\left(N_1^* \delta\left(\frac{T(\tau) - T_0}{\Phi}\right)\right.\right.$$

$$+ N_{01} \exp\left(-\frac{Q_N}{RT(\tau)}\right)\right)g$$

$$\times \left.\left(\int_{T(\tau)}^{T(t)} v_0 \exp\left(-\frac{Q_G}{RT(t)}\right)d\frac{T(t)}{\Phi}\right)^{\frac{d}{m}} d\frac{T(\tau)}{\Phi}\right]$$

$$(27)$$

In principle, the following treatment is analogous to that given for isothermal transformation in Section 3.1. However, the integrals in Equation 27 cannot be evaluated analytically in general. The integral

TABLE I Expressions for the growth exponent, n, the overall activation energy, Q, and the rate constant, K_0, to be inserted in Equations 25 and 36 for isothermal annealing and isochronal annealing, respectively. Results are given for mixed nucleation (site saturation and continuous nucleation) and Avrami nucleation. For C_c, $f(\lambda t)$ and $f(\lambda \frac{RT^2}{Q_N \Phi})$, see Tables II–IV

	Isothermal	Isochronal
Mixed nuc		
n	$\frac{d}{m} + \dfrac{1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}$	$\frac{d}{m} + \dfrac{1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}$
Q	$\dfrac{\frac{d}{m}Q_G + \left(n - \frac{d}{m}\right)Q_N}{n}$	$\dfrac{\frac{d}{m}Q_G + \left(n - \frac{d}{m}\right)Q_N}{n}$
K_0^n	$\dfrac{gv_0^{\frac{d}{m}}}{4\left(\frac{d}{m}+1\right)^{\frac{1}{1+(r_2/r_1)^{-1}}}} \left[\begin{array}{c} \left(N_1^*\left(1+\frac{r_2}{r_1}\right)\right)^{\frac{1}{1+r_2/r_1}} \\ \left(N_{01}\left(1+\left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+(r_2/r_1)^{-1}}} \end{array} \right]$	$\dfrac{gv_0^{\frac{d}{m}}}{\left(\frac{d}{m}+1\right)^{\frac{1}{1+(r_2/r_1)^{-1}}}} \left[\begin{array}{c} \left(\frac{N_1^*}{(Q_G)^{\frac{d}{m}}}\left(1+\frac{r_2}{r_1}\right)\right)^{\frac{1}{1+r_2/r_1}} \\ \left(C_c N_{01}\left(1+\left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+(r_2/r_1)^{-1}}} \end{array} \right]$
$\frac{r_2}{r_1}$	$\dfrac{\left(1/\left(\frac{d}{m}+1\right)\right)N_{01}\exp\left(-\frac{Q_N}{RT}\right)t}{N_1^*}$	$\dfrac{C_c Q_G^{\frac{d}{m}} N_{01}\exp\left(-\frac{Q_N}{RT}\right)}{\left(\frac{d}{m}+1\right)N_1^*}\left(\frac{RT^2}{\Phi}\right)$
Avrami		
n	$n = \frac{d}{m} + \dfrac{1}{1+\left(\frac{r_2}{r_1}\right)}$	$n = \frac{d}{m} + \dfrac{1}{1+\left(\frac{r_2}{r_1}\right)}$
Q	$\dfrac{\frac{d}{m}Q_G + \left(n - \frac{d}{m}\right)Q_N}{n}$	$\dfrac{\frac{d}{m}Q_G + \left(n - \frac{d}{m}\right)Q_N}{n}$
K_0^n	$\dfrac{gN'f(\lambda t)v_0^{\frac{d}{m}}}{\left(\frac{d}{m}+1\right)}(\lambda_0)^{\frac{1}{1+r_2/r_1}}(\lambda t)^{\frac{1}{1+(r_2/r_1)^{-1}}}$	$\left[\dfrac{gv_0^{\frac{d}{m}}N'f\left(\lambda\frac{RT^2}{Q_N\Phi}\right)}{\frac{d}{m}+1}(\lambda_0)^{\frac{1}{1+r_2/r_1}}\left(\lambda\frac{RT^2}{\Phi}\right)^{\frac{1}{1+(r_2/r_1)^{-1}}}C_c\right]$
$\frac{r_2}{r_1}$	$\dfrac{\lambda t}{\frac{d}{m}+1}$	$\dfrac{C_c Q_G^{\frac{d}{m}}}{\frac{d}{m}+1}\left(\frac{RT^2}{\Phi}\lambda\right)$

Note: v_0 and Q_G have to be substituted by D_0 and Q_D in case of volume diffusion controlled growth.

$\int_{T(\tau)}^{T(t)}\exp(-\frac{Q_G}{RT})\,dT$ in Equation 27 is called temperature integral and can be rewritten as [7]:

$$\int_{T(\tau)}^{T(t)}\exp\left(-\frac{Q_G}{RT}\right)dT = \left[\int_0^{T(t)}\exp\left(-\frac{Q_G}{RT}\right)dT\right.$$
$$\left. - \int_0^{T(\tau)}\exp\left(-\frac{Q_G}{RT}\right)dT\right]$$
$$= T(t)\left[\int_1^\infty \frac{\exp\left(-\frac{Q_G}{RT}z\right)}{z^2}\,dz\right]$$
$$- T(\tau)\left[\int_1^\infty \frac{\exp\left(-\frac{Q_G}{RT(\tau)}z\right)}{z^2}\,dz\right] \quad (28)$$

by using the substitutions $z = T(t)/T$ and $z = T(\tau)/T$ [7], respectively. Thus an analytical approximation of the integrals becomes possible, using a series expansion of the type [7, 14],

$$T\left[\int_1^\infty \frac{\exp\left(-\frac{Q_G}{RT}z\right)}{z^2}\,dz\right]$$
$$= \frac{RT^2}{Q_G}\exp\left(-\frac{Q_G}{RT}\right)\left(1 - 2\frac{RT}{Q_G} + \cdots\right) \quad (29)$$

Recognizing that in an alternating series the absolute error upon series truncation is less than the absolute value of the first term neglected and that in most transformation reactions $\frac{Q_G}{RT} \gg 1$ (usually $\frac{Q_G}{RT} \geq 25$), it is possible to use only the first term of the series expansion in Equation 29 without making an appreciable error. Hence, upon applying twice the series expansion

discussed, Equation 28 becomes

$$\int_{T(\tau)}^{T(t)}\exp\left(-\frac{Q_G}{RT}\right)dT = \frac{R}{Q_G}\left[T(t)^2\exp\left(-\frac{Q_G}{RT}\right)\right.$$
$$\left. - T(\tau)^2\exp\left(-\frac{Q_G}{RT(\tau)}\right)\right] \quad (30)$$

Using Equation 30, Equation 27 can be given as

$$V^e = Vgv_0^{\frac{d}{m}}\int_{T_0}^{T(t)}\left(\frac{1}{\Phi^{\frac{d}{m}}}N_1^*\delta(T(\tau) - T_0)\right.$$
$$\left. + \frac{1}{\Phi^{\frac{d}{m}+1}}N_{01}\exp\left(-\frac{Q_N}{RT(\tau)}\right)\right)$$
$$\times\left(\frac{R}{Q_G}\left(T(t)^2\exp\left(-\frac{Q_G}{RT}\right)\right.\right.$$
$$\left.\left. - T(\tau)^2\exp\left(-\frac{Q_G}{RT(\tau)}\right)\right)\right)^{\frac{d}{m}}dT(\tau) \quad (31)$$

Applying the result of the Dirac function, $\int f(T(\tau))\delta(T(\tau) - T_0)dT(\tau) = f(T_0)$, using again the approximation for the temperature integral as in Equation 30 and recognizing that $T > T_0$ the analytical solution for V^e can be given as (see Appendix A)

$$V^e = Vgv_0^{\frac{d}{m}}N_1^*\left(\frac{1}{Q_G}\right)^{\frac{d}{m}}\exp\left(-\frac{\frac{d}{m}Q_G}{RT}\right)\left(\frac{RT^2}{\Phi}\right)^{\frac{d}{m}}$$
$$+ \frac{1}{\frac{d}{m}+1}Vgv_0^{\frac{d}{m}}N_{01}C_c\exp\left(-\frac{\frac{d}{m}Q_G + Q_N}{RT}\right)$$
$$\times\left(\frac{RT^2}{\Phi}\right)^{\frac{d}{m}+1} \quad (32)$$

TABLE II Expressions for the correction factor, C_c, (c.f., Table I)

	$\frac{d}{m}$	C_c
Interface-controlled growth	1	$\frac{2}{Q_N(Q_N+Q_G)}$
	2	$\frac{6}{Q_N(Q_N+Q_G)(Q_N+2Q_G)}$
	3	$\frac{24}{Q_N(Q_N+Q_G)(Q_N+2Q_G)(Q_N+3Q_G)}$
Diffusion-controlled growth	1/2	$\left[\frac{Q_D}{2Q_N\left(Q_N+\frac{1}{2}Q_D\right)}\right]$
	1	$\left[\frac{2}{Q_N(Q_N+Q_D)}\right]$
	3/2	$\left[\frac{5}{2}\frac{Q_G^{\frac{1}{2}}(3Q_D+4Q_N)}{4Q_N\left(Q_N+\frac{1}{2}Q_D\right)(Q_N+Q_D)\left(Q_N+\frac{3}{2}Q_D\right)}\right]$

where $T = T(t)$ and C_c is a constant, defined by the activation energies of nucleation and growth (see Table II).

Again, as in the isothermal case, the extended volume consists of two parts: V_s^e due to pure site saturation and V_c^e due to pure continuous nucleation (c.f., Equation 16). Now the ratio of V_s^e and V_c^e is given by,

$$\frac{V_c^e}{V_s^e} = \frac{C_c Q_G^{\frac{d}{m}} N_{01}\exp\left(-\frac{Q_N}{RT}\right)}{\left(\frac{d}{m}+1\right)N_1^*}\left(\frac{RT^2}{\Phi}\right) = \frac{r_2}{r_1} \quad (33)$$

Next, a treatment as performed between Equations 17 and 22 can be applied to rewrite V^e in a similar way. The result is:

$$V^e = \frac{Vgv_0^{\frac{d}{m}}}{\left(\frac{d}{m}+1\right)^{\frac{1}{1+(r_2/r_1)^{-1}}}}\left[\left(\frac{N_1^*}{(Q_G)^{\frac{d}{m}}}\left(1+\frac{r_2}{r_1}\right)\right)^{\frac{1}{1+r_2/r_1}}\right.$$
$$\times\left(C_c N_{01}\left(1+\left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+(r_2/r_1)^{-1}}}\right]$$
$$\times\left[\exp\left(-\frac{\frac{d}{m}Q_G+\frac{1}{1+(r_2/r_1)^{-1}}Q_N}{RT}\right)\right.$$
$$\times\left(\frac{RT^2}{\Phi}\right)^{\left(\frac{d}{m}+\frac{1}{1+(r_2/r_1)^{-1}}\right)}\right] \quad (34)$$

After substitution of Equation 34, Equation 12 can be rewritten as:

$$\ln\left(-\ln\left(1-f\right)\right)$$
$$= \ln\left[\frac{gv_0^{\frac{d}{m}}}{\left(\frac{d}{m}+1\right)^{\frac{1}{1+(r_2/r_1)^{-1}}}}\left(\frac{N_1^*}{(Q_G)^{\frac{d}{m}}}\left(1+\frac{r_2}{r_1}\right)\right)^{\frac{1}{1+r_2/r_1}}\right.$$
$$\left.\left(C_c N_{01}\left(1+\left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+(r_2/r_1)^{-1}}}\right]$$
$$-\left(\frac{\frac{d}{m}Q_G+\frac{1}{1+(r_2/r_1)^{-1}}Q_N}{RT}\right)$$
$$+\left(\frac{d}{m}+\frac{1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}\right)\ln\left(\frac{RT^2}{\Phi}\right) \quad (35)$$

This result can be compared with the correspondingly rewritten Equation 13, i.e., Equation 24. By comparing Equations 35 and 24, temperature dependent values of n, Q and K_0^n result, which have been gathered in Table I. Apparently, in the case of isochronal annealing, α can be identified with $\frac{RT^2}{\Phi}$.

It is concluded that the degree of transformation in this case of isochronal annealing can be represented by,

$$f = 1 - \exp\left(K_0(T)^{n(T)}\exp\left(-\frac{n(T)Q(T)}{RT}\right)\right.$$
$$\times\left(\frac{RT^2}{\Phi}\right)^{n(T)}\right) \quad (36)$$

where the kinetic parameters, n, Q and K_0 are temperature dependent. It should be noted that Equation 36 does not hold for transformations upon cooling because of the approximation used for the temperature integral in Equation 32 (see Appendix A).

3.3. Isothermal transformation: Avrami nucleation and interface-controlled growth

Using Equations 8b and 9a, the extended volume can then be given as (c.f., Equation 10):

$$V^e = V\int_0^t gN'\lambda\exp\left(-\lambda\tau\right)$$
$$\times\left(\int_\tau^t v_0\exp\left(-\frac{Q_G}{RT}\right)dt\right)^{\frac{d}{m}}d\tau$$
$$= VgN'v_0^{\frac{d}{m}}\exp\left(-\frac{\frac{d}{m}Q_G}{RT}\right)$$
$$\times\int_0^t \lambda\exp\left(-\lambda\tau\right)(t-\tau)^{\frac{d}{m}}d\tau \quad (37)$$

During isothermal annealing, λ is a constant, so analytical integration of Equation 37 is possible. It is obtained (c.f., Appendix B),

$$V^e = VgN'v_0^{\frac{d}{m}}\exp\left(-\frac{\frac{d}{m}Q_G}{RT}\right)t^{\frac{d}{m}}\left(\frac{\lambda t}{\frac{d}{m}+1}\right)f(\lambda t)$$
$$= V_s^e\left(\frac{\lambda t}{\frac{d}{m}+1}\right)f(\lambda t) \quad (38)$$

where V_s^e is defined according to Equation 16a. Expressions for $f(\lambda t)$ for different $\frac{d}{m}$ ratios have been gathered in Table III. By rewriting Equation 38, an alternative formulation is possible,

$$V^e = \frac{1}{\frac{d}{m}+1}VgN'\lambda_0 v_0^{\frac{d}{m}}\exp\left(-\frac{\frac{d}{m}Q_G+Q_N}{RT}\right)t^{\frac{d}{m}+1}f(\lambda t)$$
$$= V_c^e f(\lambda t) \quad (39)$$

TABLE III Expressions for $f(\lambda t)$, (c.f., Table I)

	$\frac{d}{m}$	$f(\lambda t)$
Interface-controlled growth	1	$\left(\frac{2\exp(-\lambda t)+2\lambda t-2}{(\lambda t)^2}\right)$
	2	$\left(\frac{6+3(\lambda t)^2-6\exp(-\lambda t)-6\lambda t}{(\lambda t)^3}\right)$
	3	$\left(\frac{4(\lambda t)^3+24\exp(-\lambda t)-12(\lambda t)^2+24\lambda t-24}{(\lambda t)^4}\right)$
Diffusion-controlled growth	1/2	$\left(\frac{1+\lambda t-\exp(-\lambda t)}{2\lambda t}+\frac{2\exp(-\lambda t)+2\lambda t-(\lambda t)^2-2}{2(\lambda t)^2}\right)$
	1	$\left(\frac{2\exp(-\lambda t)+2\lambda t-2}{(\lambda t)^2}\right)$
	3/2	$\left(\frac{6-6\exp(-\lambda t)+3(\lambda t)^2+(\lambda t)^3-6\lambda t}{2(\lambda t)^3}\right.$ $\left.+\frac{2\exp(-\lambda t)+2\lambda t-(\lambda t)^2-2}{2(\lambda t)^2}\right)$

where V_c^e is defined according to Equation 16b. Thus, V^e can be described as,

$$V^e = \frac{1}{2}\left(V_s^e\left(\frac{\lambda t}{\frac{d}{m}+1}\right)f(\lambda t)+V_c^e f(\lambda t)\right) \quad (40)$$

The ratio of V_s^e and V_c^e is now given by,

$$\frac{V_c^e}{V_s^e}=\frac{\lambda t}{\frac{d}{m}+1}=\frac{r_2}{r_1} \quad (41)$$

Next, a treatment as performed between Equations 17 and 22 can be applied, to rewrite V^e in a similar way (see also Appendix B). The result is,

$$V^e = V\frac{gN'}{\left(\frac{d}{m}+1\right)}v_0^{\frac{d}{m}}(\lambda_0 f(\lambda t))^{\frac{1}{1+r_2/r_1}}(\lambda t f(\lambda t))^{\frac{1}{1+(r_2/r_1)^{-1}}}$$
$$\times\exp\left(-\frac{\frac{d}{m}Q_G+\frac{1}{1+(r_2/r_1)}Q_N}{RT}\right)t^{(\frac{d}{m})+\frac{1}{1+(r_2/r_1)}} \quad (42)$$

Combining Equations 42 and 12, it is concluded that the degree of transformation can be represented with analytical expressions for the time dependent kinetic parameters, n, Q and K_0^n, as gathered in Table I. Again (c.f., Section 3.1), α can be identified by t.

3.4. Isochronal transformation: Avrami nucleation and interface-controlled growth

Using Equations 8a and 9b with the the definitions for T_0 and Φ given below Equation 26, the extended volume can then be given as (c.f., Equation 10):

$$V^e = V\int_0^t gN'\lambda\exp\left(-\int_0^\tau \lambda dt\right)$$
$$\times\left(\int_{T(\tau)}^{T(t)}\frac{v}{\Phi}dT(t)\right)^{\frac{d}{m}}d\tau$$
$$= V\int_{T_0}^{T(t)}\frac{N'gv_0^{\frac{d}{m}}}{\Phi^{\frac{d}{m}+1}}\lambda$$
$$\times\exp\left(-\int_{T_0}^{T(\tau)}\lambda_0\exp\left(-\frac{Q_N}{RT(t)}\right)d\frac{T(t)}{\Phi}\right)$$

$$\times\left(\int_{T(\tau)}^{T(t)}\exp\left(-\frac{Q_G}{RT}\right)dT(t)\right)^{\frac{d}{m}}dT(\tau)$$
$$= V\int_{T_0}^{T(t)}\frac{N'gv_0^{\frac{d}{m}}}{\Phi^{\frac{d}{m}+1}}\lambda\exp\left(-\frac{R\lambda}{Q_N\Phi}T(\tau)^2\right)$$
$$\times\left(\int_{T(\tau)}^{T(t)}\exp\left(-\frac{Q_G}{RT(t)}\right)dT(t)\right)^{\frac{d}{m}}dT(\tau) \quad (43)$$

where, for the last line of Equation 43 the same procedure as indicated by Equations 28–30 has been applied, and the term involving T_0 is deleted (see Appendix A). Adopting in the following the same procedures as indicated by Equations 28–32 and by Equations 38–40 and using a series expansion for the first exponential function in Equation 43, Equation 43 can be written as (see Appendix C),

$$V^e = V\int_{T_0}^T\frac{N'gv_0^{\frac{d}{m}}}{\Phi^{\frac{d}{m}+1}}\lambda\left[1-T(\tau)^2\frac{R\lambda}{Q_N\Phi}\right.$$
$$+\frac{1}{2!}\left(T(\tau)^2\frac{R\lambda}{Q_N\Phi}\right)^2+\cdots$$
$$\left.+(-1)^n\frac{1}{n!}\left(T(\tau)^2\frac{R\lambda}{Q_N\Phi}\right)^n\right]$$
$$\times\left[\frac{R}{Q_G}\left(T^2\exp\left(-\frac{Q_G}{RT}\right)\right.\right.$$
$$\left.\left.-T(\tau)^2\exp\left(-\frac{Q_G}{RT(\tau)}\right)\right)\right]^{\frac{d}{m}}dT(\tau)$$
$$= \frac{1}{2}\left(V_s^e\frac{C_cQ_G^{\frac{d}{m}}}{\frac{d}{m}+1}\left(\frac{RT^2}{\Phi}\lambda\right)f\left(\lambda\frac{RT^2}{Q_N\Phi}\right)\right.$$
$$\left.+V_c^e f\left(\lambda\frac{RT^2}{Q_N\Phi}\right)\right) \quad (44)$$

It should be noted that Equation 44 does not hold for transformation on cooling, because of the approximation used for the temperature integral (see Appendix A). In this case, V_s^e and V_c^e, as incorporated in Equation 44, are given by,

$$V_s^e = VgN'v_0^{\frac{d}{m}}\left(\frac{1}{Q_G}\right)^{\frac{d}{m}}\exp\left(-\frac{\frac{d}{m}Q_G}{RT}\right)\left(\frac{RT^2}{\Phi}\right)^{\frac{d}{m}} \quad (45a)$$

$$V_c^e = \frac{1}{\frac{d}{m}+1}VgN'v_0^{\frac{d}{m}}\lambda_0 C_c$$
$$\times\exp\left(-\frac{Q_N+\frac{d}{m}Q_G}{RT}\right)\left(\frac{RT^2}{\Phi}\right)^{\frac{d}{m}+1} \quad (45b)$$

The ratio of the two extended volumes equals,

$$\frac{V_c^e}{V_s^e}=\frac{r_2}{r_1}=\frac{C_cQ_G^{\frac{d}{m}}}{\frac{d}{m}+1}\left(\frac{RT^2}{\Phi}\lambda\right) \quad (46)$$

TABLE IV Expressions for $f(\lambda \frac{RT^2}{Q_N\Phi})$, (c.f., Table I)

	$\frac{d}{m}$	$f\left(\lambda \frac{RT^2}{Q_N\Phi}\right)$
Interface-controlled growth	1	$\left[\left(1 + \sum_{n=1}^{n} (-1)^n \frac{1}{(n+1)!} \frac{Q_N + Q_G}{(n+1)Q_N + Q_G}\left(\lambda \frac{RT^2}{Q_N\Phi}\right)^n\right)\right]$
	2	$\left[\left(1 + \sum_{n=1}^{n} (-1)^n \frac{1}{(n+1)!} \frac{(Q_N + Q_G)(Q_N + 2Q_G)}{((n+1)Q_N + Q_G)((n+1)Q_N + 2Q_G)}\left(\lambda \frac{RT^2}{Q_N\Phi}\right)^n\right)\right]$
	3	$\left[\left(1 + \sum_{n=1}^{n} (-1)^n \frac{1}{(n+1)!} \frac{(Q_N + Q_G)(Q_N + 2Q_G)(Q_N + 3Q_G)}{((n+1)Q_N + Q_G)((n+1)Q_N + 2Q_G)((n+1)Q_N + 3Q_G)}\left(\lambda \frac{RT^2}{Q_N\Phi}\right)^n\right)\right]$
Diffusion-controlled growth	1/2	$\left[\left(1 + \sum_{n=1}^{n} (-1)^n \frac{1}{(n+1)!} \frac{\left(Q_N + \frac{1}{2}Q_D\right)}{\left((n+1)Q_N + \frac{1}{2}Q_D\right)}\left(\lambda \frac{RT^2}{Q_N\Phi}\right)^n\right)\right]$
	1	$\left[\left(1 + \sum_{n=1}^{n} (-1)^n \frac{1}{(n+1)!} \frac{\left(Q_N + \frac{1}{2}Q_D\right)(Q_N + Q_G)}{\left((n+1)Q_N + \frac{1}{2}Q_D\right)((n+1)Q_N + Q_G)}\left(\lambda \frac{RT^2}{Q_N\Phi}\right)^n\right)\right]$
	3/2	$\left[\left(1 + \sum_{n=1}^{n} (-1)^n \frac{1}{(n+1)!} \frac{\left(Q_N + \frac{1}{2}Q_D\right)(Q_N + Q_D)\left(Q_N + \frac{3}{2}Q_D\right)}{\left((n+1)Q_N + \frac{1}{2}Q_D\right)((n+1)Q_N + Q_D)\left((n+1)Q_N + \frac{3}{2}Q_D\right)}\left(\lambda \frac{RT^2}{Q_N\Phi}\right)^n\right)\right]$

The expressions for C_c and $f(\lambda \frac{RT^2}{Q_N\Phi})$ have been gathered in Tables II and IV. Next, a treatment as performed between Equations 17 and 22 can be applied, to rewrite V^e in a similar way. The result is

$$V^e = \left[\frac{Vgv_0^{\frac{d}{m}} N' f\left(\lambda \frac{RT^2}{Q_N\Phi}\right)}{\left(\lambda \frac{RT^2}{\Phi}\right)^{\frac{1}{1+(r_2/r_1)-1}}}(\lambda_0)^{\frac{1}{1+r_2/r_1}} C_c\right]$$

$$\times \exp\left(-\frac{\frac{d}{m}Q_G + \frac{1}{1+(r_2/r_1)}Q_N}{RT}\right)$$

$$\times \left(\frac{RT^2}{\Phi}\right)^{\left(\frac{d}{m} + \frac{1}{1+r_2/r_1}\right)} \tag{47}$$

Combining Equations 47 and 12, it is concluded that the degree of transformation can be represented by Equation 36 with analytical expressions for the temperature dependent kinetic parameters, n, Q and K_0^n, as gathered in Table I. Again (c.f., Section 3.2), α can be identified with RT^2/Φ.

4. Analytical models for transformations involving volume diffusion-controlled growth

Detailed calculations analogous to those performed in Section 3 for transformations involving interface-controlled growth have been carried out for transformations involving volume diffusion controlled growth. The results demonstrate that no principal difference occurs between the kinetic parameters for these two growth modes, but different values occur for $\frac{d}{m}$ and different expressions result for $f(\lambda t)$ (isothermal annealing), $f(\lambda \frac{RT^2}{Q_N\Phi})$ (isochronal annealing), $\frac{r_2}{r_1}$ and C_c (see Tables I–IV). Furthermore, the pre-exponential factor, v_0 and the activation energy, Q_G for growth have to be substituted in the principal expressions presented for n, Q and K_0^n, in Table I by D_0 and Q_D, the pre-exponential factor and the activation energy for diffusion.

No matter which kind of the considered nucleation or growth mode prevails, the transformed fraction can always be described with Equation 25 for isothermal

TABLE V Values of the kinetic parameters used for the numerical calculations of isothermally and isochronally conducted phase transformations for the case of mixed nucleation or Avrami nucleation and interface controlled growth

Mixed nucleation		Avrami nucleation	
Q_G (kJ/mol)	200	Q_G (kJ/mol)	200
Q_N (kJ/mol)	100	Q_N (kJ/mol)	100
v_0 (s^{-1})	10^9	v_0 (s^{-1})	10^9
d/m	3	d/m	3
N_{01} (s^{-1} m^{-3})	5×10^{15}	N' (m^{-3})	10^{15}
N_1^* (m^{-3})	From 0 to 10^{12}	λ_0 (s^{-1})	From 10^4 to 10^8

transformation and with Equation 36 for isochronal transformation, and the relation between the effective activation energy, Q and the growth exponent, n, (Equation 1), can always be validated.

5. The analytical model

The general analytical model presented here allows identification of the individual roles of nucleation, growth and experimental parameters and explains variations in n and Q during progressing transformations.

5.1. Influences of nucleation model parameters and temperature on isothermal transformation behaviour

Using the analytical description (Equation 25) in combination with Tables I and III and values for the model parameters as given in Table V, results of df/dt vs. t and n vs. t for the case of isothermal transformation with mixed nucleation, have been calculated for a fixed temperature and for specific values of N_1^* and N_{01} (see Fig. 1a and b); the influence of the temperature is shown in Fig. 2a and b. The analogous results for the case of isothermal transformation involving Avrami nucleation have been calculated for different values of λ_0 (see Fig. 3a and b). The influence of N' is not given here because it is small as compared to the effect of variations in λ_0.

If $N_1^* = 0$ or $\lambda_0 \to 0$, continuous nucleation prevails, and the value of n is constant ($=4$) throughout the transformation (Figs 1 and 3). With increasing N_1^*

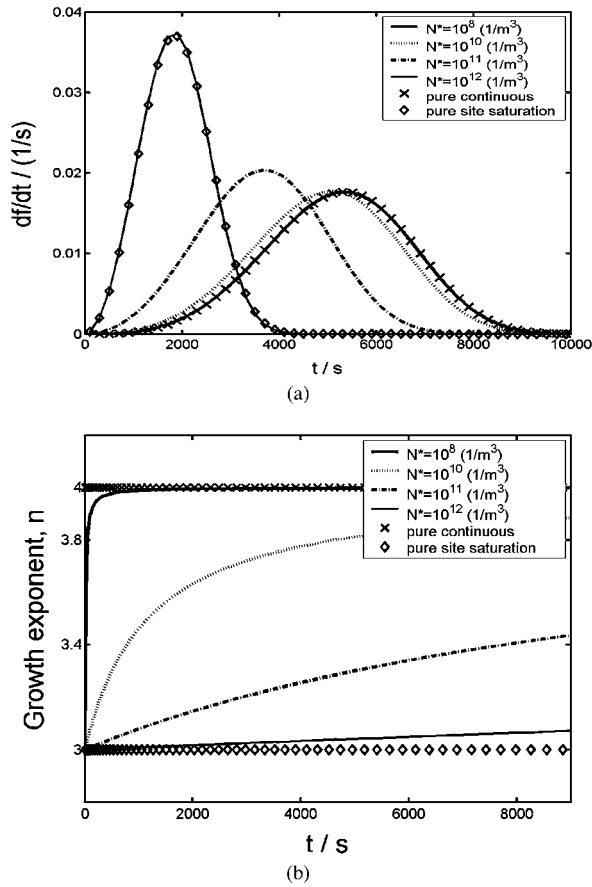(a)

(b)

Figure 1 The transformation rate df/dt (a), and the growth exponent n (b) as a function of time at 640 K, for mixed nucleation with $N_{01} = 5 \times 10^{15}$ (s^{-1} m^{-3}).

or λ_0, implying increasing importance of site saturation, the value of n decreases progressively, and depends distinctly on transformation time, t. If $N_{01} = 0$ or $\lambda \to \infty$, pure site saturation prevails and the value of n is constant (=3) throughout the transformation (Figs 1 and 3). Clearly, if extreme cases of nucleation do not occur, the assumption of a growth (Avrami) exponent that is constant during the transformation (as is often assumed in practice) is unjustified.

It is apparent from Fig. 2 that the transformation rate, df/dt, peak maximum, is very sensitive to T. If, for the case considered (c.f., Table V), T decreases from 680 to 620 K, the df/dt peak becomes very much broader, indicating that much more time is needed for the transformation. The variation of n during the transformation increases upon decreasing temperature, but this effect is relatively less propounced than the discussed effect on df/dt.

5.2. Influence of the heating rate on isochronal transformation behaviour

Obviously, the heating rate strongly influences the transformation rate as a function of temperature upon isochronal annealing (Fig. 4a). Upon isochronal annealing, the value of n (i) changes pronouncedly upon annealing and (ii) the variation of n upon annealing strongly depends on the heating rate (Fig. 4b). Only if extreme cases of nucleation occur, pure continuous nucleation or pure site saturation, the value of
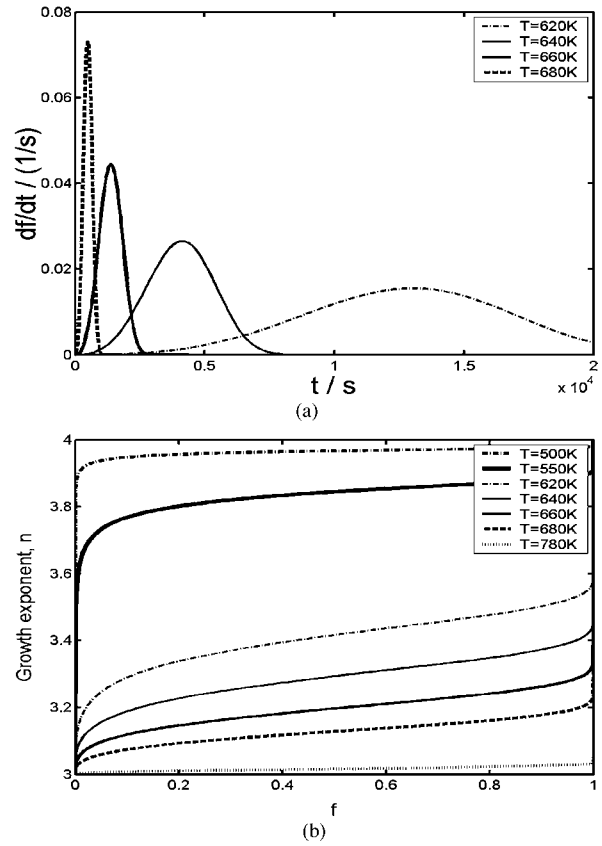

(a)

(b)

Figure 2 The transformation rate df/dt as a function of time (a), and the growth exponent n as a function of fraction transformed (b) for isothermal annealing at temperatures of 500, 550, 620 640, 660, 680, and 780 K, for mixed nucleation with $N_{01} = 5 \times 10^{15}$ (s^{-1} m^{-3}) and $N_1^* = 5 \times 10^{10}$ (m^{-3}). (Note that Fig. 2a exhibits the results of four intermediate temperatures).
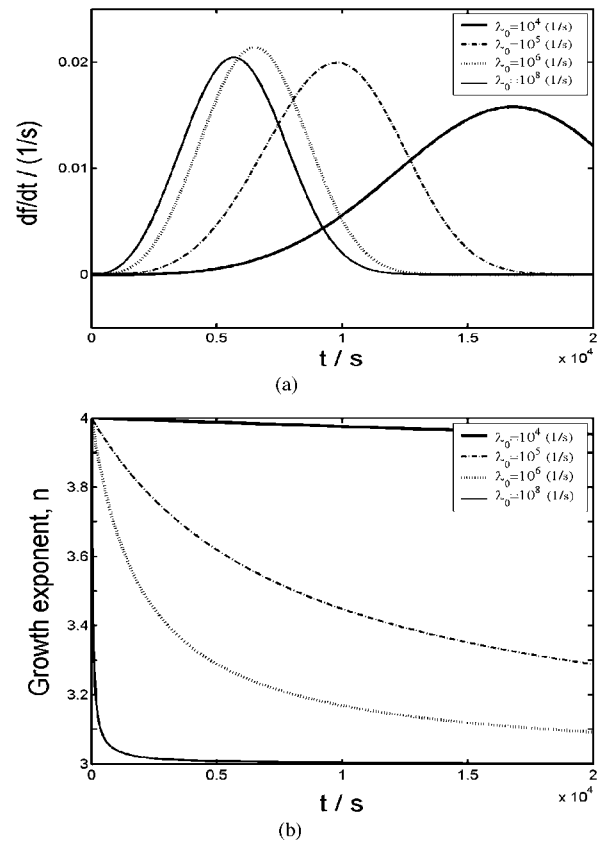

(a)

(b)

Figure 3 The transformation rate df/dt (a), and the growth exponent n (b) as a function of time at 580 K, for Avrami nucleation with $N' = 10^{15}$ (m^{-3}), and different values for λ_0 (s^{-1}).
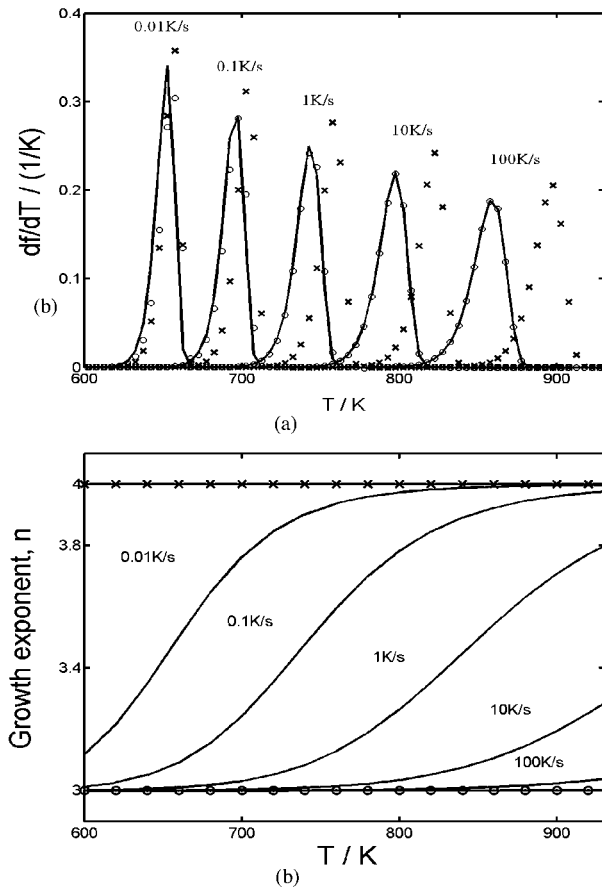
Figure 4 The transformation rate df/dt (a), and the growth exponent n (b) as a function of temperature, for isochronal annealing at heating rates: 0.01, 0.1, 1, 10, 100 K/s, (($\times$) with $N_{01} = 5 \times 10^{15}$ (s^{-1} m^{-3}) and $N_1^* = 0$ (m^{-3}) i.e., pure continuous nucleation; ($-$) with $N_{01} = 5 \times 10^{15}$ (s^{-1} m^{-3}) and $N_1^* = 10^{11}$ (m^{-3}) i.e., mixed nucleation; ($\circ$) with $N_{01} = 0$ (s^{-1} m^{-3}) and $N_1^* = 10^{12}$ (m^{-3}) i.e., pure site saturation).

n is independent of Φ, and is constant (4 or 3; see Fig. 4b).

5.3. Variation of the effective activation energy

The relation between the effective, overall activation energy, Q, and the separate activation energies for nucleation and growth, Q_N and Q_G (c.f., Equation 1) has been proposed in [8] on a numerical basis; the present paper has analytically validated Equation 1 for also not extreme, not limiting cases of transformation kinetics (Table I). Because Q_N and Q_G (or Q_D) are taken to be constant (see Equations 6–11), according to Equation 1 the effective activation energy, Q, therefore, depends on time and/or temperature through the growth exponent, n. Only if extreme, limiting kinetic conditions hold, Q is constant during the transformation. In practice, a genuine variation of Q with progressing transformation is often ignored until now and some average values for Q is determined upon fitting a kinetic model.

6. Applicability of the analytical model

The transformation rate can be numerically calculated exactly, as a function of time (isothermal annealing) or temperature (isochronal annealing), on the basis of Equation 12 by numerical integration of Equation 10

for V_e. This exact result can then be compared with corresponding results from the analytical approaches, Equations 25 and 36, respectively. Thereby the validity of approximations used in the analytical treatment (see Sections 3 and 4) is tested.

Using the values for the model parameters given in Table V the numerical calculation of the transformation rate has been performed for five different temperatures (isothermal annealing) and five different heating rates (isochronal annealing). Using the same values for the model parameters and the values of T or Φ chosen for the numerical calculation, the corresponding results of the (approximate) analytical relations for df/dt, or df/dT (see Equations 25 and 36) have been calculated as well. The results have been depicted in Fig. 5.

Alternatively, fitting of the analytical model to the exact numerical data provides a set of values for the model parameters (this resembles the procedure performed in practice [8]), which can then be compared with the exact values used in the numerical calculation. This fitting is performed by fitting Equations 25 and 36, using the appropriate analytical solutions for the kinetic parameters gathered in Tables I–IV, to, respectively, the isothermal anneals simultaneously (Fig. 5a and Equation 25) and the isochronal anneals simultaneously (Fig. 5b and Equation 36). The results are presented in Table VI. It follows from Fig. 5 and Table VI that the analytical results obtained in this work agree very well, i.e., in
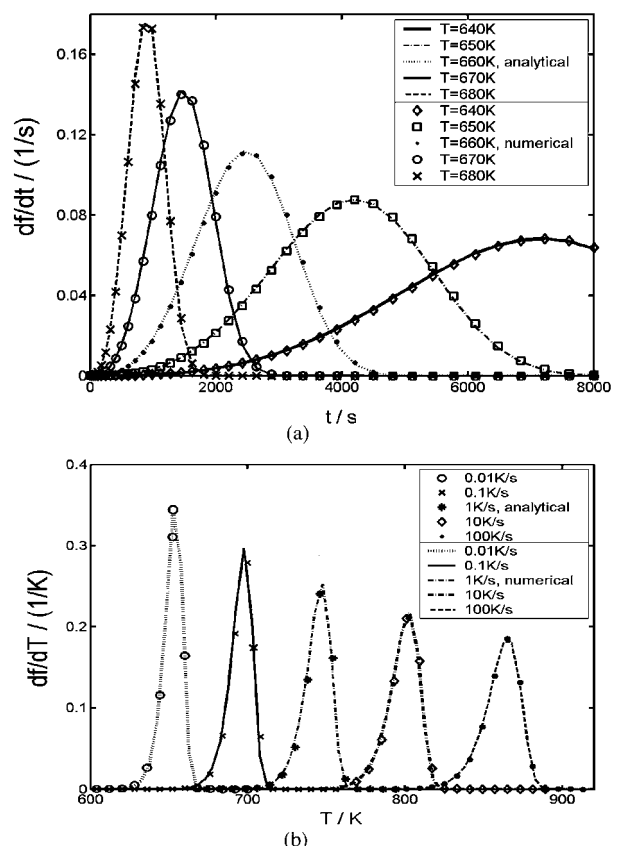

Figure 5 The transformation rate as a function of time at various temperatures (a) and as a function of temperature at various heating rates (b) calculated, exactly numerically and approximately analytically. The results shown in (a) pertain to mixed nucleation with $N_{01} = 5 \times 10^{15}$ (s^{-1} m^{-3}) and $N_1^* = 5 \times 10^{10}$ (m^{-3}); the results shown in (b) pertain to Avrami nucleation with $N' = 10^{15}$ (m^{-3}) and $\lambda_0 = 2 \times 10^6$ (s^{-1}).

	Q_N	Q_G	N_{01}	N_1^*	N'	λ_0
Isothermal transformation						
Mixed nucleation	100	200	5×10^{15}	5×10^{10}		
	100 ± 0.1	200 ± 0.1	From 2×10^{15} to 7×10^{15}	From 3×10^{10} to 7×10^{10}		
Avrami nucleation	100	200			10^{15}	2×10^6
	100 ± 1	200 ± 2			From 8×10^{14} to 4×10^{15}	From 10^6 to 5×10^6
Isochronal transformation						
Mixed nucleation	100	200	5×10^{15}	10^8		
	100 ± 1	200 ± 2	From 10^{15} to 8×10^{15}	From 5×10^7 to 3×10^8		
Avrami nucleation	100	200			10^{15}	10^8
	100 ± 3	200 ± 4			From 5×10^{14} to 5×10^{15}	From 5×10^7 to 5×10^8

any case within experimental accuracy, with the exact solutions.

7. Conclusions

The analytical model presented in this work provides a precise description of phase transformation kinetics during both isothermal and isochronal anneals, for cases where extreme kinetic conditions (site saturation or continuous nucleation) cannot be supposed. The proposed formulas have been derived in particular considering mixed nucleation (a mixture of site saturation and continuous nucleation), Avrami nucleation, interface-controlled growth and volume diffusion controlled growth. No matter which of these nucleation or growth modes determine the transformation mechanism, the degree of isothermal or isochronal transformation can be described adequately by combinations of the kinetics parameters, n, Q and K_0, according to Equations 25 and 36

$$f = 1 - \exp\left(K_0(t)^{n(t)} \exp\left(-\frac{n(t)Q(t)}{RT}\right)t^{n(t)}\right),$$
for isothermal anneals

$$f = 1 - \exp\left(K_0(T)^{n(T)} \exp\left(-\frac{n(T)Q(T)}{RT}\right)\right.$$
$$\left.\times\left(\frac{RT^2}{\Phi}\right)^{n(T)}\right), \quad \text{for isochronal anneals}$$

Analytical formulations for the time and temperature dependencies of the kinetic parameters can be given (Tables I–IV).

The effective, overall, time and temperature dependent activation energy can always be analytically interpreted as a combination of the constant activation energies for nucleation and growth, according to

$$Q = \frac{\frac{d}{m}Q_G + \left(n - \frac{d}{m}\right)Q_N}{n}$$

Therefore an observation of change of Q with time or temperature need **not** be considered as an experimental artifact or as a consequence of change of transformation mechanism.

Appendix A

Equation 31 can be described (with $T = T(t)$ and to avoid unnecessary, nonessential complications in the following formulas, $d/m = 1$) as

$$V^e = Vg\nu_0 \int_{T_0}^{T} \left(\frac{1}{\Phi}N_1^*\delta(T(\tau) - T_0) + \frac{1}{\Phi^2}N_{01}\exp\left(-\frac{Q_N}{RT(\tau)}\right)\right)$$

$$\times \left(\frac{R}{Q_G}\left(T^2\exp\left(-\frac{Q_G}{RT}\right) - T(\tau)^2\exp\left(-\frac{Q_G}{RT(\tau)}\right)\right)\right) dT(\tau)$$

$$= Vg\nu_0 \int_{T_0}^{T} \left(\frac{1}{\Phi}N_1^*\delta(T(\tau) - T_0)\right) \times \left(\frac{R}{Q_G}\left(T^2\exp\left(-\frac{Q_G}{RT}\right) - T(\tau)^2\exp\left(-\frac{Q_G}{RT(\tau)}\right)\right)\right) dT(\tau)$$

$$+ Vg\nu_0 \int_{T_0}^{T} \left(\frac{1}{\Phi^2}N_{01}\exp\left(-\frac{Q_N}{RT(\tau)}\right)\right) \times \left(\frac{R}{Q_G}\left(T^2\exp\left(-\frac{Q_G}{RT}\right) - T(\tau)^2\exp\left(-\frac{Q_G}{RT(\tau)}\right)\right)\right) dT(\tau)$$

$$= Vg\nu_0 N_1^*\left(\frac{R}{Q_G}\right)\left[\exp\left(-\frac{Q_G}{RT}\right)\frac{T^2}{\Phi} - \exp\left(-\frac{Q_G}{RT_0}\right)\frac{T_0^2}{\Phi}\right]$$

$$+ Vg\nu_0\frac{RT^2}{Q_G}\exp\left(-\frac{Q_G}{RT}\right)\int_{T_0}^{T} \left(\frac{1}{\Phi^2}N_{01}\exp\left(-\frac{Q_N}{RT(\tau)}\right)\right) dT(\tau)$$

$$- Vg\nu_0\frac{R}{Q_G}\int_{T_0}^{T} \left(\frac{T(\tau)^2}{\Phi^2}N_{01}\exp\left(-\frac{Q_N + Q_G}{RT(\tau)}\right)\right) dT(\tau) \tag{A-1}$$

Recognizing the exponential integral in Equation 28, the exponential terms in Equation A-1 can be described as,

$$
\int_{T_0}^{T} \left(\frac{1}{\Phi^2} N_{01} \exp\left(-\frac{Q_N}{RT(\tau)}\right) \right) dT(\tau)
$$

$$
= \frac{N_{01}}{\Phi^2} \left[\int_0^T \exp\left(-\frac{Q_G}{RT(\tau)}\right) dT(\tau) \right.
$$

$$
\left. - \int_0^{T_0} \exp\left(-\frac{Q_G}{RT(\tau)}\right) dT(\tau) \right]
$$

$$
= \frac{N_{01}}{\Phi^2} T \left[\int_1^\infty \frac{\exp\left(-\frac{Q_G}{RT}z\right)}{z^2} dz \right]
$$

$$
- \frac{N_{01}}{\Phi^2} T_0 \left[\int_1^\infty \frac{\exp\left(-\frac{Q_G}{RT_0}z\right)}{z^2} dz \right] \qquad \text{(A-2)}
$$

$$
\int_{T_0}^{T} \left(\frac{T(\tau)^2}{\Phi^2} N_{01} \exp\left(-\frac{Q_N + Q_G}{RT(\tau)}\right) \right) dT(\tau)
$$

$$
= \frac{N_{01}}{\Phi^2} \left[\int_0^T T(\tau)^2 \exp\left(-\frac{Q_N + Q_G}{RT(\tau)}\right) dT(\tau) \right.
$$

$$
\left. - \int_0^{T_0} T(\tau)^2 \exp\left(-\frac{Q_N + Q_G}{RT(\tau)}\right) dT(\tau) \right]
$$

$$
= \frac{N_{01}}{\Phi^2} T^3 \left[\int_1^\infty \frac{\exp\left(-\frac{Q_N + Q_G}{RT}z\right)}{z^4} dz \right]
$$

$$
- \frac{N_{01}}{\Phi^2} T_0^3 \left[\int_1^\infty \frac{\exp\left(-\frac{Q_N + Q_G}{RT_0}z\right)}{z^4} dz \right] \qquad \text{(A-3)}
$$

by using the substitutions $z = T/T(\tau)$ and $z = T_0/T(\tau)$, respectively.

Applying the approximations as indicated by Equation 29 to Equations A-2 and A-3, Equation A-1 can then be written as,

$$
V^e = V g v_0 N_1^* \left(\frac{R}{Q_G} \right)
$$

$$
\times \left[\frac{T^2}{\Phi^2} \exp\left(-\frac{Q_G}{RT}\right) - \frac{T_0^2}{\Phi^2} \exp\left(-\frac{Q_G}{RT_0}\right) \right]
$$

$$
+ V g v_0 N_{01} \frac{R^2 T^2}{Q_N Q_G} \exp\left(-\frac{Q_G}{RT}\right)
$$

$$
\times \left[\frac{T^2}{\Phi^2} \exp\left(-\frac{Q_N}{RT}\right) - \frac{T_o^2}{\Phi^2} \exp\left(-\frac{Q_N}{RT_0}\right) \right]
$$

$$
- V g v_0 N_{01} \frac{R^2}{Q_G(Q_N + Q_G)} \left[\frac{T^4}{\Phi^2} \exp\left(-\frac{Q_N + Q_G}{RT}\right) \right.
$$

$$
\left. - \frac{T_0^4}{\Phi^2} \exp\left(-\frac{Q_N + Q_G}{RT_0}\right) \right] \qquad \text{(A-4)}
$$

Since, in the temperature range where the phase transformation occurs $T > T_0$, values of terms $[\frac{T^2}{\Phi^2} \exp(-\frac{Q_G}{RT_0})]$, $[\frac{T_0^2}{\Phi^2} \exp(-\frac{Q_N}{RT_0})]$ and $[\frac{T_0^4}{\Phi^2} \exp(-\frac{Q_N + Q_G}{RT_0})]$ can be neglected, in comparison with the

values of the corresponding terms at T. Thus Equation A-4 becomes,

$$
V^e = V g v_0 N_1^* \left(\frac{1}{Q_G} \right) \exp\left(-\frac{Q_G}{RT}\right) \left(\frac{RT^2}{\Phi} \right)
$$

$$
+ \frac{1}{2} V g v_0 N_{01} C_c \exp\left(-\frac{Q_G + Q_N}{RT}\right) \left(\frac{RT^2}{\Phi} \right)^2
$$

with $C_C = \frac{2}{Q_N(Q_N + Q_G)}$;
Analogously, for $d/m = 2$

$$
V^e = V g v_0 N_1^* \left(\frac{1}{Q_G} \right)^2 \exp\left(-\frac{2Q_G}{RT}\right) \left(\frac{RT^2}{\Phi} \right)^2
$$

$$
+ \frac{1}{3} V g v_0 N_{01} C_c \exp\left(-\frac{2Q_G + Q_N}{RT}\right) \left(\frac{RT^2}{\Phi} \right)^3
$$

with $C_C = \frac{6}{Q_N(Q_N + Q_G)(Q_N + 2Q_G)}$ and for $d/m = 3$

$$
V^e = V g v_0 N_1^* \left(\frac{1}{Q_G} \right)^3 \exp\left(-\frac{3Q_G}{RT}\right) \left(\frac{RT^2}{\Phi} \right)^3
$$

$$
+ \frac{1}{4} V g v_0 N_{01} C_c \exp\left(-\frac{3Q_G + Q_N}{RT}\right) \left(\frac{RT^2}{\Phi} \right)^4
$$

with $C_c = \frac{24}{Q_N(Q_N + Q_G)(Q_N + 2Q_G)(Q_N + 3Q_G)}$.

Appendix B
Employing $\int u \, dv = uv - \int v \, du$, the analytical integration in Equation 37 yields for $d/m = 1$

$$
\int_0^t \lambda \exp(-\lambda \tau)(t - \tau) \, d\tau
$$

$$
= -\exp(\lambda t)(t - \tau)_0^t - \int_0^t \exp(-\lambda \tau) \, d\tau
$$

$$
= \frac{\exp(-\lambda t) + \lambda t - 1}{\lambda} \qquad \text{(B-1)}
$$

Substituting B-1 into Equation 37 results in,

$$
V^e = (V g N' v_0 \exp\left(\frac{Q_G}{RT}\right)) \left(\frac{\exp(-\lambda t) + \lambda t - 1}{\lambda t} \right) t \qquad \text{(B-2)}
$$

B-2 can be rewritten as,

$$
V^e = \left(1/2 V g N' v_0 \lambda_0 \exp\left(-\frac{Q_G + Q_N}{RT}\right) \right)
$$

$$
\times \left(\frac{2 \exp(-\lambda t) + 2\lambda t - 2}{(\lambda t)^2} \right) t^2 \qquad \text{(B-3)}
$$

If $f(\lambda t)$ is given by $f(\lambda t) = (\frac{2 \exp(-\lambda t) + 2\lambda t - 2}{(\lambda t)^2})$, then Equation 40 results. Analogously, Equation 40 can also be obtained, as a form, for $d/m = 2, 3$, with the corresponding expressions for $f(\lambda t)$ shown in Table III.

For the values N' and λ_0 in Equations B-2 and B-3, different values $(N')'$ and $(\lambda_0)'$ can be chosen in such a way that V^e is due to only site saturation,

$$V_{s'}^e = V(N')'gv_0^{\frac{d}{m}}\exp\left(-\frac{\frac{d}{m}Q_G}{RT}\right)t^{\frac{d}{m}} \tag{B-4}$$

or that V^e is due to only continuous nucleation

$$V_{c'}^e = \left(\frac{1}{\frac{d}{m}+1}\right)V(N')'(\lambda_0)'gv_0^{\frac{d}{m}}$$
$$\times\exp\left(-\frac{\frac{d}{m}Q_G+Q_N}{RT}\right)t^{\frac{d}{m}+1} \tag{B-5}$$

$$V_{s'}^e = V_{c'}^e = V^e \tag{B-6}$$

From Equations B-2 and B-3 it then follows,

$$V_{c'}^e = f(\lambda t)V_c^e \tag{B-7}$$

$$V_{s'}^e = f(\lambda t)\frac{\lambda t}{\frac{d}{m}+1}V_s^e \tag{B-8}$$

Combining Equations 40 and 41 results in

$$V^e = \frac{1}{2}\left(V_s^e\left(\frac{\lambda t}{\frac{d}{m}+1}\right)f(\lambda t)+V_c^e f(\lambda t)\right)$$
$$= \frac{1}{2}f(\lambda t)\left(1+\frac{\lambda t}{\frac{d}{m}+1}\right)\left[\frac{r_2}{r_1+r_2}V_s^e+\frac{r_1}{r_1+r_2}V_c^e\right]$$
$$= \frac{1}{2}\frac{1}{r_1+r_2}\left[r_2 f(\lambda t)\frac{\lambda t}{\frac{d}{m}+1}V_s^e\right.$$
$$+ r_1\frac{\lambda t}{\frac{d}{m}+1}f(\lambda t)V_s^e + r_1 f(\lambda t)V_c^e + r_2 f(\lambda t)V_c^e\right]$$
$$= \frac{1}{r_1+r_2}\left[r_2 f(\lambda t)\frac{\lambda t}{\frac{d}{m}+1}V_s^e + r_1 f(\lambda t)V_c^e\right]$$
$$\tag{B-9}$$

Finally, substitution of Equations B-7 and B-8 in Equation B-9 gives,

$$V^e = \frac{1}{r_1+r_2}\left[r_2 V_{s'}^e + r_1 V_{c'}^e\right] \tag{B-10}$$

Appendix C

For Avrami nucleation, the extended volume in case of isochronal annealing can be expressed as:

$$V^e = V\int_{T_0}^{T(t)}\frac{N'gv_0^{\frac{d}{m}}}{\Phi^{\frac{d}{m}+1}}\lambda\left[1-T(\tau)^2\frac{R\lambda}{Q_N\Phi}\right.$$
$$+\frac{1}{2!}\left(T(\tau)^2\frac{R\lambda}{Q_N\Phi}\right)^2+(-1)^n\frac{1}{n!}\left(T(\tau)^2\frac{R\lambda}{Q_N\Phi}\right)^n\right]$$
$$\times\left[\frac{R}{Q_G}\left(T(t)^2\exp\left(-\frac{Q_G}{RT}\right)\right.\right.$$
$$\left.\left.-T(\tau)^2\exp\left(-\frac{Q_G}{RT(\tau)}\right)\right)\right]^{\frac{d}{m}}dT(\tau) \tag{C-1}$$

with $\lambda=\lambda_0\exp(-\frac{Q_N}{RT(\tau)})$.

When $d/m=1$,

$$V^e = VgN'v_0\frac{RT(t)^2}{Q_G\Phi^2}\exp\left(-\frac{Q_G}{RT}\right)\int_{T_0}^{T(t)}$$
$$\times\lambda\left[\begin{array}{c}1-T(\tau)^2\frac{R\lambda}{Q_N\Phi}+\frac{1}{2!}\left(T(\tau)^2\frac{R\lambda}{Q_N\Phi}\right)^2\\+\cdots+(-1)^n\frac{1}{n!}\left(T(\tau)^2\frac{R\lambda}{Q_N\Phi}\right)^n\end{array}\right]dT(\tau)$$
$$-VgN'v_0\frac{R}{Q_G\Phi^2}\int_{T_0}^{T(t)}$$
$$\times\lambda\left[\begin{array}{c}1-T(\tau)^2\frac{R\lambda}{Q_N\Phi}+\frac{1}{2!}\left(T(\tau)^2\frac{R\lambda}{Q_N\Phi}\right)^2\\+\cdots+(-1)^n\frac{1}{n!}\left(T(\tau)^2\frac{R\lambda}{Q_N\Phi}\right)^n\end{array}\right]$$
$$\times\left[\left(T(\tau)^2\exp\left(-\frac{Q_G}{RT_\tau}\right)\right)\right]dT(\tau) \tag{C-2}$$

After some arrangement, Equation C-2 can be rewritten as,

$$V^e = VgN'v_0\frac{RT(t)^2}{Q_G\Phi^2}\exp\left(-\frac{Q_G}{RT}\right)\left\{\begin{array}{c}\left[\int_{T_0}^{T(t)}\lambda_0\exp\left(-\frac{Q_N}{RT(\tau)}\right)dT(\tau)\right]\\-\left[\frac{R}{Q_N\Phi}\int_{T_0}^{T(t)}\lambda_0^2(T(\tau))^2\exp\left(-\frac{2Q_N}{RT(\tau)}\right)dT(\tau)\right]\\\cdots\cdots\cdots\\+\left[(-1)^n\frac{1}{n!}\left(\frac{R}{Q_N\Phi}\right)^n\int_{T_0}^{T(t)}\lambda_0^{n+1}(T(\tau))^{2n}\exp\left(-\frac{(n+1)Q_N}{RT(\tau)}\right)dT(\tau)\right]\end{array}\right.$$
$$-VgN'v_0\frac{R}{Q_G\Phi^2}\left\{\begin{array}{c}\left[\int_{T_0}^{T(t)}\lambda_0(T(\tau))^2\exp\left(-\frac{Q_N+Q_G}{RT(\tau)}\right)dT(\tau)\right]\\-\left[\frac{R}{Q_N\Phi}\int_{T_0}^{T(t)}\lambda_0^2(T(\tau))^4\exp\left(-\frac{2Q_N+Q_G}{RT(\tau)}\right)dT(\tau)\right]\\\cdots\cdots\\+\left[(-1)^n\frac{1}{n!}\left(\frac{R}{Q_N\Phi}\right)^n\int_{T_0}^{T(t)}\lambda_0^{n+1}(T(\tau))^{2n+2}\exp\left(-\frac{(n+1)Q_N+Q_G}{RT(\tau)}\right)dT(\tau)\right]\end{array}\right\} \tag{C-3}$$

Using the procedure as indicated in Equations 28–30 and Equations A-1 to A-4, the exponential integration incorporated in Equation C-3 can be given with $T(t) = T$ as,

$$\int_{T_0}^{T} \left(\lambda_0 \exp\left(-\frac{Q_N}{RT(\tau)}\right) \right) dT(\tau) = \frac{RT^2}{Q_N} \lambda$$

$$\int_{T_0}^{T} \left(\lambda_0^2 T(\tau)^2 \exp\left(-\frac{2Q_N}{RT(\tau)}\right) \right) dT(\tau) = \frac{RT^4}{2Q_N} \lambda^2$$

$$\cdots$$

$$\int_{T_0}^{T} \left(\lambda_0^{n+1} T(\tau)^{2n} \exp\left(-\frac{(n+1)Q_N}{RT(\tau)}\right) \right) dT(\tau)$$

$$= \frac{RT^{2n+2}}{(n+1)Q_N} \lambda^{n+1}$$

$$\cdots$$

$$\int_{T_0}^{T} \left(\lambda_0^{n+1} T(\tau)^{2n+2} \exp\left(-\frac{(n+1)Q_N + Q_G}{RT(\tau)}\right) \right) dT(\tau)$$

$$= \frac{RT^{2n+4}}{(n+1)Q_N + Q_G} \lambda^{n+1}$$

Substitution of these expressions into Equation C-3 results in

$$V^e = VgN'\nu_0 \frac{1}{Q_N Q_G} \exp\left(-\frac{Q_N + Q_G}{RT}\right)\left(\frac{RT^2}{\Phi}\right)^2$$

$$\times \left(1 - \left(\lambda \frac{RT^2}{Q_N \Phi}\right)\frac{Q_N Q_G}{2Q_N Q_G} + \cdots - \right.$$
$$\left. \cdots + (-1)^n \frac{1}{n!}\left(\lambda \frac{RT^2}{Q_N \Phi}\right)^n \frac{Q_N Q_G}{(n+1)Q_n Q_G} \right)$$

$$- VgN'\nu_0^{\frac{d}{m}} \frac{1}{Q_G(Q_N + Q_G)} \exp\left(-\frac{Q_N + Q_G}{RT}\right)$$

$$\times \left(\frac{RT^2}{\Phi}\right)^2 \left(1 - \left(\lambda \frac{RT^2}{Q_N \Phi}\right)\frac{Q_N + Q_G}{2Q_N + Q_G} + \cdots - \cdots + \right.$$
$$\left. (-1)^n \frac{1}{n!}\left(\lambda \frac{RT^2}{Q_N \Phi}\right)^n \frac{Q_N + Q_G}{(n+1)Q_N + Q_G} \right)$$

$$= VgN'\nu_0 \lambda_0 \frac{1}{2} \frac{2}{Q_N(Q_N + Q_G)}$$

$$\times \exp\left(-\frac{Q_N + Q_G}{RT}\right)\left(\frac{RT^2}{\Phi}\right)^2$$

$$\times \left[\left(1 + \sum_{n=1}^{n} (-1)^n \frac{1}{(n+1)!} \frac{Q_N + Q_G}{(n+1)Q_N + Q_G} \right.\right.$$

$$\left.\left. \times \left(\lambda \frac{RT^2}{Q_N \Phi}\right)^n \right) \right]$$

$$= VgN'\nu_0 \frac{1}{Q_G} \exp\left(-\frac{Q_G}{RT}\right)\left(\frac{RT^2}{\Phi}\right)$$

$$\times \left(\frac{Q_G}{Q_N(Q_N + Q_G)} \frac{RT^2}{\Phi} \lambda \right)$$

$$\times \left(1 + \sum_{n=1}^{n} (-1)^n \frac{1}{(n+1)!} \frac{Q_N + Q_G}{(n+1)Q_N + Q_G} \right.$$

$$\left. \times \left(\lambda \frac{RT^2}{Q_N \Phi}\right)^n \right)$$

$$= \frac{1}{2}\left(V_s^e \frac{C_c Q_G}{2}\left(\frac{RT^2}{\Phi}\lambda\right) f\left(\lambda \frac{RT^2}{Q_N \Phi}\right) \right.$$

$$\left. + V_c^e f\left(\lambda \frac{RT^2}{Q_N \Phi}\right) \right) \qquad \text{(C-4)}$$

The expressions for the extended volume in the case of $d/m = 2$, and 3, are similar to the given above for $d/m = 1$. Finally, a general expression can be given as Equation 44 with C_c and $f(\lambda \frac{RT^2}{Q_N \Phi})$ given in Tables II and IV.

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