

# Comparison between an analytical model and JMA kinetics for isothermally and isochronally conducted transformations

F. Liu<sup>a,\*</sup>, G.C. Yang<sup>a</sup>, J.N. Liu<sup>b</sup>

<sup>a</sup> State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China

<sup>b</sup> Materials Department, Xi'an Institute of Technology, Xi'an, Shaanxi 710032, PR China

Received 11 June 2005; received in revised form 2 August 2005; accepted 13 August 2005

Available online 3 October 2005

## Abstract

Applying an analytical model, both isothermally and isochronally conducted transformations are formulated, using time/temperature-dependent kinetic parameters. In specific cases, the analytical model reduces to the Johnson–Mehl–Avrami (JMA) kinetics. Fits of JMA kinetics to exact numerical calculations and analytical solutions using the same values for model parameters (as chosen in the numerical calculation) have been performed for different temperatures (isothermal) or different heating rates (isochronal), respectively. According to the error analysis, only in the extreme cases where pure site saturation or pure continuous nucleation prevails, JMA kinetics with constant kinetic parameters is applicable; but for intermediate cases where mixed nucleation or Avrami nucleation dominates, kinetic parameters change with progressing transformation. This implies that the effective activation energy and the growth exponent generally depend on time/temperature, even if the transformation mechanism is constant (isokinetic).

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Nucleation; Growth; Isothermal; Isochronal; Crystallization kinetics

## 1. Introduction

Solid-state phase transformations are important means for the adjustment of the microstructure and thus the tuning of the properties of materials. In order to exploit this tool to full extent, much effort is spent on the modeling of phase transformations [1–18]. In the classical treatment (c.f. ref. [5]) Johnson–Mehl–Avrami (JMA) approach [1–4] plays a central role in studies of transformations where nucleation and growth mechanisms operate. Very many experimental results of phase transformation kinetics have been fitted with a JMA model. It should however be recognized that the JMA model can only be validated for certain extreme, limiting cases, in particular for nucleation (see Section 2). The JMA model implies that the growth exponent  $n$  and the effective activation energy  $Q$  should be constant during the course of the transformation. New development in experimental techniques allow high accuracy in the experimental data on transformation kinetics and have unambiguously determined that, as a rule,  $n$

and  $Q$  are not constant (e.g. [8,15–22]): 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 [16–22], i.e. the transformation process is not isokinetic. Fitting of JMA kinetics to such phase transformations therefore only yields a phenomenological description. However, the limited validity of the classical JMA approach may be the cause for this, then only seemingly, incompatibility with isokinetics [23] and a critical reappraisal of the modeling of phase transformation kinetics appears in order.

Against this background, an *analytical* model for solid-state phase transformations has been developed that incorporates the three mechanisms: nucleation (e.g. mixed nucleation and/or Avrami nucleation), growth (interface-controlled and/or volume diffusion-controlled growth) and impingement [24]. The model has been developed for both isothermally and isochronally conducted transformations, with time  $n(t)$ ,  $Q(t)$ ,  $K_0(t)$  or temperature  $n(T)$ ,  $Q(T)$ ,  $K_0(T)$ -dependent kinetic parameters (for which analytical descriptions have been given [24–26]). It should be noted that, consequently, a transformation can still be considered as “isokinetic” in the sense indicated above, although a kinetic parameter, as the growth exponent  $n$ , can distinctly vary during the course of a transformation.

\* Corresponding author. Tel.: +86 29 88460372; fax: +86 29 88492374.

E-mail address: [liufeng@nwpu.edu.cn](mailto:liufeng@nwpu.edu.cn) (F. Liu).

<sup>1</sup> On leave from Max-Planck-Institute for Metals Research.

Basing on exact numerical calculations, analytical solutions were herein given using the same values for model parameters; meanwhile the corresponding fits of JMA kinetics were provided. Detailed comparison between analytical solutions/fits of JMA kinetics and exact numerical calculations has been carried out. It can be proved from the error analysis that JMA kinetics with constant kinetic parameters is applicable only for the extreme cases; but for intermediate cases where mixed nucleation or Avrami nucleation occurs, the kinetic parameters change with progressing transformation.

## 2. Phase transformation kinetics

### 2.1. The path variable for isothermal and non-isothermal transformations

Time and temperature in general are not state variables which would determine the stage of transformation: the thermal history of a material determines the degree of transformation,  $f$  ( $0 \leq f \leq 1$ ). Therefore, it appears appropriate to introduce a path variable,  $\beta$ , which fully determines  $f$  and depends on the thermal history, i.e. the path followed in the temperature–time diagram:  $T(t)$  prescribes  $\beta$  [6]. The transformed fraction,  $f$ , can then be given as [6]

$$f = F(\beta) \quad (1)$$

The dependence of the path variable  $\beta$  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  $T$

$$\beta = \int K(T(t)) dt \quad (2)$$

This equation is compatible with the additively rule [5,6,23], which supposes that throughout the temperature/time range of interest the transformation mechanism is the same (which is called isokinetic). A change of transformation mechanism in the course of the transformation, as might be caused by a rate constant  $K(T(t))$  that is not solely dependent on  $T(t)$ , would cause a breakdown of the additively rule and the applicability of Eq. (2) for the path variable. For many applications,  $K(T)$  can be given by an Arrhenius-type equation

$$K(T(t)) = K_0 \exp\left(-\frac{Q}{RT(t)}\right) \quad (3)$$

with  $Q$  as the overall, effective activation energy,  $K_0$  the temperature- and time-independent rate and  $R$  as the gas constant. It follows from Eqs. (2) and (3) for isothermal annealing [6]

$$\beta = K(T)t \quad (4a)$$

According to a detailed description for the temperature integral and its approximation, for isochronal annealing with a constant heating rate  $\Phi$ , it holds (c.f. refs. [6,10,15])

$$\beta \cong \left[ \frac{K_0 \Phi R t'^2}{Q} \exp\left(-\frac{Q}{R\Phi t'}\right) \right] \quad (4b)$$

where  $t' = t + T_0/\Phi$  with  $T_0$  as the start temperature of the transformation (i.e. at  $t=0$ ). Eq. (4b) is only valid for heating.

### 2.2. Modes of nucleation, growth and impingement

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 [15,24]

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

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 [15,24]

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

where  $N_0$  is a temperature-independent nucleation rate constant and  $Q_N$  is the temperature- and time-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 [15,24]

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

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 [1–4,15,24]

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

where  $\lambda$  is the rate at which an individual sub-critical nucleus becomes supercritical  $\lambda(t = \tau) = \lambda_0 \exp\left(-\frac{Q_N}{RT(\tau)}\right)$ , with  $\lambda_0$  as a temperature-independent rate and  $N'$  as the total number of sub-critical nuclei per unit volume at  $t=0$ .

The *diffusion-controlled and the interface-controlled growth* modes can be given in a compact form. At time  $t$ , the volume  $Y$ , of a particle nucleated at time  $\tau$  is given by refs. [15,24]

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

with  $g$  as a particle-geometry factor and  $v(t) = v_0 \exp\left(-\frac{Q_G}{RT(t)}\right)$  with  $Q_G$  the temperature- and time-independent activation energy of growth and 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 ( $d=1, 2$  and  $3$ ).

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*,  $v_0$  equals the pre-exponential factor for diffusion  $D_0$  and  $Q_G$  represents the activation energy for diffusion,  $Q_D$ .

The number of supercritical nuclei formed in a unit volume, at time  $\tau$  during a time lapse  $d\tau$ , is given by  $\dot{N}(T(\tau))d\tau$  according to Eqs. (5)–(8). The volume of each of these nuclei grows from  $\tau$  until  $t$  according to Eq. (10) 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

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

with  $V$  as the sample volume, which is supposed to be constant throughout the transformation. A relation between the actually transformed volume,  $V^t$ , and the extended transformed volume,  $V^e$ , or between the real transformed fraction,  $f = V^t/V$ , and the extended transformed fraction  $x_e = V^e/V$  is required. The expressions for the extended transformed volume/fraction do not account for the overlap of growing particles (hard 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  $dt$ , the extended and the actual transformed volumes will increase by  $dV^e$  and  $dV^t$ . From the change of the extended volume  $dV^e$ , only a part will contribute to the change of the actually transformed volume  $dV^t$ , namely a part as large as the untransformed volume fraction [1–3,5]. Hence

$$dV^t = \left( \frac{V - V^t}{V} \right) dV^e \quad \frac{df}{dx_e} = 1 - f \quad (11)$$

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

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

In case of anisotropically growing particles, the time interval that particles, after their randomly dispersed nucleation can grow before “blocking” by other particles occurs, is, on average, smaller than for isotropic growth [12,16–18]. This blocking effect due to anisotropic growth leads to hard impingement that results in strong deviations from classical JMA kinetics [12,16–18]. Considering this blocking effect, one phenomenological approach accounting for impingement in this case has been proposed [12,16] by extending Eq. (12) to

$$\frac{df}{dx_e} = (1 - f)^\xi \quad (13)$$

where  $\xi \geq 1$ . Impingement due to Eq. (13) is more severe, i.e. the difference between  $f$  and  $x_e$  is *larger*, than due to Eq. (11) and increases with  $\xi$ .

Further, in diffusion-controlled transformations, as the nano-crystallization of amorphous alloys [27–29] and the gamma–alpha transformation in (carbon-containing) alloyed steels [30,31], overlap of diffusion fields surrounding the growing particles has to be considered (soft impingement). Some

specific analytical and numerical approaches to account for the diffusion fields surrounding the product phase particles have been proposed (e.g. [30–32]), which, however, are unsuited for general applications. The applicability of Eqs. (11) and (12) to diffusion-controlled reactions has been discussed in several recent works [10,12,33–35]. Approximately, within the context of the general analytical transformation model [24,25], models for (hard) impingement are discussed below for both interface- and diffusion-controlled transformations.

### 2.3. General equation for the transformed fraction

According to Eqs. (4)–(9) and for cases for nucleation considered here (as mixed nucleation and Avrami nucleation), the overall extended volume 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. By extensive calculation an explicit analytical expression for the extended volume can be obtained [24]. The degree of transformation can then be derived considering the impingement for example according to Eq. (12).

No matter which of the nucleation or growth modes considered determine the transformation mechanism, the degree of isothermal or isochronal transformation can be uniquely described by combinations of the time-dependent kinetic parameters:  $n(t)$ ,  $Q(t)$  and  $K_0(t)$  (i.e. for isothermal transformation) or the temperature-dependent kinetic parameters  $n(T)$ ,  $Q(T)$  and  $K_0(T)$  (i.e. for isochronal transformation) as

$$f = 1 - \exp\left(K_0(t)^{n(t)} t^{n(t)} \exp\left(-\frac{n(t)Q(t)}{RT}\right)\right) \quad (14)$$

$$f = 1 - \exp\left(K_0(T)^{n(T)} \left(\frac{RT^2}{\Phi}\right)^{n(T)} \exp\left(-\frac{n(T)Q(T)}{RT}\right)\right) \quad (15)$$

It should be noted that these results are fully compatible with Eqs. (1)–(4), see refs. [6,24]. Only if pure site saturation or pure continuous nucleation occurs, Eqs. (14) and (15) are compatible with the description of Johnson–Mehl–Avrami [1–6]

$$f = 1 - \exp\left(-K_0^n \alpha^n \exp\left(-\frac{nQ}{RT}\right)\right) \quad (16)$$

where the kinetic parameters:  $n$ ,  $Q$  and  $K_0$  are constants (i.e. do not depend on time and temperature) and  $\alpha$  can be identified with either the annealing time  $t$  for isothermal transformation, or with  $RT^2/\Phi$  for isochronal transformation.

The effective, overall activation energy,  $Q$ , can always be analytically interpreted as a combination of the activation energies for nucleation and growth,  $Q_N$  and  $Q_G$  [24]

$$Q = \frac{\frac{d}{m} Q_G + \left(n - \frac{d}{m}\right) Q_N}{n} \quad (17)$$

where the value of  $n$  is equal to  $d/m$  for site saturation and equal to  $d/m + 1$  for continuous nucleation. Eq. (17) is also deduced analytically in Ref. [15] for transformations controlled by extreme cases, i.e. pure site saturation and pure continuous nucleation.

Table 1  
Expressions for the (time and temperature dependencies of the) growth exponent,  $n$ , the overall activation energy,  $Q$  and the rate constant,  $K_0$  to be inserted in Eqs. (14) and (15) for isothermal annealing and isochronal annealing, respectively

	Isothermal	Isochronal
<b>Mixed nucleation</b>		
$n$	$\frac{d}{m} + \frac{1}{1 + \left(\frac{r_2}{r_1}\right)^{-1}}$	$\frac{d}{m} + \frac{1}{1 + \left(\frac{r_2}{r_1}\right)^{-1}}$
$Q$	$\frac{\frac{d}{m} Q_G + \left(n - \frac{d}{m}\right) Q_N}{n}$	$\frac{\frac{d}{m} Q_G + \left(n - \frac{d}{m}\right) Q_N}{n}$
$K_0^n$	$\frac{g v_0^{d/m}}{\left(\frac{d}{m} + 1\right)^{1/(1+(r_2/r_1)^{-1})}} \left[ \left( N_1^* \left( 1 + \frac{r_2}{r_1} \right) \right)^{1/(1+(r_2/r_1))} \times \left( N_{01} \left( 1 + \left( \frac{r_2}{r_1} \right)^{-1} \right) \right)^{1/(1+(r_2/r_1)^{-1})} \right]$	$\frac{g v_0^{d/m}}{\left(\frac{d}{m} + 1\right)^{1/(1+(r_2/r_1)^{-1})}} \left[ \left( \frac{N_1^*}{(Q_G)^{d/m}} \left( 1 + \frac{r_2}{r_1} \right) \right)^{1/(1+(r_2/r_1))} \times \left( C_c N_{01} \left( 1 + \left( \frac{r_2}{r_1} \right)^{-1} \right) \right)^{1/(1+(r_2/r_1)^{-1})} \right]$
$\frac{r_2}{r_1}$	$\frac{\frac{1}{\frac{d}{m} + 1} N_{01} t \exp\left(-\frac{Q_N}{RT}\right)}{N_1^*}$	$\frac{C_c Q_G^{d/m} N_{01} \exp\left(-\frac{Q_N}{RT}\right)}{\left(\frac{d}{m} + 1\right) N_1^*} \left( \frac{RT^2}{\Phi} \right)$
<b>Avrami nucleation</b>		
$n$	$n = \frac{d}{m} + \frac{1}{1 + \frac{r_2}{r_1}}$	$n = \frac{d}{m} + \frac{1}{1 + \frac{r_2}{r_1}}$
$Q$	$\frac{\frac{d}{m} Q_G + \left(n - \frac{d}{m}\right) Q_N}{n}$	$\frac{\frac{d}{m} Q_G + \left(n - \frac{d}{m}\right) Q_N}{n}$
$K_0^n$	$\frac{g N' f(\lambda t) v_0^{d/m}}{\frac{d}{m} + 1} (\lambda_0)^{1/(1+(r_2/r_1))} (\lambda t)^{1/(1+(r_2/r_1)^{-1})}$	$\left[ \frac{g v_0^{d/m} N' f\left(\lambda \frac{RT^2}{Q_N \Phi}\right)}{\frac{d}{m} + 1} (\lambda_0)^{1/(1+(r_2/r_1))} \left( \lambda \frac{RT^2}{\Phi} \right)^{1/(1+(r_2/r_1)^{-1})} C_c \right]$
$\frac{r_2}{r_1}$	$\frac{\lambda t}{\frac{d}{m} + 1}$	$\frac{C_c Q_G^{d/m}}{\frac{d}{m} + 1} \left( \frac{RT^2}{\Phi} \lambda \right)$

For  $C_c$ ,  $f(\lambda t)$  and  $f(\lambda RT^2/Q_N \Phi)$ , see ref. [24].

Unlike the extreme cases for which the JMA equation holds strictly, in general,  $n$ ,  $Q$  and  $K_0$  are not constant but will be time (isothermal transformation) or temperature (isochronal transformation)-dependent. They depend on the model parameters, as  $N_1^*$  and  $N_{01}$  (mixed nucleation) or  $N'$  and  $\lambda_0$  (Avrami nucleation),  $Q_N$  and  $Q_G$ , as well as on the annealing temperature  $T$  (isothermal transformations) or the heating rate  $\Phi$  (isochronal transformations); see the analytical functions summarized in Table 1. Fitting of Eqs. (14) and (15), with the appropriate expressions for  $n$ ,  $Q$  and  $K_0$ , to a series of isothermal anneals or to a series of isochronal anneals leads to determination of the model parameters which are for the cases considered here:  $Q_N$ ,  $Q_G$  and  $v_0$  together with either  $N_1^*$  and  $N_{01}$ , or  $N'$  and  $\lambda_0$  [25].

As above mentioned (Section 2.2), it should be noted that the same expressions (Table 1) occur for the kinetic parameters  $n$ ,  $Q$  and  $K_0$  for the two growth modes considered (see Eq. (9)), provided, in case of volume diffusion-controlled growth, the pre-exponential factor,  $v_0$ , and the activation energy,  $Q_G$ , are substituted by  $D_0$  and  $Q_D$ , the pre-exponential factor and the activation energy for diffusion.

Hence, isokinetic transformation (c.f. Section 2.1) does not necessarily require that  $n$ ,  $Q$  and  $K_0$  have to be constants during the course of the transformation, as has very often been stated erroneously (e.g. see refs. [19,21]). Obviously, various combinations of nucleation and growth modes represent different transformation mechanisms, and result in different expressions for  $n(t)$ ,  $Q(t)$ ,  $K_0(t)$  or  $n(T)$ ,  $Q(T)$ ,  $K_0(T)$  and for the transformed fraction subjected to the general expressions Eqs. (14) and (15).

### 3. Calculation results

The following calculations are carried out:

- (1) According to the recipe in Section 2.2, numerical calculation of the transformation rate was performed for a range of model parameters  $Q_G$ ,  $v_0$  and  $d/m$  and  $Q_N$  and  $N_0$  and  $N^*$  or  $\lambda_0$  and  $N'$  (see Table 2). Parameters are chosen such that a mixture of nucleation mechanisms is employed.
- (2) Then JMA fit to the transformation rate and analytical calculation using the same values for model parameters as chosen in the numerical calculations are carried out.
- (3) Rigorous numerical application of the recipe given in Section 2.3 provides the transformation rate,  $df/dt$  or  $df/dT$ , as a

Table 2

Values of the model parameters as used in the numerical calculations for isothermal and isochronal annealing for mixed nucleation or Avrami nucleation and the growth mechanism pertaining to volume diffusion or interface-controlled growth

Mixed nucleation	Values	Avrami nucleation	Values
$Q_G$ (kJ mol <sup>-1</sup> )	300	$Q_G$ (kJ mol <sup>-1</sup> )	200
$Q_N$ (kJ mol <sup>-1</sup> )	200	$Q_N$ (kJ mol <sup>-1</sup> )	100
$v_0$ (m s <sup>-1</sup> )	10 <sup>9</sup>	$v_0$ (m s <sup>-1</sup> )	10 <sup>9</sup>
$d/m$	3/(3/2)	$d/m$	3/(3/2)
$N_0$ (m <sup>-3</sup> s <sup>-1</sup> )	Start 10 <sup>30</sup> , end 10 <sup>27</sup>	$N'$ (m <sup>-3</sup> )	5 × 10 <sup>15</sup>
$N^*$ (m <sup>-3</sup> )	Start 10 <sup>17</sup> , end 10 <sup>20</sup>	$\lambda_0$ (m <sup>-3</sup> s <sup>-1</sup> )	Start 10 <sup>5</sup> , end 10 <sup>8</sup>

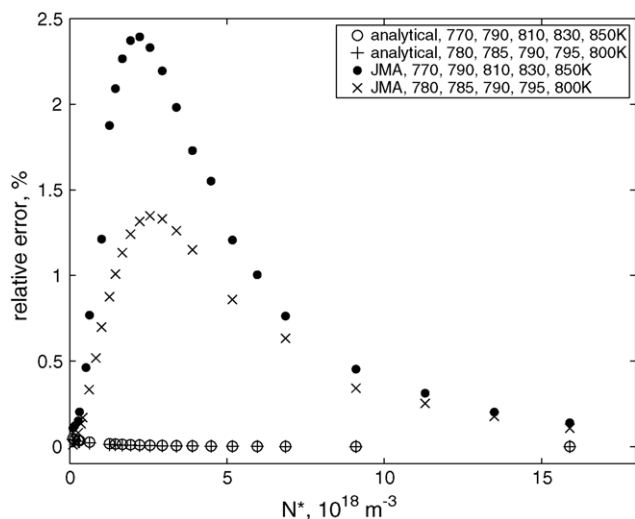


Fig. 1. Relative error (of  $df/dt$ ) from analytical solutions or JMA fits as a function of model parameter,  $N^*$  for isothermal annealing assuming mixed nucleation and interface-controlled growth at two sets of annealing temperatures.

function of time/temperature. This calculation is performed for five different temperatures (isothermal annealing) or five different heating rates (isochronal annealing), assuming interface-controlled growth mode.

- (4) JMA kinetics (see Eqs. (1)–(4)) is fitted to the transformation rate as obtained in step 3 simultaneously for the five different temperatures,  $T$  (isothermal annealing) or five different heating rates,  $\Phi$  (isochronal annealing). Thus values for the kinetics parameters,  $n$ ,  $Q$  and  $K_0$  are obtained [15].
- (5) Using the same values for the model parameters and the values of  $T$  or  $\Phi$  as chosen in the numerical calculation, the corresponding analytical expressions for  $df/dt$ , or  $df/dT$  (see Eq. (14) or (15) and Table 1) result as well.

The above procedure has been performed for a range of values of  $N_0$  and  $N^*$  or  $\lambda_0$  (see Table 2), and good agree-

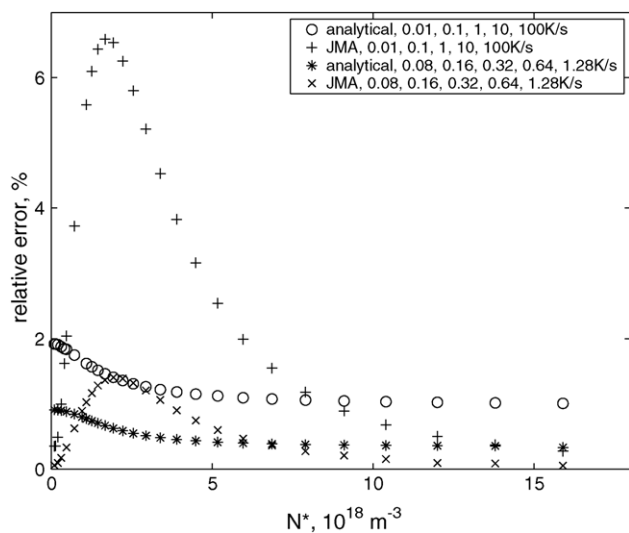


Fig. 2. Relative errors (of  $df/dT$ ) from analytical solutions or JMA fits as a function of model parameter  $N^*$  for isochronal transformation assuming mixed nucleation and interface-controlled growth at two sets of heating rates.

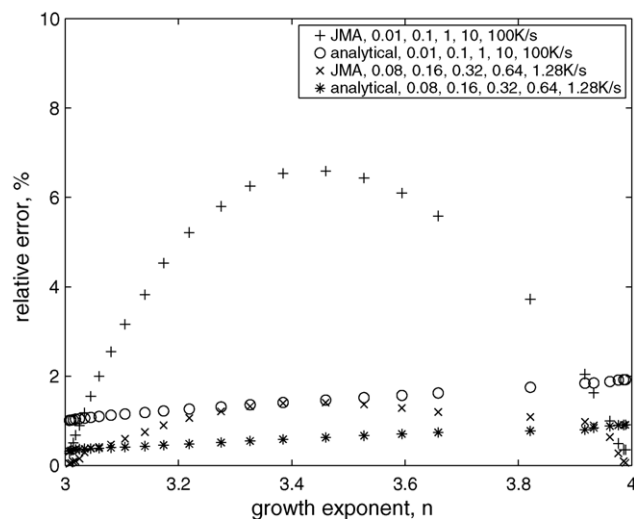


Fig. 3. Relative errors (of  $df/dT$ ) from analytical solutions or JMA fits as function of the growth exponent for isochronal transformation assuming mixed nucleation and interface-controlled growth at two sets of heating rates.

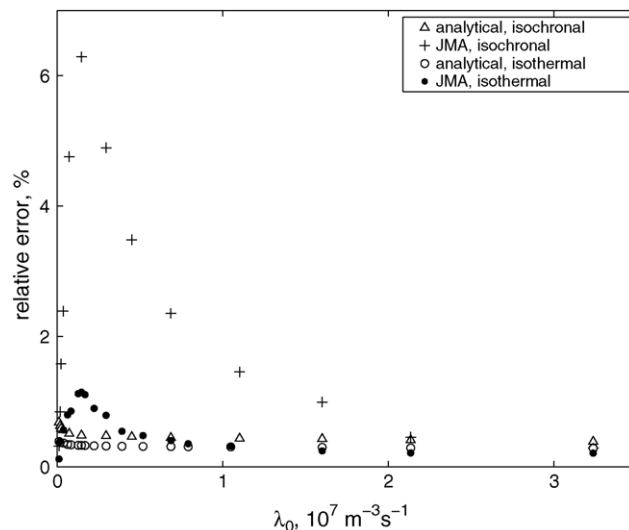


Fig. 4. Relative error (of  $df/dt$  or  $df/dT$ ) from analytical solutions or JMA fits as a function of model parameter  $\lambda_0$  for isothermal and isochronal transformation assuming Avrami nucleation and interface-controlled growth at five different temperatures (580, 590, 600, 610 and 620 K) or five different heating rates (0.01, 0.1, 1, 10 and 100 K s<sup>-1</sup>).

ment between exact numerical calculations and analytical solutions results within the whole range of  $N_0$  and  $N^*$  or  $\lambda_0$  (see Figs. 1–5). Analogous calculations for transformations assuming volume diffusion-controlled growth are also performed and similar results have been obtained, for which a detail description is not given here.

#### 4. Error analysis

The applicability of the analytical model and its superiority to JMA kinetics for the intermediate cases can be judged from the error analysis between JMA fits/analytical solutions and the exact numerical calculations.



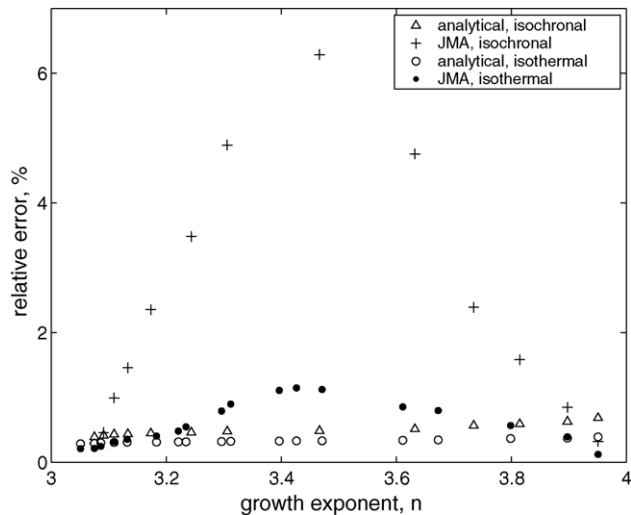


Fig. 5. Relative errors (of  $df/dt$  or  $df/dT$ ) from analytical solutions or JMA fits as function of the growth exponent for isothermal and isochronal transformation assuming Avrami nucleation and interface-controlled growth at five different temperatures (580, 590, 600, 610 and 620 K) or five different heating rates (0.01, 0.1, 1, 10 and 100 K s<sup>-1</sup>).

#### 4.1. JMA fits

As shown in Figs. 1–5, JMA kinetics provides good fits to the exact numerical calculations for the extreme cases where pure site saturation or pure continuous nucleation prevails (see Figs. 1–5), but the resultant error becomes much higher for the intermediate cases. Furthermore, the resultant error is drastically dependent on the annealing temperature (isothermal) or the heating rate (isochronal), e.g. higher error of fits results for wider range of annealing temperatures or of heating rates as chosen; see Figs. 1 and 2.

#### 4.2. The analytical solution

For all the analytical solutions using the same values for the model parameters chosen in numerical calculations, the resultant error reduces with increasing  $N^*$  or  $\lambda_0$ , i.e. with changing nucleation mechanism from pure continuous nucleation to pure site saturation [24] (see Figs. 1, 2 and 4). For the exact numerical calculation for isothermal transformation assuming mixed nucleation, the resultant error of analytical solution is nearly zero throughout the overall range of  $N^*$  from  $10^{17}$  to  $10^{20}$ , and is much lower than that of JMA fits (see Fig. 1). This can be ascribed to the fact that the analytical solution corresponds mathematically to the exact numerical calculations for isothermal transformations assuming mixed nucleation [24]. Owing to approximations applied for isochronal transformations and/or Avrami nucleation [24], the resultant error is increased (see Figs. 2 and 4). However, it should be noted that the dependence of the resultant error on the annealing temperature (isothermal) or the heating rate (isochronal) is not as serious as that of JMA fits (see Figs. 1 and 2).

According to step 4 in Section 3, the growth exponent,  $n$ , is obtained from JMA fits to the numerical calculations with specific model parameters:  $N_0$  and  $N^*$  or  $\lambda_0$  and  $N'$ ; meanwhile

the corresponding  $n$  values can be calculated from the analytical solutions obtained according to step 5 in Section 3. Accordingly, the resultant errors from JMA fits and from analytical solutions as a function of the growth exponent,  $n$ , are obtained, as illustrated in Figs. 3 and 5. Obviously, the resultant error of JMA fits is lower for the extreme cases (e.g. close to  $n=3$  or 4), but much higher for the intermediate cases (e.g. around  $n=3.4$ – $3.5$ ), whereas the resultant error from the analytical solution is continuously increased with the growth exponent,  $n$ .

### 5. Discussion

According to the classical JMA kinetics, the kinetic parameters:  $n$ ,  $Q$  and  $K_0$  hold constant throughout the time/temperature range of interest for isothermal transformations assuming pure site saturation or pure continuous nucleation. Analogously, for the numerical calculation (isothermal transformation) assuming specific values, e.g.  $N_0 = 10^{30} \text{ m}^{-3} \text{ s}^{-1}$  and  $N^* = 10^{17} \text{ m}^{-3}$  or  $N_0 = 10^{27} \text{ m}^{-3} \text{ s}^{-1}$  and  $N^* = 10^{20} \text{ m}^{-3}$ , the growth exponent,  $n$  is fitted to be 3.9982 or 3.0001 by JMA kinetics, and is calculated using analytical solutions to be nearly four or three over the whole transformation (see Fig. 6), respectively. Furthermore, the growth exponent obtained using analytical solutions is close to three or four for transformations assuming Avrami nucleation, provided that  $\lambda_0 = 10^8$  or  $10^5$  is chosen, respectively; see Fig. 7. Therefore, JMA kinetics, which solely provides good fit for the extreme cases, can be considered as the specific case of the analytical model where pure continuous nucleation or pure site saturation prevails.

Taking  $N_0$  and  $N^*$  or  $\lambda_0$  and  $N'$  as between the extreme values, the extended volume for the intermediate cases consists of two parts: one part is contributed from site saturation, and the other from continuous nucleation. With increasing  $N^*$  or  $\lambda_0$ , the contribution from pure site saturation become more and more predominant [15,24]. Since the resultant error of the analyti-

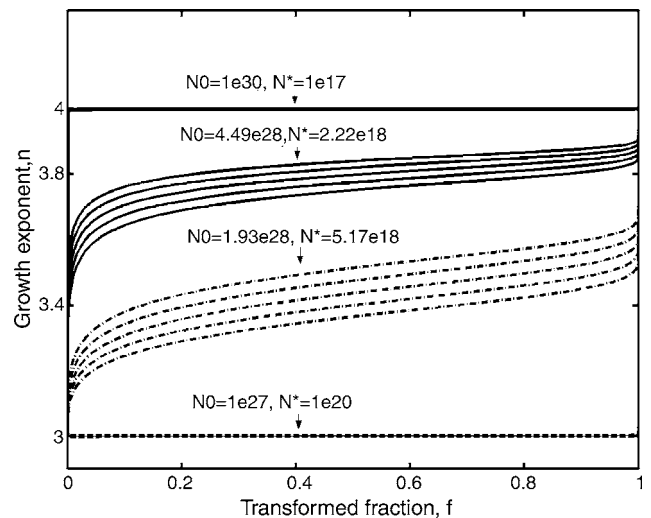


Fig. 6. Growth exponent as function of transformed fraction for isothermal transformation assuming mixed nucleation (choosing different values for  $N_0$  and  $N^*$ ) and interface-controlled growth at five different temperatures (770, 790, 810, 830 and 850 K).

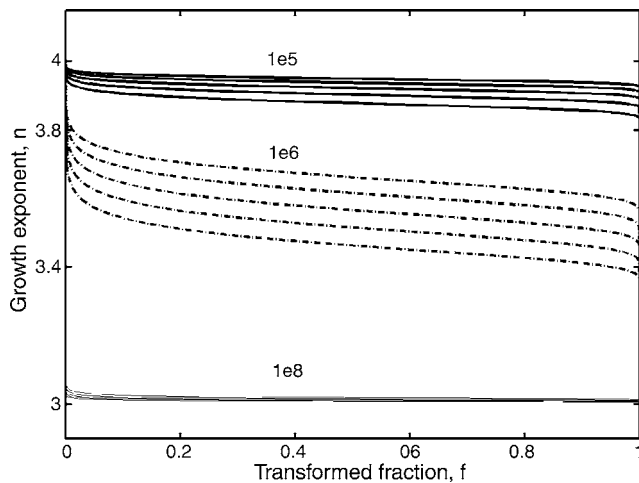


Fig. 7. Growth exponent as function of transformed fraction for isochronal annealing at five different heating rates (0.01, 0.1, 1, 10 and 100 K s<sup>-1</sup>) choosing specific values for  $\lambda_0$  and assuming Avrami nucleation and interface-controlled growth.

cal solution is mainly due to the contribution from continuous nucleation as a result of approximations applied [24], it reduces with increasing  $N^*$  or  $\lambda_0$  (see Figs. 1, 2 and 4).

Applying a JMA-like model to a phase transformation assumes that throughout the temperature/time range of interest the transformation mechanism is the same (which is called “isokinetic”), i.e. constant kinetic parameters with respect to time and temperature [6,15]. Actually, this assumption corresponds to assuming a constant ratio between the two contributions, i.e. from site saturation and continuous nucleation, independent of transformation time/temperature. According to the analytical model, the ratio between the two contributions changes with progressing transformation [24]. Therefore,  $n$  (as well as  $Q$  and  $K_0$ ) should change as a function of time (isothermal) or temperature (isochronal) (as shown in Figs. 6 and 7). This accounts for the large deviations of the resultant error in reaction to different temperatures (isothermal) or heating rates (isochronal), as obtained between JMA fits and analytical solutions.

Therefore, the analytical solution, applying time- or temperature-dependent kinetic parameters gives better description to the intermediate cases, as compared to the JMA fits. From Figs. 3 and 5, the resultant error from the analytical solution is much lower than that from the JMA fit, corresponding to  $n$  between 3.1 and 3.9. This implies that the JMA kinetics is only applicable for the extreme cases.

## 6. Conclusion

1. The analytical solution, applying time- or temperature-dependent kinetic parameters, provides a precise description for isothermal or isochronal phase transformation assuming different nucleation or growth mechanisms. In the extreme cases where pure continuous nucleation or pure site saturation prevails, the analytical model reduces to the so-called JMA kinetics.
2. According to the error analysis, JMA fit with constant kinetic parameters,  $n$ ,  $Q$  and  $K_0$  is only applicable for the extreme

cases where pure continuous nucleation or pure site saturation prevails; but for the intermediate cases where mixed nucleation or Avrami nucleation dominates, JMA fits results in much higher error, as compared to analytical solutions. This indicates that the kinetic parameters should change with progressing transformation, i.e. as a function of time (isothermal) or temperature (isochronal), and that the effective activation energy and the growth exponent generally depend on time/temperature, even if the transformation mechanism is constant (isokinetic).

## Acknowledgements

F. Liu is grateful to Prof. E.J. Mittemeijer and Prof. F. Sommer for their valuable and essential instruction and cooperation and to Dipl.-Ing. H. Nitsche for support with the numerical calculations in Max-Planck-Institute for Metals Research. The authors are grateful to the National Natural Science Foundation of China and Fundamental Research Project of Natural Science in Shaanxi Province for the financial support under Grant Nos. 50395103, 50432020 and 2001C55.

## References

- [1] M. Avrami, *J. Chem. Phys.* 7 (1939) 1109.
- [2] M. Avrami, *J. Chem. Phys.* 8 (1940) 212.
- [3] M. Avrami, *J. Chem. Phys.* 9 (1941) 177.
- [4] A.N. Kolmogorov, *Izv. Akad. Nauk, SSSR, Ser. Mat.* 3 (1937) 355.
- [5] J.W. Christian, *The theory of transformation in metals and alloys*, in: Part 1 Equilibrium and General Kinetics Theory, Pergamon Press, Oxford, 1975.
- [6] E.J. Mittemeijer, *J. Mater. Sci.* 27 (1992) 3977.
- [7] S. Vyazovkin, *Thermochim. Acta* 355 (2000) 155.
- [8] D.W. Henderson, *J. Non-Cryst. Solids* 30 (1979) 301.
- [9] J. Vazquez, P.L. Lopez-Alemany, P. Villares, R. Jimenez-Garay, *J. Phys. Chem. Solids* 61 (2000) 493.
- [10] M.J. Starink, *Thermochim. Acta* 404 (2003) 163.
- [11] M.J. Starink, A.M. Zahra, *Thermochim. Acta* 298 (1997) 179.
- [12] M.J. Starink, *J. Mater. Sci.* 36 (2001) 4433.
- [13] D. Crespo, T. Pradell, *Phys. Rev. B* 54 (5) (1995) 3101.
- [14] E. Pineta, T. Pradell, D. Crespo, *Philos. Mag. A* 82 (2002) 107.
- [15] A.T.W. Kempen, F. Sommer, E.J. Mittemeijer, *J. Mater. Sci.* 37 (2002) 1321.
- [16] B.J. Kooi, *Phys. Rev. B* 70 (22) (2004) 224108.
- [17] D.P. Birnie III, M.C. Weinberg, *J. Non-Cryst. Solids* 219 (1979) 89.
- [18] D.P. Birnie III, M.C. Weinberg, *J. Non-Cryst. Solids* 202 (1979) 290.
- [19] G. Ghosh, M. Chandrasekaran, L. Delay, *Acta Mater.* 39 (1991) 925.
- [20] H. Nitsche, F. Sommer, E.J. Mittemeijer, *J. Non-Cryst. Solids*, in press.
- [21] A. Calka, A.P. Radlinski, *Acta Mater.* 35 (1987) 1823.
- [22] C.W. Price, *Acta Metall. Mater.* 38 (1990) 727.
- [23] O. Grong, O.R. Myhr, *Acta Mater.* 48 (2) (2000) 445.
- [24] F. Liu, F. Sommer, E.J. Mittemeijer, *J. Mater. Sci.* 39 (2004) 1621.
- [25] F. Liu, F. Sommer, E.J. Mittemeijer, *J. Mater. Res.* 19 (9) (2004) 2586.
- [26] F. Liu, F. Sommer, E.J. Mittemeijer, *Acta Mater.* 52 (2004) 3207.
- [27] H. Nitsche, F. Sommer, E.J. Mittemeijer, unpublished.
- [28] D.E. Coates, *Metall. Trans.* 3A (1972) 1203.
- [29] D.R. Allen, J.C. Foley, J.H. Perepezko, *Acta Mater.* 46 (1998) 431.
- [30] C. Capidevila, F.G. Caballero, *Metall. Mater. Trans.* 32A (2001) 661–669.
- [31] C. Capidevila, F.G. Caballero, *Scripta Mater.* 39 (7) (1998) 853.
- [32] T. Pradell, D. Crespo, N. Clavaguera, *J. Phys. Condens. Matter* 10 (17) (1998) 3833.
- [33] K.D. Li, E. Chang, *Acta Mater.* 52 (2004) 219.
- [34] B.B. Kappes, J.E. Shield, *J. Non-Cryst. Solids* 317 (1979) 106.
- [35] G. Sasikala, S.K. Ray, S.L. Mannan, *Mater. Sci. Eng.* 359A (2003) 86.