Analysis of the kinetics of phase transformations; roles of nucleation index and temperature dependent site saturation, and recipes for the extraction of kinetic parameters

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Abstract A general analytical model for the description of phase transformation kinetics, with kinetic parameters that are time and temperature dependent, can be given that exhibits the roles of (i) the nucleation index, a, and (ii) the temperature dependence of site saturation. Recipes for straightforward deduction of the growth exponent, n, and the effective activation energy, Q, have been presented. It has also been shown how the values of the constant activation energies for nucleation and growth, Q_N and Q_G, can be derived from the dependence of n and Q on time and temperature. The applicability of the kinetic model and of the recipes for isothermally and isochronally conducted phase transformations has been tested by analytical and numerical calculations and by application to the crystallization kinetics of amorphous $Zr_{50}Al_{10}Ni_{40}$, as measured by means of isochronal differential scanning calorimetry.

Introduction

Solid-state phase transformations play an important role in the production of very many materials as they provide the means to optimize the microstructure and thereby the properties of materials. Therefore, a great interest exists for a comprehensive description of the kinetics, i.e. the time-temperature behaviour, of phase transformations [1–3].

Solid-state phase transformations are generally the outcome, for both isothermally and non-isothermally conducted annealings, of three, often simultaneously operating, mechanisms: nucleation, growth and impingement. Recently, a general, modular, numerical kinetic model [2, 3] has been proposed that recognizes the three mechanisms, nucleation, growth, and impingement of growing new phase particles, as entities that can be modelled separately. The modular approach is applicable to both isothermally conducted (time dependent) and isochronally conducted (temperature dependent) transformations, as verified by experiments [4, 5].

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". It has been often claimed that occurrence of "isokinetics" implies that the kinetic parameters are assumed to be constant with respect to time and temperature. Indeed, this is compatible with the well-known and very often used analytical description of transformation kinetics according to Johnson, Mehl and Avrami (JMA) [6–9], that in fact only holds for special, extreme cases of nucleation, growth and impingement. However, many experimental results of phase transformation kinetics that have been reported and fitted with a JMA (-like) model, show that often the measured kinetics cannot be described with constant values for the kinetic parameters as the growth exponent, n, and the effective activation energy, Q

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(e.g. [10–12]): the fitted parameters, n and Q, appear to be different for different stages of the transformation, i.e. the transformation would not be iso-kinetic and fitting of JMA kinetics to such phase transformations therefore only yields a phenomenological description.

To deal with such complications and recognizing the strong need for a comprehensive description of phase transformation kinetics, a general, analytical phase transformation model was proposed that incorporates a range of nucleation and growth mechanisms [13–15]. Use of analytical expressions has an advantage over numerical calculations because e.g. the influence of different nucleation, growth and impingement models can be easily identified and investigated and is generally preferred, if possible. This model has been applied successfully to practical cases [14, 15]. The model leads to equations for the degree of transformation, $f(0 \leq f \leq 1)$, that have the structure of the JMA equation but with *time dependent kinetic parameters*, as $n(t)$ and $Q(t)$, for isothermal transformation, or *temperature dependent kinetic parameters*, as $n(T)$ and $Q(T)$, for isochronal transformation [13, 15]:

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

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

with K_0 as the time/temperature dependent pre-exponential factor and Φ as the constant heating rate (= isochronal annealing).

The effective, overall, *time or temperature dependent* activation energy can be interpreted as a combination of the *constant* activation energies for nucleation and growth, Q_N and Q_G, according to [2, 13],

$$Q = \frac{\frac{d}{m}Q_G + (n - d/m)Q_N}{n} \quad (3)$$

with m as the growth mode parameter ($m = 1$ for interface-controlled growth; $m = 2$ for volume diffusion controlled growth) and d as the dimensionality of the growth ($d = 1, 2, 3$).

On the basis of the general, analytical model, a transformation can still be considered as "iso-kinetic" in the sense indicated above, even if kinetic parameters as n and Q distinctly vary during the course of a transformation.

It was found that isothermal JMA kinetics on the basis of the traditional description of the continuous nucleation mechanism (constant nucleation rate) cannot be used to interpret available experimental results [16]: a nucleation rate increasing with time (e.g. autocatalytic nucleation [17]) or decreasing with time can occur. Hence, an extension of classical continuous nucleation can be proposed by incorporating the so-called nucleation index, a [16, 18]: $N(t) = n' t^a$ for isothermal annealing, with n' as a constant and a as the nucleation index: $a = 0$ implies zero nucleation rate; $a = 1$ implies constant nucleation rate ($dN(t)/dt = n'$); $a > 1$ implies a nucleation rate increasing with time and $0 < a < 1$ implies a nucleation rate decreasing with time.

In the case of site saturation it is usually assumed (as in isothermal decomposition of substitutional solid solutions) that the number of supercritical particles (=nuclei) is temperature independent. This assumption in general does not hold. Accordingly, it appears appropriate to introduce an "activation energy", Q_s, controlling the temperature dependency of the number of frozen-in supercritical particles (= nuclei) acting in the site saturation mechanism upon progressing transformation.

Both complications discussed above and symbolized by the parameters a and Q_S need to be addressed in a generally applicable, quantitative description of transformation kinetics. This is the purpose of sections 'The nucleation, a and Temperature dependence of site saturation'.

Although, in principle, fitting of the analytical model, on the basis of different combinations of nucleation, growth and impingement mechanisms, to the experimental results can be made, this procedure can be very time-consuming and cumbersome (see e.g. Refs. [13–15]). The most important kinetic parameters for phase transformation are the growth exponent, n, the effective activation energy, Q, and the activation energies of nucleation and growth, Q_N and Q_G, respectively. Recipes for the direct extraction of values for these kinetic parameters from transformation-rate data will be given in section 'Recipes for determination of kinetic parameters from isothermally and isochronally conducted transformations'.

Synopsis of theoretical background [13, 15]

The term *site saturation* is used in those cases where the number of supercritical particles (= nuclei) of the new phase does not change during the transformation: all nuclei, of number N^* per unit volume, are present at $t = 0$ already. This implies for the nucleation rate:

$$\dot{N}(T) = N^*\delta(t-0); \quad \text{for isothermal transformation} \tag{4a}$$

$$\dot{N}(T(t)) = N^*\delta\left(\frac{T(t)-T_0}{\Phi}\right); \tag{4b}$$

for isochronal transformation

with $\delta(t-0)$ and $\delta\left(\frac{T(t)-T_0}{\Phi}\right)$ denoting Dirac functions and N as the number of nuclei per unit volume. For isochronal annealing with a constant heating rate, Φ, $T(t) = T_0 + \Phi t$ with $T_0 = T(t=0)$ and $\Phi = dT(t)/dt$.

According to the classical nucleation theory the nucleation rate is determined by the number of new phase particles of critical size and the rate of jumping of atoms through the interface between the particles of critical size and the parent phase. The frequency of jumping through the interface is given by an Arrhenius term, the argument of which thus varies with temperature as $-A/T$, where A is a positive constant (see Eq. 5). The number of particles of critical size depends on an activation energy ΔG^*, which can be approximated as $B/\Delta T^2$ [19], where B is a positive 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^* is very small. This is the case for a frozen-in metastable state, which transforms to the stable state upon heating. The so-called *continuous* nucleation rate per unit volume $\dot{N}(T(t))$ (i.e. the rate of formation of particles of supercritical size (= nuclei)) is then only determined by the atomic mobility for transport through the interface, which for isothermal and non-isothermal annealing can be given by an Arrhenius term:

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

where N_0 is a temperature-independent nucleation rate constant, and Q_N is the activation energy for transfer through the interface, defined as the temperature- and time-independent activation energy for nucleation. The number of nuclei equals 0 at $t = 0$.

It should be noted that for small undercooling or overheating, ΔG^* is not very small, and the argument of the exponential term describing the number of particles of critical size varies with temperature as $-B'/T\Delta T^2$, where B' is a positive constant. Then the temperature dependence of the rate of jumping through the marix/particle interface may be neglected with respect to the temperature dependence of the formation of nuclei and the nucleation rate is given by

$$\dot{N}(T(t)) = N_0 \exp\left(-\frac{\Delta G^*(T(t))}{RT(t)}\right) \tag{5b}$$

Note that ΔG^* in Eq. 5b depends on temperature and therefore on the basis of Eq. 5b an analytical treatment is only possible for isothermal transformation.

So-called *Avrami nucleation* involves that the rate of formation of supercritical particles at time t is given by,

$$\dot{N}(T(t)) = N'\lambda \exp\left(-\int_0^t \lambda d\tau\right) \tag{6a}$$

where λ is the rate at which an individual sub-critical particle becomes supercritical: $\lambda(t=\tau) = \lambda_0 \exp(-Q_N/(RT(\tau)))$, with λ_0 as a temperature-independent rate and N' as the total number of sub-critical particles at $t = 0$. 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).

For isothermal annealing, λ is constant, and Eq. 6a becomes,

$$\dot{N}(T,t) = N'\lambda \exp(-\lambda t) \tag{6b}$$

For isochronal annealing (with $T_0 < T(t)$) and $\frac{Q_N}{RT} \gg 1$ (usually $\frac{Q_N}{RT} \geq 25$),

Equation (6a) can be rewritten as [13],

$$\dot{N}(T(t)) \cong N'\lambda \exp\left(-\frac{R\lambda}{Q_N\Phi}T(t)^2\right) \tag{6c}$$

Physically meaningful combinations of the singular nucleation modes presented above can be considered.

The so-called *mixed nucleation* mode involves that the nucleation rate is equal to some weighted sum of the nucleation rates according to site saturation and continuous nucleation (here given for isothermal transformation):

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

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

Avrami nucleation (Eq. 6) is intermediate between site saturation and continuous nucleation: Avrami nucleation tends to be continuous nucleation and site saturation at the start and at the end of the transformation, respectively. Therefore, *site saturation plus Avrami nucleation* could be considered as a modified type of mixed nucleation discussed above (here given for isothermal transformation; for a practical example, see Ref. [15]),

$$\dot{N}(T,t) = N^* \delta(t-0) + N'\lambda \exp(-\lambda t) \tag{8}$$

A combination of *continuous nucleation* with *Avrami nucleation* is physically not worthwhile to consider: according to both nucleation modes the number of nuclei continuously increases with progressing transformation.

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

$$Y(t,\tau) = g \left[\int_\tau^t v\,\mathrm{d}t \right]^{d/m} \tag{9}$$

where g is a particle-geometry factor and $v(t) = v_0 \exp(-Q_G/(RT(t)))$ with Q_G as the temperature and time independent activation energy of growth. For interface-controlled growth, v_0 is a temperature-independent interface velocity constant and Q_G represents the energy barrier at the interface. For volume diffusion-controlled growth (particle thickening obeys a parabolic growth law), v_0 equals the pre-exponential factor for diffusion D_0 and Q_G represents the activation energy for diffusion, Q_D. For d and m see below Eq. 3.

The number of nuclei (= number of supercritical particles) formed per 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 Eqs. 4–8. The volume of each of these nuclei grows from τ until t according to Eq. 9 if it is supposed that every particle grows into an infinitely large parent phase, in the absence of the other growing particles. In this hypothetical case, the volume of all particles of the new phase at time t, which is called the extended volume, V^e, is given by,

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

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

According to Eqs. 4–10, the extended volume for cases of nucleation considered here (single nucleation modes or mixtures of nucleation modes) can be shown to be given by the addition of two parts: one part that can be conceived as due to pure site saturation and one part that can be conceived as due to pure continuous nucleation. Then, by extensive calculation, explicit analytical expressions for the extended volume can be obtained (see Ref. [13]).

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. The degree of transformation, f, is then given by,

$$f = V^t/V = 1 - \exp\left(-\frac{V^e}{V}\right) \tag{11}$$

with V^t as the actual transformed volume.

On the basis of the mechanisms given in this section, it can be shown that an analytical formulation for the degree of transformation is possible that has the structure of the JMA equation [13–15]:

$$f = 1 - \exp\left(-K_0^n \alpha^n \exp\left(-\frac{nQ}{RT}\right)\right) \tag{12}$$

where α is identified either with the annealing time t for isothermal transformation or with RT^2/Φ for isochronal transformation with $\Phi = \mathrm{d}T/\mathrm{d}t$ as the constant heating rate (cf. Eqs. 1 and 2).

Unlike the extreme cases for which the JMA equation holds strictly (site saturation and continuous nucleation), in general, n, Q, and K_0 are not constant but will be time (isothermal transformation) or temperature (isochronal transformation) dependent. Analytical formulations for these time and temperature dependencies of the kinetic parameters, n, Q, and K_0, are given in Tables 1–3.

The nucleation index, *a*

A nucleation rate accelerating or decelerating with progressing transformation, can be described by the incorporation of a nucleation index, a in the model for continuous nucleation. To allow for a nucleation rate increasing with progressing transformation, values of a larger than one have to be considered, as done, for only isothermal transformation, in Refs.[16, 18]. A nucleation rate decreasing with progressing transformation, implying, according to the treatment in this paper, $0 < a < 1$, is also described by Avrami nucleation; therefore the case for $0 < a < 1$ is not considered further here.

In the following, the effect of the nucleation index is analyzed for the (more general) case of mixed nucleation (i.e. combined site saturation and continuous

Table 1 Expressions for the (time and temperature dependency of the) growth exponent, n, the overall activation energy, Q, and the rate constant, K_0, to be inserted in Eqs. 1 and 2 for isothermal annealing and isochronal annealing, respectively

Mixed	Isothermal	Isochronal
Mixed nucleation and Avrami nucleation Ref. [13]		
n	$d/m + \dfrac{1}{1+(r_2/r_1)^{-1}}$	$d/m + \dfrac{1}{1+(r_2/r_1)^{-1}}$
Q	$\dfrac{\frac{d}{m}Q_G+(n-\frac{d}{m})Q_N}{n}\; Q = \dfrac{d/m\left(Q_G-\frac{Q_S}{d/m}\right)+(n-d/m)(Q_N+Q_S)}{n}$ (*)	$\dfrac{\frac{d}{m}Q_G+(n-\frac{d}{m})Q_N}{n}$
K_0^n	$\dfrac{g v_0^{d/m}}{(d/m+1)^{1+(r_2/r_1)^{-1}}}\left[\left(N^*\left(1+\frac{r_2}{r_1}\right)\right)^{\frac{1}{1+\frac{r_2}{r_1}}}\times\left(N_0\left(1+\left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}}\right]$	$\dfrac{g v_0^{d/m}}{(d/m+1)^{1+(r_2/r_1)^{-1}}}\left[\left(\frac{N^*}{(Q_G)^{d/m}}\left(1+\frac{r_2}{r_1}\right)\right)^{\frac{1}{1+\frac{r_2}{r_1}}}\times\left(C_c N_0\left(1+\left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}}\right]$
r_2/r_1	$\dfrac{\frac{1}{d/m+1}N_0 t\exp\left(-\frac{Q_N}{RT}\right)}{N^*}$ (*)	$\dfrac{C_c Q_G^{d/m}N_0\exp\left(-\frac{Q_N}{RT}\right)}{(d/m+1)N^*}\left(\frac{RT^2}{\Phi}\right)$
Avrami		
n	$n = d/m + \dfrac{1}{1+(r_2/r_1)^{-1}}$	$n = d/m + \dfrac{1}{1+(r_2/r_1)^{-1}}$
Q	$\dfrac{\frac{d}{m}Q_G+(n-\frac{d}{m})Q_N}{n}$	$\dfrac{\frac{d}{m}Q_G+(n-\frac{d}{m})Q_N}{n}$
K_0^n	$\dfrac{g N^* f(\lambda t)v_0^{d/m}}{(d/m+1)}(\lambda_0)^{1+\frac{r_2}{r_1}}(\lambda t)^{1+\left(\frac{r_2}{r_1}\right)^{-1}}$	$\left[\dfrac{g v_0^{d/m}N' f}{d/m+1}\left(\frac{\lambda RT^2}{Q_N\Phi}\right)^{\frac{1}{1+\frac{r_2}{r_1}}}(\lambda_0)^{1+\frac{r_2}{r_1}}\left(\lambda\frac{RT^2}{\Phi}\right)^{1+\left(\frac{r_2}{r_1}\right)^{-1}}\right]C_c$
r_2/r_1	$\dfrac{\lambda t}{d/m+1}$	$\dfrac{C_c Q_G^{d/m}}{d/m+1}\left(\frac{RT^2}{\Phi}\lambda\right)$
Site saturation plus Avrami nucleation Ref. [15]		
n	$n = d/m + \dfrac{1}{1+(r_2/r_1)^{-1}}$	$n = d/m + \dfrac{1}{1+(r_2/r_1)^{-1}}$
Q	$\dfrac{\frac{d}{m}Q_G+(n-\frac{d}{m})Q_N}{n}\; Q = \dfrac{d/m\left(Q_G-\frac{Q_S}{d/m}\right)+(n-d/m)(Q_N+Q_S)}{n}$ (*)	$\dfrac{\frac{d}{m}Q_G+(n-\frac{d}{m})Q_N}{n}$
K_0^n	$\left[\dfrac{g v_0^{d/m}}{(d/m+1)^{1+\left(\frac{r_2}{r_1}\right)}}\left(\left(N^*+\frac{N'\lambda f(\lambda t)}{2(d/m+1)}\right)\left(1+\left(\frac{r_2}{r_1}\right)^{-1}\left(\frac{\lambda t}{d/m+1}\right)\right)\right)^{\frac{1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}}\times\left(\frac{N'\lambda_0 f(\lambda t)}{2}\right)\left(1+\left(\frac{r_2}{r_1}\right)\left(\frac{\lambda t}{d/m+1}\right)^{-1}\right)^{\frac{1}{1+\left(\frac{r_2}{r_1}\right)}}\right]$ (isothermal transformation)	$\left[\dfrac{g v_0^{d/m}}{(d/m+1)^{1+\left(\frac{r_2}{r_1}\right)}}\left(\left(N^*+\frac{N'\lambda f(\lambda t)}{2(d/m+1)\exp\left(\frac{Q_S}{RT}\right)}\right)\left(1+\left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}}\times\left(\frac{N'\lambda_0 f()}{2}\right)\left(1+\left(\frac{r_2}{r_1}\right)\left(\frac{\exp\left(\frac{Q_S}{RT}\right)}{d/m+1}\right)^{-1}\right)\right]$ (isothermal transformation*)

Table 1 continued

Mixed	Isothermal	Isochronal
K_0^n	$\left[\dfrac{gv_0^{d/m}}{(d/m+1)^{1+(\frac{r_2}{r_1})}}\left(\dfrac{1}{Q_G^{d/m}}\right)\left(N^* + \dfrac{N'\lambda_0 f\left(\lambda\frac{RT^2}{Q_N\Phi}\right)}{2}\right)\right.$ $\times\left(\dfrac{N'\lambda_0 f\left(\lambda\frac{RT^2}{Q_N\Phi}\right)}{2}\right)\left(1+\left(\dfrac{r_2}{r_1}\right)\left(\dfrac{1}{d/m+1}C_cQ_G^{d/m}\frac{RT^2}{\Phi}\lambda\right)^{-1}\right)^{\frac{1}{1+(\frac{r_2}{r_1})}}$ (isochronal transformation)	$\left(N^* + \dfrac{N'Q_G^{d/m}C_c\lambda\frac{RT^2}{\Phi}f\left(\lambda\frac{RT^2}{Q_N\Phi}\right)}{2(d/m+1)}\right)\times\left(1+\left(\dfrac{1}{d/m+1}C_cQ_G^{d/m}\frac{RT^2}{\Phi}\lambda\right)^{-1}\right)^{\frac{1}{1+(\frac{r_2}{r_1})}-1}$
r_2/r_1	$\dfrac{\frac{N^*}{N'} + \frac{\lambda t}{2(d/m+1)\exp\left(-\frac{Q_G}{RT}\right)}f(\lambda t)}{\frac{1}{2}f(\lambda t)}$ (*)	$\dfrac{\frac{N^*}{N'} + \frac{C_cQ_G^{d/m}\lambda\frac{RT^2}{\Phi}}{2(d/m+1)}f\left(\lambda\frac{RT^2}{Q_N\Phi}\right)}{\frac{1}{2}f\left(\lambda\frac{RT^2}{Q_N\Phi}\right)}$

For C_c (this correction factor depends on Q_N and Q_G), $f(\lambda t)$ and $f(\lambda RT^2/Q_N\Phi)$, see [13]; these values are valid for the analytical model based on mixed nucleation and site saturation plus Avrami nucleation, as presented in this paper

v_0 and Q_G can be substituted by D_0 and Q_D in case of volume diffusion-controlled growth

* Incorporation of "activation energy" for the supercritical particle formation in site saturation

nucleation; cf. section 'Synopsis of theoretical background') and for both isothermally and isochronally conducted transformations.

Isothermal transformation

Anticipating the analysis of non-isothermal (isochronal) kinetics, and differing from the earlier work where the nucleation index was proposed originally [16, 18], the nucleation index should be introduced such that both time and temperature dependences of the nucleation density can be considered. Thus the linear relation between N and t for mixed nucleation becomes,

$$N(T,t) = N^* + \left[N_0 t \exp\left(-\frac{Q_N}{RT}\right)\right]^a \tag{13}$$

and the corresponding nucleation rate is then given by (cf. Eq. 7), (Note that if $a > 1$ N_0 and Q_N have only empirical meaning)

$$\dot{N}(T,t) = N^*\delta(t-0) + aN_0^a t^{a-1}\exp\left(-\frac{aQ_N}{RT}\right) \tag{14}$$

Thus the extended volume can be given as (cf. Eq. 10),

$$V^e = V\int\limits_0^t\left(N^*\delta(\tau-0) + aN_0^a\tau^{a-1}\exp\left(-\frac{aQ_N}{RT}\right)\right)$$
$$g\left(\int\limits_\tau^t v_0\exp\left(-\frac{Q_G}{RT}\right)\mathrm{d}t\right)^{d/m}\mathrm{d}\tau \tag{15}$$

where N^* and N_0 represent the relative contributions of the two modes of nucleation considered. Interface-controlled growth has been adopted (see below Eq. 9); this is not a restriction; see below. Performing the integrations in Eq. 15 results in,

$$V^e = VN^*gv_0^{d/m}\exp\left(-\frac{d/mQ_G}{RT}\right)t^{d/m}$$
$$+\left(g\prod_{i=1}^{d/m}\frac{i}{a+i}\right)VN_0^a v_0^{d/m}\exp\left(-\frac{d/mQ_G+aQ_N}{RT}\right)t^{d/m+a} \tag{16}$$

Now, applying an analogous treatment as that performed in Ref. [13] (see Eqs. (16–22) in Ref. [13]), the extended volume is rewritten as,

Table 2 Expressions for the (time and temperature dependency of the) growth exponent, n, the overall activation energy, Q, and the rate constant, K_0, to be inserted in Eqs. 1 and 2 for isothermal annealing and isochronal annealing, respectively

Mixed nuc	Isothermal	Isochronal
n	$d/m + \dfrac{a}{1+(r_2/r_1)^{-1}}$	$d/m + \dfrac{a}{1+(r_2/r_1)^{-1}}$
Q	$\dfrac{\frac{d}{m}Q_\mathrm{G}+(n-d/m)Q_\mathrm{N}}{n}$	$\dfrac{\frac{d}{m}Q_\mathrm{G}+(n-d/m)Q_\mathrm{N}}{n}$
K_0^n	$\dfrac{gv_0^{d/m}}{\left(\prod\limits_{i=1}^{d/m}\frac{i}{a+i}\right)^{\frac{1}{1+(r_2/r_1)^{-1}}}}\left[\left(N^*\left(1+\frac{r_2}{r_1}\right)\right)^{\frac{1}{1+\frac{r_2}{r_1}}}\times\left(N_0^a\left(1+\left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}}\right]$	$\dfrac{gv_0^{d/m}}{(d/m+1)^{\frac{1}{1+(r_2/r_1)^{-1}}}}$
		$\left[\left(\dfrac{N^*}{(Q_\mathrm{G})^{d/m}}\left(1+\frac{r_2}{r_1}\right)\right)^{\frac{1}{1+\frac{r_2}{r_1}}}\left(C_c^*N_0^a\left(1+\left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}}\right]$
r_2/r_1	$\dfrac{\left(\prod\limits_{i=1}^{d/m}\frac{i}{a+i}\right)N_0^a t^a\exp\left(-\frac{aQ_\mathrm{N}}{RT}\right)}{N^*}$	$\dfrac{C_c^*Q_\mathrm{G}^{d/m}N_0^a\exp\left(-\frac{aQ_\mathrm{N}}{RT}\right)}{(d/m+1)N^*}\left(\dfrac{RT^2}{\Phi}\right)^a$

For C_c^* see Table 4. These values are valid for the analytical model based on mixed nucleation incorporating the nucleation index for interface controlled growth, as presented in this paper

$$V^e = \frac{Vgv_0^{d/m}}{\left(\prod\limits_{i=1}^{d/m}\frac{i}{a+i}\right)^{\frac{-1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}}}$$
$$\left[\left(N^*\left(1+\frac{r_2}{r_1}\right)\right)^{\frac{1}{1+\frac{r_2}{r_1}}}\times\left(N_0^a\left(1+\left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}}\right]$$
$$\times\exp\left(-\frac{d/mQ_\mathrm{G}+\frac{a}{1+(r^2/r^1)^{-1}}Q_\mathrm{N}}{RT}\right)t^{(d/m)+\frac{a}{1+(r^2/r^1)^{-1}}} \tag{17}$$

where r_2/r_1 represents the ratio between the extended volume contributions ascribed to continuous nucleation and site saturation [13]; see Table 2 and first part of Table 1.

After substitution of Eq. 17 into Eq. 11, it can be derived,

$$\ln(-\ln(1-f)) = \ln\left[\frac{gv_0^{d/m}}{\left(\prod\limits_{i=1}^{d/m}\frac{i}{a+i}\right)^{\frac{-1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}}}\left(N^*\left(1+\frac{r_2}{r_1}\right)\right)^{\frac{1}{1+\frac{r_2}{r_1}}}\right.$$
$$\left.\left(N_0^a\left(1+\left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}}\right]$$
$$-\left(\frac{d/mQ_\mathrm{G}+\frac{a}{1+(r_2/r_1)^{-1}}Q_\mathrm{N}}{RT}\right)+\left(d/m+\frac{a}{1+\left(\frac{r_2}{r_1}\right)^{-1}}\right)\ln t \tag{18}$$

This result can be compared with the correspondingly rewritten Eq. 12,

$$\ln(-\ln(1-f)) = n\ln(K_0) - \frac{nQ}{RT} + n\ln\alpha \tag{19}$$

By comparing Eqs. 19 and 18 time dependent expressions for n, Q, and K_0 result, which have been gathered

Table 3 Expressions for the (time and temperature dependency of the) growth exponent, n, the overall activation energy, Q, and the rate constant, K_0, to be inserted in Eqs. 1 and 2 for isothermal annealing and isochronal annealing, respectively

Continuous nucleation	Isothermal $a = 1$	Isothermal $a > 1$	Isochronal $a = 1$	Isochronal $a > 1$
n	$d/m + 1$	$d/m + a$	$d/m + 1$	$d/m + a$
Q	$\dfrac{\frac{d}{m}Q_\mathrm{G}+Q_\mathrm{N}}{n}$	$\dfrac{\frac{d}{m}Q_\mathrm{G}+aQ_\mathrm{N}}{n}$	$\dfrac{\frac{d}{m}Q_\mathrm{G}+Q_\mathrm{N}}{n}$	$\dfrac{\frac{d}{m}Q_\mathrm{G}+aQ_\mathrm{N}}{n}$
K_0^n	$\dfrac{gN_0v_0^{d/m}}{n}$	$\dfrac{gN_0v_0^{d/m}}{n}$	$\dfrac{gN_0v_0^{d/m}C_c^*Q^n}{n}$	$\dfrac{gN_0v_0^{d/m}C_c^*Q^n}{n}$
Site saturation	Isothermal $Q_S = 0$	Isothermal $Q_S > 0$	Isochronal $Q_S = 0$	
n	d/m	d/m	d/m	
Q	Q_G	$\dfrac{\frac{d}{m}Q_\mathrm{G}-Q_S}{d/m}$	Q_G	
K_0^n	$gN^*v_0^{d/m}$	$gN^*v_0^{d/m}$	$\dfrac{gN^*v_0^{d/m}}{Q_\mathrm{G}^{d/m}}$	

For C_c^* see Table 4. These values are valid for the analytical model based on continuous nucleation incorporating the nucleation index and site saturation incorporating Q_S, as presented in this paper

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

in Table 2. Hence, incorporating a nucleation index ($a \neq 1$) does *not* affect the general equation for the degree of transformation in case of isothermal transformation (cf. Eq. 1). Similar results are obtained if volume diffusion controlled growth is considered.

Isochronal transformation

The mixed nucleation rate for isochronal annealing, i.e. with a constant heating rate Φ ($= dT/dt$), is given as (cf. Eq. (26) in Ref. [13]),

$$\dot{N}(T(t)) = N^* \delta\left(\frac{T(t) - T_0}{\Phi}\right) + N_0 \exp\left(-\frac{Q_N}{RT(t)}\right) \quad (20)$$

where, $T(t) = T_0 + \Phi t$ and $T_0 = T(t = 0)$. The number of nuclei per unit volume of untransformed material can be expressed as an integration of the nucleation rate from T_0 to $T(t)$, i.e. as a function of $T(t)$,

$$N = \int_{T_0}^{T(t)} \left[N^* \delta\left(\frac{T(t') - T_0}{\Phi}\right) + N_0 \exp\left(-\frac{Q_N}{RT(t')}\right)\right] d\frac{T(t')}{\Phi}$$

$$\cong N^* + \frac{RN_0}{Q_N \Phi} T(t)^2 \exp\left(-\frac{Q_N}{RT(t)}\right) \quad (21)$$

Equation 21 holds for the case of isochronal heating with $T_0 < T(t)$ and $\frac{Q_N}{RT} >> 1$ (usually $\frac{Q_N}{RT} \geq 25$))[1].

Now, adopting the philosophy as described above Eq. 13 for the case of isothermal annealing, it appears appropriate for isochronal annealing to incorporate the nucleation index a as follows,

$$N(T(t)) = N^* + \left[\frac{RN_0}{Q_N \Phi} T^2(t) \exp\left(-\frac{Q_N}{RT(t)}\right)\right]^a \quad (22)$$

and the corresponding nucleation rate is given by,

$$\dot{N}(T(t)) \cong N^* \delta\left(\frac{T(t) - T_0}{\Phi}\right) + aN_0^a \left(\frac{R}{Q_N \Phi}\right)^{a-1}$$

$$T(t)^{2(a-1)} \exp\left(-\frac{aQ_N}{RT(t)}\right) \quad (23)$$

Thus the extended volume can be given as (see Eq. 10),

$$V^e = V \left[\int_{T_0}^{T(t)} \left(\begin{array}{c} N^* \delta\left(\frac{T(\tau) - T_0}{\Phi}\right) \\ + aN_0^a \left(\frac{R}{Q_N \Phi}\right)^{a-1} \exp\left(-\frac{aQ_N}{RT(\tau)}\right) T(\tau)^{2(a-1)} \end{array}\right) g \right.$$

$$\left. \left(\int_{T(\tau)}^{T(t)} v_0 \exp\left(-\frac{Q_G}{RT(t')}\right) d\frac{T(t')}{\Phi}\right)^{d/m} d\frac{T(\tau)}{\Phi}\right] \quad (24)$$

where N^* and N_0 represent the relative contributions of the two modes of nucleation considered. Interface-controlled growth has been adopted (see below Eq. (9)); this is not a restriction; see below. Now, applying an analogous treatment as that performed in Ref. [13] (see Eqs. 28–34 in Ref. [13]), the extended volume is rewritten as,

$$V^e = \frac{Vgv_0^{d/m}}{(d/m + 1)^{\frac{1}{1 + (r_2/r_2)^{-1}}}} \left[\left(\frac{N^*}{(Q_G)^{d/m}}\left(1 + \frac{r_2}{r_1}\right)\right)^{\frac{1}{1 + \frac{r_2}{r_1}}}\right.$$

$$\times \left.\left(C_c^* N_0^a \left(1 + \left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1 + \left(\frac{r_2}{r_1}\right)^{-1}}}\right]$$

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

$$\times \left.\left(\frac{RT^2}{\Phi}\right)^{d/m + \frac{a}{1 + \left(\frac{r_2}{r_1}\right)^{-1}}}\right] \quad (25)$$

with C_c^* as a constant, defined by the activation energies of nucleation and growth as well as the nucleation index, a (see Table 4); for r_2/r_1, see Table 2.

After substitution of Eq. 25 into Eq. 11 it can be derived,

$$\ln(-\ln(1-f)) = \ln\left[\frac{\frac{gv_0^{d/m}}{(d/m+1)^{1+(r_2/r_1)^{-1}}}\left(\frac{N^*}{(Q_G)^{d/m}}\left(1 + \frac{r_2}{r_1}\right)\right)^{\frac{1}{1+\frac{r_2}{r_1}}}}{\left(C_c^* N_0^a \left(1 + \left(\frac{r_2}{r_1}\right)^{-1}\right)\right)^{\frac{1}{1+\left(\frac{r_2}{r_1}\right)^{-1}}}}\right]$$

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

$$+ \left(d/m + \frac{a}{1 + \left(\frac{r_2}{r_1}\right)^{-1}}\right)\ln\left(\frac{RT^2}{\Phi}\right) \quad (26)$$

By comparing Eqs. 19 and 26 temperature dependent values of n, Q and K_0 result, which have been gathered in Table II. Hence, incorporating a nucleation index ($a > 1$) does not affect the general equation for the degree of transformation in case of isochronal transformation (cf. Eq. 2). Similar results are obtained if volume diffusion controlled growth is considered.

Table 4 Expressions for the correction factor, C_c^*, (c.f. Table 2)

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

Experimental example: crystallization of amorphous $Zr_{50}Al_{10}Ni_{40}$

To illustrate the importance of including the nucleation index into the description of transformation kinetics, the transformation model has been applied, using different combinations of nucleation and growth modes (see sections 'Synopsis of theoretical background and The nucleation index, a'), to describe the rate of enthalpy change, measured by DSC, due to isochronal crystallization of amorphous $Zr_{50}Al_{10}Ni_{40}$. For details about the experiments performed, see Ref. [20]. The measured heat release due to crystallization is proportional to df/dT i.e. $\frac{d\Delta H}{dT} = \Delta H_t \frac{df}{dT}$ with ΔH_t as the total enthalpy of crystallization. $\Delta H_t \frac{df}{dT}$ has been calculated on the basis of Eqs. 25 and 11 and has been fitted to the experimental DSC data $\frac{d\Delta H}{dT}$. The general fitting procedure as proposed and described in Ref. [15] was applied.

The best fit was obtained adopting mixed nucleation and interface-controlled growth as modes of nucleation and growth. Incorporation of the nucleation index was essential to arrive at a good fit: Results obtained by fitting using an imposed value of $a = 1$ (implying no effect of the nucleation index) can be compared with the results obtained by the general fitting yielding $a = 4.6$: see Fig. 1(a, b). A value of the nucleation index significantly larger than one indicates that the nucleation rate is substantially increased during the transformation. This is reflected in the occurrence of relatively high transformation-rate maxima, which cannot be described by classical nucleation modes, as continuous nucleation in a JMA description (Fig. 1).

Temperature dependence of site saturation: "activation energy" for supercritical particle formation

Upon rapid cooling/quenching of a phase stable at elevated temperature this phase can become metasta-

ble at lower temperatures, e.g. an amorphous alloy or a supersaturated crystalline solid solution may occur, which strives for crystallization or decomposition, respectively. Depending on the precise thermal history of such metastable phases a certain amount of particles of a new, stable phase may have been "frozen in". If a heat treatment is applied subsequently to such a metastable phase with "frozen-in" particles of the new, stable phase, then those particles larger than the critical size (which are called the nuclei of the new, stable phase [3]) can grow, implying occurrence of site saturation (cf. section 'Synopsis of theoretical background'). Given a certain size distribution for the "frozen-in" particles of the new, stable phase, it is evident that the number of nuclei (= supercritical particles) acting in the site saturation nucleation mechanism is temperature dependent. Hence it
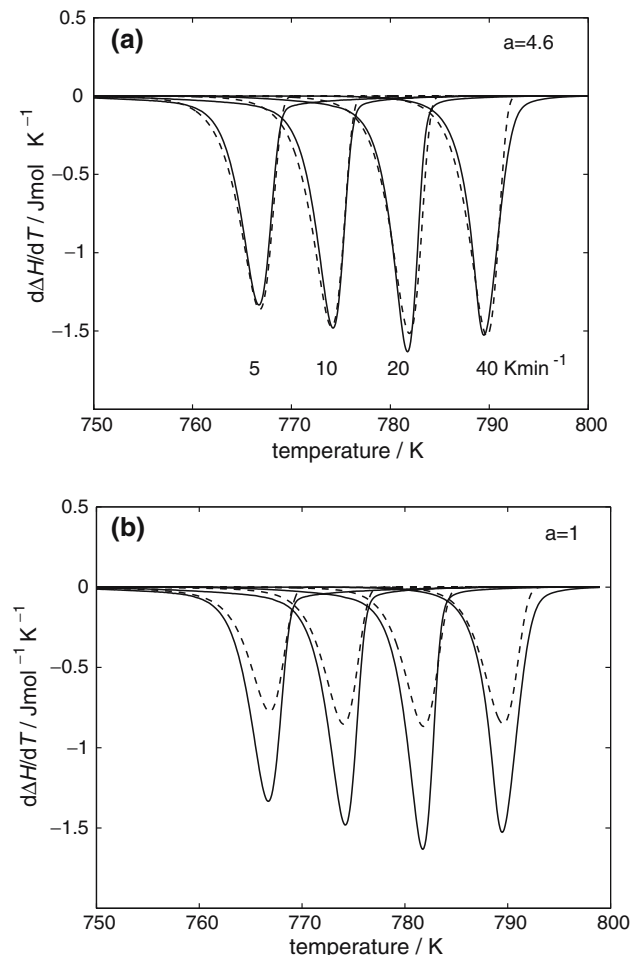

Fig. 1 Rate of enthalpy change, $d\Delta H/\Phi\ dt = d\Delta H/dT$ due to isochronal crystallization of amorphous $Zr_{50}Al_{10}Ni_{40}$, at the heating rates indicated, as measured (solid lines) and as fitted (dotted lines) by adopting mixed nucleation as nucleation mode (**a**) $a = 4.6$ and (**b**) $a = 1$, and interface-controlled growth as growth mode

appears appropriate to introduce an "activation energy", Q_s, controlling the number of frozen-in nuclei acting in the transformation.

The critical size of the frozen-in new phase particles depends on temperature as $C/(\Delta T)$[19]. Hence the critical size increases with decreasing undercooling, ΔT, i.e. generally with increasing annealing temperature. Assuming that the size distribution of the frozen-in particles of the new, stable phase exhibits an exponential tail, i.e. the number of particles decreases exponentially for increasing particle size, a description of the temperature dependence of the number of supercritical particles operating in the site saturation nucleation mode according to $\exp\left(\frac{Q_S}{RT}\right)$ appears reasonable. (Note that the number of active sites decreases with increasing annealing temperature: thus Q_S is *not* an activation energy in the usual sense, which would have required a minus sign in the argument of the exponent).

It is important to distinguish between isothermal and non-isothermal transformations. Evidently, at constant temperature Q_S fully determines the constant number of nuclei at $t \geq 0$. However, a complication occurs for non-isothermal transformations. Consider the case of increasing temperature during the transformation (as in isochronal annealing experiments). Without more ado it cannot be excluded that particles of the new phase which are supercritical at T_1 become subcritical at $T_2(> T_1)$, albeit growth has occurred during heating up from T_1 to T_2. Hence, in order to know the number of active sites in the site saturation mechanism in non-isothermal experiments, the competition between the heating rate and the growth rate has to be considered. Here the analytical treatment is only performed for the isothermal case.

For isothermal transformations conducted at different annealing temperatures, different values for the number of the supercritical particles occur for each annealing temperature T. Equation 4 can then be rewritten as,

$$\dot{N}(T,t) = N_S^* \exp\left(\frac{Q_S}{RT}\right)\delta(t-0) \qquad (27)$$

with N_S^* as a constant. It follows for the extended volume (cf. Eq. 10),

$$
\begin{aligned}
V^e = V \int_0^t & \left(N_S^* \exp\left(\frac{Q_S}{RT}\right)\delta(\tau-0)\right)g \\
& \times \left(\int_\tau^t v_0 \exp\left(-\frac{Q_G}{RT}\right)dt'\right)^{d/m} d\tau
\end{aligned}
\qquad (28)
$$

where interface-controlled growth has been adopted (see below Eq. 9); this is not a restriction; see below. Proceeding analogously to the treatment in section 'Isochronal transformation', it is obtained,

$$V^e = V g v_0^{d/m} N_S^* \exp\left(-\frac{d/mQ_G - Q_S}{RT}\right)t^{(d/m)} \qquad (29)$$

After substitution of Eq. 29 into Eq. 11 it is obtained for the dependence on time for the degree of transformation,

$$
\begin{aligned}
\ln(-\ln(1-f)) = & \ln\left[g v_0^{d/m} N_S^*\right] \\
& - \left(\frac{d/mQ_G - Q_S}{RT}\right) + (d/m)\ln t
\end{aligned}
\qquad (30)
$$

Comparing Eq. 30 with Eq. 19 it follows that constant values of n, Q and K_0 occur in this case; see Table III.

Time dependent values for n, Q and K_0 were derived in this work for the combination of site saturation with either continuous nucleation or Avrami nucleation; see the results presented in Table 1. The introduction of Q_S leads to the following modified expression for the effective, overall, activation energy (cf. Eq. 3):

$$Q = \frac{d/m\left(Q_G - \frac{Q_S}{d/m}\right) + (n - d/m)(Q_N + Q_S)}{n} \qquad (31)$$

Similar results are obtained if volume diffusion controlled growth is considered. Hence, incorporating Q_S does not affect the general equation for the degree of transformation in case of isothermal transformation (cf. Eq. 1).

Recipes for determination of kinetic parameters from isothermally and isochronally conducted transformations

Fitting of the general Eqs. 1 and 2, after insertion of the appropriate expressions for n, Q, and K_0 (see Tables 1–3) to a series of isothermal anneals or to a series of isochronal anneals, respectively, leads to determination of the model parameters which are for the cases considered here: Q_N and Q_G, or Q_N and Q_G and a (i.e. incorporating the nucleation index), and v_0, together with either N^* and N_0 (site saturation and continuous nucleation) or N' and λ_0 (Avrami nucleation) or N^*, N', and λ_0 (site saturation plus Avrami nucleation). Note that the incorporation of Q_S changes the model parameters Q_N and Q_G into $Q'_N = Q_N + Q_S$ and

$Q'_G = Q_G - Q_S/d/m$ (see Eq. 31); in the following only the symbols Q_N and Q_G will be used. The numerical procedure for fitting and a discussion on independent vs. dependent fit parameters have been given in Ref. [15].

The most important kinetic parameters for phase transformation obviously are the growth exponent, n, the effective activation energy, Q, and the nucleation and growth activation energies, Q_N and Q_G. It would be very useful if a simple, direct method, instead of the elaborate numerical approach discussed in Ref. [15], could be proposed to obtain values for these particular kinetic parameters. It is shown in this section that, indeed, simple recipes can be given for determination of the time and/or temperature dependent growth exponent, n, and effective activation energy, Q. Subsequently, the constant Q_N and Q_G values can be determined from the dependence of Q on n using Eq. 3.

The following recipes are derived here on the basis of mixed nucleation incorporating the nucleation index a; for general validity of the recipes, see section 'General applicability of the recipes; determination of the constant activation energies for nucleation, Q_N, and growth, Q_G'.

Isothermal transformation

Growth exponent, n(f)

In classical JMA analysis (then n, Q, and K_0 do *not* depend on transformation time), a plot is made of $\ln(-\ln(1-f))$ vs. $\ln(t)$ (cf. Eq. 19). Thus a straight line occurs with slope $n = d/m + 1$ in case of pure continuous nucleation or $n = d/m$ in case of pure site saturation. This is also valid if a and Q_S are introduced in case of pure continuous nucleation and pure site saturation, respectively.

According to the kinetic model (cf. Tables 1 and 2), n is in general a function of both transformation time and temperature. The ratio r_2/r_1 can be rewritten for isothermal transformation, for mixed nucleation incorporating the nucleation index, as ct^a (with c as a constant; cf. Tables 1 and 2). It then follows from Eq. 19 that,

$$\frac{d(\ln(-\ln(1-f)))}{d\ln t} = d/m + \frac{a}{1 + \left(\frac{r_2}{r_1}\right)^{-1}} = n(t)_T = n(f)_T$$

(32)

The curve obtained by plotting $\ln(-\ln(1-f))$ vs. $\ln(t)$ also not yield truly straight line. The slope at time t provides the value of $n(t)$ at time t. Only for the limiting cases, $r_2/r_1 \to 0$ or $r_2/r_1 \to \infty$, the $\ln(-\ln(1-f))$ vs. $\ln(t)$ curve becomes a straight line with $d(\ln(-\ln(1-f)))/d\ln(t)$ equal to d/m or $d/m + a$, respectively. Once the dependence of n on t is known the dependence of n on f, *for the annealing temperature considered*, can be determined straightforwardly from each isothermal annealing experiment as the relation between t and f has been determined experimentally for each annealing temperature.

Effective activation energy, Q(f)

Values for the activation energy can be obtained from the lengths of time, t_f, needed to attain a certain fixed value of f at different isothermal annealing temperatures. The data points in a plot of $\ln(t_f)$ vs. $1/T$ are usually approximated by a straight line, from the slope of which, a value for $Q(f)$ independent of the annealing temperature is obtained [1]. This linearity in the plot of $\ln(t_f)$ vs. $1/T$ occurs only if the effective activation energy, Q, is constant during the transformation.

According to the kinetic model (cf. Tables 1 and 2), Q is in general both a function of transformation time and temperature. The ratio r_2/r_1 can be expressed as $c't^a \exp(-aQ_N/RT)$ (with c' as a constant; cf. Tables 1 and 2). Differentiation of both sides of Eq. 19 with respect to $1/T$ then gives,

$$\frac{d(\ln t_f)}{d(1/T)} = \frac{d/mQ_G + \frac{a}{1 + \left(\frac{r_2}{r_1}\right)^{-1}} Q_N}{\left(d/m + \frac{a}{1 + \left(\frac{r_2}{r_1}\right)^{-1}}\right) R} = \frac{Q(f)_T}{R},$$

$$\text{with } Q(f)_T = \frac{d/mQ_G + (n(f)_T - d/m)Q_N}{n(f)_T}$$

(33)

Plotting of $\ln(t_f)$ vs. $1/T$ will not yield a truly straight line. Thus the value of $Q(f)$ depends on the temperature where the slope of the plot of $\ln(t_f)$ vs. $1/T$ is taken. To determine the slope in practice, several annealing temperatures are required. The slope of the straight lines drawn through the data points of two of these temperatures can then be considered as an approximation for $Q(f)$ corresponding to a temperature between these two annealing temperatures.

Only for the limiting cases, $r_2/r_1 \to 0$ or $r_2/r_1 \to \infty$, the $\ln(t_f)$ vs. $1/T$ curve becomes a truly straight line and Q then equals Q_G or $(d/mQ_G + aQ_N)/n$, corresponding to $n = d/m$ and $n = d/m + a$, respectively. The dependence of Q on f at different temperatures can be

determined by repeating the above procedure for a chosen number of f values.

Isochronal transformation

Growth exponent, n(f)

Values for the growth exponent can be obtained from the transformed fraction, f_T, attained at a certain fixed value of T, as measured for different heating rates. The data points in a plot of $\ln(-\ln(1 - f_T))$ vs. $\ln(\Phi)$ can be represented by a straight line if the growth exponent, n, is constant during the transformation. The slope of this straight line then equals n.

According to the kinetic model (cf. Tables 1 and 2), $n(f)$ is in general a function of both transformation temperature and heating rate. Differentiation of both sides of Eq. 26 with respect to $\ln\Phi$ then gives,

$$\frac{d(\ln(-\ln(1 - f_T)))}{d\ln(\Phi)} = d/m + \frac{a}{1 + \left(\frac{r_2}{r_1}\right)^{-1}} \quad (34)$$
$$= n(T)_\Phi = n(f)_\Phi$$

Plotting of $\ln(-\ln(1 - f_T))$ vs. $\ln(\Phi)$ will not yield a truly straight line. Thus the value of $n(T)_\Phi$ depends on the heating rate where the slope of the plot of $\ln(-\ln(1 - f_T))$ vs. $\ln(\Phi)$ is taken. To determine the slope in practice, several heating rates are required. The slope of the straight lines drawn through the data points of two of these heating rates can be considered as an approximation for $n(T)_\Phi$ corresponding to a heating rate between these two heating rates. Only for the limiting cases, $r_2/r_1 \rightarrow 0$ or $r_2/r_1 \rightarrow \infty$, the above curve becomes a straight line with their slopes equal to d/m or $d/m + a$, respectively. The dependence of n (at a fixed Φ) on T can be determined by repeating the above procedure for a chosen number of T values. Once for a certain heating rate the dependence of n on T is known, the dependence of n on f, for the heating rate considered, can be determined as the relation between f and T has been determined experimentally.

Effective activation energy, Q(f)

Values for the activation energy can be obtained upon isochronal annealing from the temperature, T_f, needed to attain a certain fixed value of f, as measured for different heating rates. The data points in a plot of $\ln(T_f^2/\Phi)$ vs. $1/T_f$ are usually approximately by a straight line, from the slope of which a value for $Q(f)$ independent of the heating rate is obtained [1]. This linearity in the plot of $\ln(T_f^2/\Phi)$ vs. $1/T_f$ occurs only if

the effective activation energy, Q, is constant during the transformation.

For the case of constant effective activation energy, the above approach was proposed originally by Kissinger [21] for special cases of reaction kinetics, although, instead of T_f, the temperature where the transformation-rate maximum occurs was used. The corresponding, so-called Kissinger procedure has been and is often used, usually without justification. Mittemeijer [1] was the first to derive the general validity of the analysis, provided that the temperature of maximal transformation rate is replaced by the temperature of the same degree of transformation, T_f.

According to the kinetic model (cf. Table 2), Q is in general a function of both transformation temperature and heating rate. Differentiation of both sides of Eq. 26 with respect to $1/T_f$ gives,

$$\frac{d\left(\ln T_f^2/\Phi\right)}{d(1/T_f)R} = -\frac{\frac{d}{m}Q_G + \frac{a}{1 + \left(\frac{r_2}{r_1}\right)^{-1}}Q_N}{d/m + \frac{a}{1 + \left(\frac{r_2}{r_1}\right)^{-1}}} = -Q(f)_\Phi,$$
$$\text{with } Q(f)_\Phi = \frac{d/m Q_G + (n(f)_\Phi - d/m)Q_N}{n(f)_\Phi} \quad (35)$$

Plotting of $\ln(T_f^2/\Phi)$ vs. $1/T_f$ will not yield a truly straight line. Thus the value of $Q(f)$ depends on the heating rate where the slope of the plot of $\ln(T_f^2/\Phi)$ vs. $1/T_f$ is taken. To determine the slope in practice, several heating rates are required. The slope of the straight lines drawn through the data points of two of these heating rates can be considered as an approximation for $Q(f)$ corresponding to a heating rate between these two heating rates. Only for the limiting cases, $r_2/r_1 \rightarrow 0$ or $r_2/r_1 \rightarrow \infty$, $\ln(T_f^2/\Phi)$ vs. $1/T_f$ becomes a truly straight line and Q then equals to Q_G or $(d/m Q_G + a Q_N)/n$, respectively. The dependence of Q on f at different heating rates can be determined by repeating the above procedure for a chosen number of f values.

Product of growth exponent and effective activation energy, Q(f)n(f)

Analogous to section 'Growth exponent, $n(f)$' for isothermal transformation, in classical JMA analysis (then n, Q, and K_0 do *not* depend on transformation temperature) and for isochronal transformation, a plot can be made of $\ln(-\ln(1 - f))$ vs. $\ln(1/T)$ (cf. Eq. 26) at constant heating rate. Thus a straight line occurs with slope $-nQ/R = -(d/m Q_G + Q_N)/R$ in case of pure continuous nucleation or $-nQ/R = -d/m Q_G/R$ in case of pure site saturation. This is also valid if a is introduced in case of pure continuous nucleation.

According to the kinetic model (cf. Tables 1 and 2), n and Q are in general a function of both transformation temperature and heating rate. Differentiation of both sides of Eq. 26 with respect to $1/T$ then gives,

$$
\frac{d(\ln(-\ln(1-f)))}{d(1/T)} = -\frac{d/mQ_G + \frac{a}{1+\left(\frac{r_2}{r_1}\right)^{-1}}Q_N}{R}
$$
$$
-2\left(d/m + \frac{a}{1+\left(\frac{r_2}{r_1}\right)^{-1}}Q_N\right)T
$$
$$
= -\frac{[n(T)Q(T)]_\Phi}{R} - 2n(T)_\Phi T
$$

(36)

If $Q \gg RT$, plotting of $\ln(-\ln(1-f))$ versus $1/T$ gives a curve (or straight line) with slope equal to $-\frac{[n(T)Q(T)]_\Phi}{R}$. Hence the slope of the curve of $\ln(-\ln(1-f))$ vs. $1/T$ at temperature T provides the value of $[n(T)Q(T)]$ at heating rate Φ. Only for the limiting cases, $r_2/r_1 \to 0$ or $r_2/r_1 \to \infty$, the $\ln(-\ln(1-f))$ vs. $1/T$ curve becomes a straight line with $d(\ln(-\ln(1-f)))/d(1/T)$ equal to $-d/mQ_G/R$ or $-(d/mQ_G + aQ_N)/R$, respectively. Thus the dependence of $(n(T)Q(T))_\Phi$ on f, *for the heating rate considered*, can be determined from each isochronal annealing experiment as the relation between T and f has been determined experimentally for each heating rate.

General applicability of the recipes; determination of the constant activation energies for nucleation, Q_N, and growth, Q_G

The above recipes have been deduced analytically here for phase transformations controlled by mixed nucleation (site saturation and continuous nucleation (incorporating the nucleation index)), and either interface-controlled growth or diffusion-controlled growth.

For Avrami nucleation or site saturation plus Avrami nucleation as nucleation mechanisms, these recipes cannot be derived analytically. However, as will be shown below by numerical calculations, the principles of the recipes given hold also in these cases.

Using the values for the model parameters as given in Table 5, numerical calculations of f have been performed for four different temperatures ($T = 580$, 590, 600, and 610 K) as a function of time (isothermal annealing) and for four different heating rates ($\Phi = 0.05$, 0.25 1.25, and 6.25 K/s) as a function of temperature (isochronal annealing).

For the case of site saturation plus Avrami nucleation as nucleation mechanism and interface-controlled growth as growth mechanism, the numerically calculated evolutions of n with f and of Q with f (on the basis of Eqs. 1 (see Table 1) and 11), for *isothermal transformation*, are shown in Fig. 2a and b, respectively. As expected, for the kinetic model considered, the values of n and Q as a function of f are both not constant and depend on the transformation temperature. Applying the recipe given by Eq. 32 for the considered temperatures gives sets of n values (data points in Fig. 2a), which agree well with the exact values of n (lines in Fig. 2a) over the entire range of f. Applying the recipe given by Eq. 33 for the considered temperatures gives sets of Q values (data points in Fig. 2b). The value of Q is determined by the slope between the data points of two applied temperatures (see discussion below Eq. 33). The results thus obtained agree very well with the exact values of Q as calculated for the mean temperature of the two applied
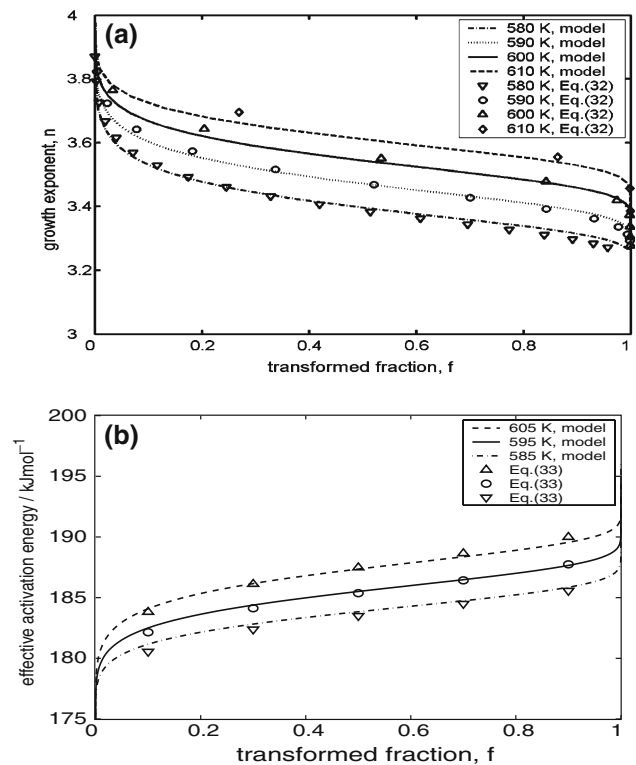

Fig. 2 The growth exponent, n (**a**) and the effective activation energy, Q (**b**), as a function of the transformed fraction, f, for isothermal transformation controlled by Avrami nucleation plus site saturation as nucleation mode and interface-controlled growth as growth mode, at temperatures of 580, 590, 600 and 610 K, calculated using the values of the kinetic parameters as given in Table 5. Lines: model results; Symbols: results obtained by application of the recipes given by Eqs. 32 and 33, respectively

Table 5 Values of the kinetic parameters used for the numerical calculations of isothermally and isochronally conducted phase transformations for the case of site saturation plus Avrami nucleation as nucleation mode and interface controlled growth as growth mode

Parameters	d/m	N^* m^{-3}	N' m^{-3} s^{-1}	λ_0 s^{-1}	Q_N kJ mol^{-1}	Q_G kJ mol^{-1}	v_0 ms^{-1}
Values	3	1×10^{10}	5×10^{15}	1×10^6	100	200	10^9

temperatures (full lines in Fig. 2b), over the entire range of f.

The n values for the temperatures and transformed fractions considered in Fig. 2b can be obtained by straightforward interpolation from the data of the temperatures given in Fig. 2a. The dependence of $Q(f)$ on $n(f)$, at a fixed temperature (here, e.g. 585, 595 and 605 K), is obtained. Fitting of Eq. 3 to these $(Q(f), n(f))$ data for the same temperature leads to values for the separate, constant activation energies for nucleation and growth, Q_N and Q_G. The values thus obtained ($Q_N = 98$ kJ/mol) and ($Q_G = 202$ kJ/mol) are (indeed) practically equal to the true values (see Table 5).

For the case of site saturation plus Avrami nucleation as nucleation mechanism and interface-controlled growth as growth mechanism, the numerically calculated evolutions of n with f and Q with f, for *isochronal transformation* (on the basis of Eqs. 2 (see Table 1) and 11), are shown in Figs. 3a and b, respectively. As expected, for the kinetic model considered, the values of n and Q as a function of f are both not constant and depend on the heating rate. Applying the recipes given by Eqs. 34 and 35 to the transformation curves at the considered heating rates gives sets of $n(f)$ and $Q(f)$ values (data points in Fig. 3). The values of $n(f)$ and $Q(f)$ are determined by the slope between data points of two applied heating rates (see discussions below Eqs. 34 and 35). Combining the results shown in Figs. 3a and b, the dependence of $Q(f)$ on $n(f)$, at a fixed heating rate, is obtained. Fitting of Eq. 3 to these $(Q(f), n(f))$ data for the same heating rate leads to values for the separate, constant activation energies for nucleation and growth, Q_N and Q_G. The values thus obtained ($Q_N = 95$ kJ/mol) and ($Q_G = 204$ kJ/mol) are practically equal to the true values (see Table 5).

Conclusions

(1) To describe phase transformation kinetics, generally applicable JMA-like equations are possible taking the growth exponent, n, the effective activation energy, Q, and the pre-exponential factor, K_0, as time and/or temperature dependent. This work has led to analytical expressions for n, Q and K_0 for two cases:

(i) adoption of the nucleation index, a, to allow for a nucleation rate increasing with progressing transformation; the resulting transformation model could be fitted very well to the isochronal crystallization of amorphous $Zr_{50}Al_{10}Ni_{40}$ alloys;

(ii) introduction of temperature dependence of site saturation, i.e. adoption of an "activation energy" for supercritical particle formation in site saturation.

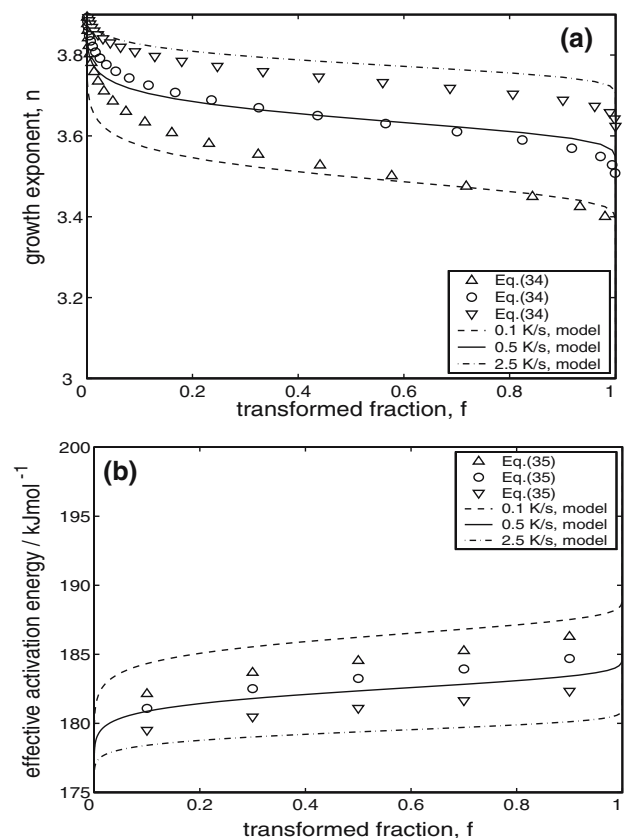(2) Several generally applicable recipes have been derived to deduce the growth exponent, n, and the

Fig. 3 The growth exponent, n (**a**) and the effective activation energy, Q (**b**), as a function of the transformed fraction, f, for isochronal transformation controlled Avrami nucleation plus site saturation as nucleation mode and interface-controlled growth as growth mode, at heating rates of 0.05, 0.25, 1.25, 6.25 K/s, calculated using the values of the kinetic parameters as given in Table 5. Lines: model results; Symbols: results obtained by application of the recipes given by Eqs. 34 and 35, respectively

effective activation energy, Q, both as function of time (isothermal transformation) or temperature (isochronal transformation), directly from measured kinetic data. The resulting dependence of Q on n leads to straightforward determination of the constant activation energies for nucleation and growth.

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