The use of the JMAYK kinetic equation for the analysis of solid-state reactions: critical considerations and recent interpretations ☆

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Abstract

The present work is concerned with the classical Johnson–Mehl–Avrami–Yerofeev–Kolmogorov (JMAYK) equation. Some critical points are presented because this kinetic relation has been extensively misused. Various aspects regarding its failure when it is applied to recrystallization of plastically deformed metals are also considered. Recent conceptual improvements, such as the new approach where the transformation is described by the superposition of single JMAYK processes, have resulted in the resurgence of this approach.

Keywords: Crystallization; Kinetics; Recrystallization

1. Introduction

Almost sixty years ago, different researchers developed independently the well-known JMAYK kinetic relation which has been extensively used to give a phenomenological description of many solid-state processes. At present, methods allowing the most simple and direct measurement of the transformed fraction come from the field of thermal analysis: DSC, TG, etc., and, perhaps, some electromagnetic measurements. From a technical viewpoint, an important advance has already been achieved in the problem of obtaining reproducible and correct kinetic data. However, even nowadays, the widespread effects of some leading questions are still an important current issue:

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☆ Dedicated to Hiroshi Suga on the Occasion of his 65th Birthday.

Why are kinetic parameters necessary? Is there a definite physical meaning behind the kinetic parameters, i.e. they allow us to obtain some fundamental information on the physics of the transformation, or do they have a purely empirical significance? Is the JMAYK kinetic relation such an oversimplified approach to the true transformation rate equation that it has become useless?

Certainly, the applicability to some specific problems (particularly to the recrystallization kinetics of metals) constitutes a serious challenge for this old formulation. At the same time, many doubts and discussions have been expressed so far in literature in relation to the extensive misuse of the JMAYK equation. Consequently, this is now a convenient time to reflect on the use and validity of this kinetic relation and to consider recent experimental observations. However, our final personal opinion is hopeful, provided recent improvements reveal that we have not reached a deadlock in this area.

2. The groundwork

The kinetics of the heterogeneous reactions of the solid state can usually be described in terms of separate nucleation and growth mechanisms. It is evident that the kinetics of such transformations is important from the point of view of both fundamental and applied research. For instance, the technological applications of many solid-state devices require the corresponding materials to be thermally stable with time and temperature during use. Recrystallization in cold-worked metals and the crystallization of amorphous alloys are representative examples of this kind of transformation. The transformed fraction α can be monitored under any thermal history by different experimental methods such as differential scanning calorimetry (DSC), electrical resistivity, transmission electron microscopy (TEM), hardness measurements, or X-ray diffraction techniques. Unfortunately, however, the theory and practice of the different methods for the evaluation of the kinetic parameters are far from being universally accepted. In this respect, the classic kinetic relation developed independently by Kolmogorov [1], Johnson and Mehl [2], Avrami [3–5] and Yerofeev [6] (the JMAYK equation) has been widely used to describe not only a great variety of solid-state transformations but also some heterogeneous chemical reactions such as solid–gas decompositions. The JMAYK kinetic relation is based on the well-known extended-volume concept which is the volume that new grains would occupy in the absence of impingement and overlap of adjacent transformed grains. The significance of this extended volume (where no correction for overlapping is made) is that it is simply related to the kinetic laws of growth, which may thus be separated from the geometrical problem of impingement.

An extensive and elegant treatment on the foundations of the JMAYK theory is due to Christian [7]. Next, we summarize concisely the main points of these foundations in steps of increasing generality.

(i) In this step we consider the following conditions:

(a) isothermal transformations which do not involve a change in mean composition, i.e. polymorphic phase changes;

(b) a constant and isotropic growth rate, Y (so the transformed regions are spherical);

(c) only the initial stages of transformations are considered; in this way the interference of neighbouring nuclei is negligible.

(d) a constant nucleation rate per unit volume, I_V.

These conditions lead to the result

$$\alpha = \frac{4\pi}{3} \int_0^t I_v Y^3 (t - \tau)^3 \, d\tau = \pi/3 \, I_v Y^3 t^4 \tag{1}$$

where τ is the incubation time for nucleation.

(ii) In a more exact treatment we must take into account the geometrical problem of the impingement. According to Avrami [3], the change in the actual transformed volume, V_t, and that of the extended volume, V_e, are related by

$$d V_t = \left(1 - \frac{V_t}{V}\right) d V_e \tag{2}$$

which describes a completely random overlap of growing crystallites, V being the full volume. Consequently, we can define an extended degree of conversion, α_e, corresponding to the omission of the ingestion of the phantom or potential nuclei

$$\frac{d\alpha}{d\alpha_e} = 1 - \alpha \tag{3}$$

and then we can write

$$-\ln(1 - \alpha) = \pi/3 \, I_v Y^3 t^4 \tag{4}$$

(iii) The previous formalism may be generalized for a number of more general conditions, i.e.:

(a) The effects of the free surface that occur in a thin sheet of solid material; in this case, growth is essentially two-dimensional;

(b) I_v may not be constant. Some physical processes leading to this situation are the cases of nuclei forming preferentially at either grain boundaries or at edges or corners. The calculation of the isothermal kinetic laws under these conditions has been performed by Cahn [8];

(c) diffusion controlled reactions where the growth laws are parabolic;

(d) the case of non-isothermal transformations.

An interesting survey on the theory of nucleation and growth controlled transformations under very general thermal conditions has been published by Kemény and Šesták [9]. For instance, for an isotropic growth confined to m dimensions, Eq. (1) can be rewritten as

$$\alpha = 1 - \exp\left\{-\int_0^t g\left[\int_\tau^t Y(\theta) \, d\theta\right]^m I_v(\tau) \, d\tau\right\} \tag{5}$$

where $Y(\theta)$ represents the growth rate for all of the m dimensions of growth and g is a geometrical factor. This equation is valid under very general thermal conditions

insofar as no assumption has been made about the origin of the time dependences of I_v and Y: so, the implicit time dependences $Y[T(\theta)]$ and $I_v[T(\tau)]$ could be easily included.

Under isothermal conditions and by assuming an Arrhenius dependence for the nucleation and growth rates

$$I_v(t) = I_o \exp(-E_N/RT) \tag{6}$$

$$Y(t) = Y_o \exp(-E_G/RT) \tag{7}$$

the integrals in Eq. (5) are easily solved and yield

$$\alpha(t) = 1 - \exp\left[-\frac{g}{m+1} Y_o^m I_o \exp\left(-\frac{E_N + mE_G}{RT} \right) t^{m+1} \right] \tag{8}$$

On the basis of all the previous expressions, we should use the general relation proposed by Avrami for isothermal transformations

$$\alpha = 1 - \exp(-Kt^n) \tag{9}$$

where n is the Avrami exponent (indicative of the transformation process) and K is a thermally activated rate constant representing both nucleation and growth rates. Eq. (9) is valid for linear growth under most circumustances and approximately valid for the early stages of diffusion-controlled growth (although Ham [10] has emphasized that a law of this kind has no fundamental significance is diffusion-limited reactions). Table 1 summarizes the values of n corresponding to a variety of experimental

Table 1
Values of n in the kinetic law $\alpha = 1 - \exp(-kt^n)$ (from Ref. [7])
(a) Polymorphic changes, discontinuous precipitation, eutectoid reactions, interface controlled growth, etc.

Conditions	n
Increasing nucleation rate	> 4
Constant nucleation rate	4
Decreasing nucleation rate	3–4
Zero nucleation rate (saturation of point sites)	3
Grain edge nucleation after saturation	2
Grain boundary nucleation after saturation	1

(b) Diffusion-controlled growth

Conditions	n
All shapes growing from small dimensions, increasing nucleation rate	$> 2\frac{1}{2}$
All shapes growing from small dimensions, constant nucleation rate	$2\frac{1}{2}$
All shapes growing from small dimensions, decreasing nucleation rate	$1\frac{1}{2} - 2\frac{1}{2}$
All shapes growing from small dimensions, zero nucleation rate	$1\frac{1}{2}$
Growth of particles of appreciable initial volume	$1 - 1\frac{1}{2}$
Needles and plates of finite long dimensions, small in comparison with their separation	1
Thickening of long cylinders (needles), e.g. after complete end impingement	1
Thickening of very large plates, e.g. after complete edge impingement	1/2
Precipitation on dislocations (very early stages)	$\simeq 2/3$

situations. Eq. (9) can also be written in the form

$$\ln[-\ln(1-\alpha)] = n\ln t + \ln K \tag{10}$$

Thus. the Avrami exponent can be evaluated from the slope of the plot of ln $[-\ln(1-\alpha)]$ against ln t. In addition, the apparent activation energy E_a can be derived from the intercepts of the plot for different temperatures, through the Arrhenius relation

$$K(T) = k_o e^{-E_a/RT} \tag{11}$$

This apparent activation energy E_a has contributions from both the activation energy of nucleation E_N and that of growth E_G. Thus, if we are dealing with crystallization processes, the effective activation energy E_c will be (E_a/n) [11, 12]. Moreover, the Avrami exponent can be partitioned [7, 12, 13] as

$$n = a + bp \tag{12}$$

where a depends on the nucleation rate (zero for existing nuclei and unity for constant nucleation rate), b represents the dimensionality of the growing phase (1–3) and p is related to the growth mechanism (1/2 for parabolic, diffusion controlled and 1 for interfacial growth). In the same way, a general equation for the effective activation energy was suggested by Von Heimendahl and Kuglstatter [14]

$$E_C = \frac{aE_N + bpE_G}{a + bp} \tag{13}$$

where E_N and E_G stand for the activation energies of nucleation and growth, respectively, as stated in Eqs. (6) and (7). These quantities can be separately determined by TEM experiments, and the E_C values predicted by Eq. (13) have been found to be in good agreement with those determined by the usual kinetic methods [15]. Therefore, it is worth noting that in conjunction with DSC methods, supplementary TEM studies based on the observation of sufficient specimens to ensure adequate statistical confidence, are a powerful tool in determining the kinetics of solid state processes [15]. Thus, in order to gain a deep understanding of the atomic processes involved in the transformation, the analysis (by means of the proper stereological relationships) of variables such as the number of particles per unit volume and the particle size distribution for each heat treatment, is very useful.

In the framework of the above considerations, extensive work has been carried out on the kinetics of solid-state reactions mainly by using methods of thermal analysis. In this respect, the present survey is concerned with a variety of serious difficulties in this field, namely the oversimplified approaches describing the kinetics of non-isothermal experiments and the indiscriminate use of the JMAYK equation for such processes, the ability to determine the actual reaction mechanism, the applicability to heterogeneous reactions of concepts founded in the field of homogeneous reactions, i.e. the rate of nth order, the criticism concerning the validity of Eqs. (2) and (3), the most recent interpretations of the JMAYK kinetic law to explain the commonly observed non-linearity in the JMAYK plots of different systems, as well as the recent improvement based on the use of an activation energy distribution (AED) for the description of

kinetic equations. It is worth noting here that the most exciting of these questions has been thoroughly considered and analysed in the classical work by Šesták [16], i.e. the question concerning the physical meaning of kinetic parameters, as well as the problems inherent in the mathematical formalism used for the description of kinetic processes.

3. Alternative models in solid state kinetics

The aim of this section is to present some alternative kinetic models different from the conventional JMAYK model. In order to express the reaction rate, $d\alpha/dt$, the form usually adopted is

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{14}$$

where $f(\alpha)$ is a function characteristic of the actual transformation mechanism and $K(T)$ is the temperature dependence which is usually believed to be of the Arrhenius form (Eq. (11)).

This dependence for the rate constant is accepted without question, although this assumption is only justified for a random distribution of energy states. However, the separability of α and T, implicit in the above equation, is almost a dogma in routine kinetic analysis.

The integration of Eq. (14) under the condition of a constant heating rate ($\beta = dT/dt$) yields

$$g(\alpha) = \frac{k_0 E}{\beta R} p(x) \tag{15}$$

where $x = E/RT$ and $p(x)$ denotes the exponential integral function, which cannot be expressed in a simple analytical form. Methods for the evaluation of kinetic parameters using as a starting point either Eqs. (14) or (15) are described, respectively, as differential or integral methods.

The correct form for the $f(\alpha)$ function, relative to the JMAYK model, is

$$f(\alpha) = n(1 - \alpha)[\ln(1 - \alpha)]^{1 - 1/n} \tag{16}$$

Almost twenty-five years ago, Šesták and Berggren [17] proposed an alternative empirical kinetic model of the form

$$f(\alpha) = \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p \tag{17}$$

Further mathematical analysis [18] has shown, however, that no more than two kinetic exponents are necessary for the description of any experimental curve $f(\alpha)$. Thus, after eliminating the third exponential term in Eq. (17), the final form obtained is

$$f(\alpha) = \alpha^m (1 - \alpha)^n \tag{18}$$

where the exponential factors m and n, in this Šesták–Berggren (SB) kinetic model have purely empirical significance. According Criado et al. [19], the behaviour of both

models (SB and JMAYK) exhibit important similarities and, moreover, it seems that the SB model is more suitable for a quantitative description of some processes, e.g. the decomposition of nickel nitrate in Ref. [19]. In contrast to this, it has been shown that the SB model cannot be successfully used as a general expression for diffusion models. This fact, together with the lack of validity of the SB exponents as universal constants for solid state reactions, has determined its rather scarce use.

With respect to recrystallization kinetic experiments, the following relation has been proposed [20, 21] as the Speich and Fisher (SF) kinetic model

$$\frac{\alpha}{1-\alpha} = k\,t^n \tag{19}$$

The above equation was based on an empirical relation between α and the interfacial area A between recrystallized and unrecrystallized material. It is well known that pure metals that have work-hardened due to deformation will soften completely when being annealed at a suitable temperature. The process responsible is called recrystallization and leads to a new grain structure of the metal. In a remarkable work on the computer simulation of recrystalization kinetics [21], Price has demonstrated the agreement between the SF model and some experimental kinetic data over a wide range of α. In this work impingement geometry (hard and soft) was studied as a function of grain shape, grain symmetry, and distribution geometry. In the same way, Price stresses how the JMAYK formulation (founded on linear growth rates) is restricted to only the early stages of recrystallization. Moreover, it seems strange or anomalous that the JMAYK model uses only volumetric terms to model a transformation which is mainly due to a surface reaction. Nevertheless, by using stereological relations, Cahn [22] showed that Eq. (19) was not rigorously correct at either extreme of α. Likewise, some criticism concerning the SF equation [21] has been reported since this equation is based on an empirical relation between the variables α and A (the interfacial area) which are not geometrically related. Finally, Table 2 summarizes the algebraic expressions for the $f(\alpha)$ and $g(\alpha)$ functions for the most frequently used mechanisms of solid state reactions.

4. Methods for determining the actual kinetics from non-isothermal data: the master plots

As soon as different alternative models have been considered, the problem about the ability to distinguish between the JMAYK model and other possible choices is raised. In this respect, the master plot is a characteristic curve independent of the condition of the measurement which is easily obtained from experimental data (an interesting and complete survey on this problem is due to Criado and coworkers [23–25]). This kind of reference theoretical curve is useful in determining the mechanism of a solid state process. In this sense, the master plots are mainly obtained from the less time-consuming non-isothermal experiments, i.e. a linear heating programme. Although some opinions are in disagreement [26, 27] with respect to the usefulness of non-isothermal experiments in determining the actual kinetic model, the most recent interpretation, Ref. [9], is conclusive and emphatic: "Non-isothermal measurements

Table 2
Algebraic expressions for the $f(\alpha)$ and $g(\alpha)$ functions for the most common mechanism operating in solid-state reactions

Mechanism	Symbol	$f(\alpha)$	$g(\alpha)$
Random nucleation and growth of nuclei (JMAYK equation)	An	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$	$[-\ln(1-\alpha)]^{1/n}$
Rate law of nth order	R$(1/(1-n))$	$(1-\alpha)^n$	$(1-(1-\alpha)^{1-n})/(1-n)$
One-dimensional diffusion (parabolic law)	D1	$(1/2)\alpha$	α^2
Two-dimensional diffusion	D2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion (Jander equation)	D3	$\dfrac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)]^{1/3}}$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (Ginstein–Brounshtein equation)	D4	$\dfrac{3}{2[(1-\alpha)^{-1/3}-1]}$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

can be used even for the determination of the mechanism of crystallization, in contrast to the belief that it is restricted to isothermal methods only".

Once the activation energy has been determined, by using the well-tried Kissinger method [28], several simple procedures allow us to ascertain the actual reaction mechanism.

The most commonly used master plots are those based on the first and the second derivatives of the transformed fraction α. Within the first group, we note the method based on the representation of $z(\alpha)$ against α, where

$$z(\alpha) = \frac{(d\alpha/dt)}{\beta}\,\pi(x)\,T = f(\alpha)\,g(\alpha) \qquad (20)$$

$\pi(x)$ being the fourth rational expression of Senum and Yang [29] which is used in an accurate approximation for the exponential integral function

$$p(x) = e^{-x}\frac{\pi(x)}{x} \qquad (21)$$

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \qquad (22)$$

It has been shown [23] that the plot corresponding to Eq. (20) leads to well-separated curves for all models considered in Table 2. Thus, by plotting the $z(\alpha)$ function obtained from the experimental data and comparing with the theoretical master curves, the proper kinetic model can be determined precisely.

In the same way, the representation of $\ln f(\alpha)$ versus $-\ln(1-\alpha)$ [30, 31] is a powerful tool for the discrimination of the kinetic models. In practice, we use the simple

relationship

$$\ln[k_o f(\alpha)] = \ln \frac{d\alpha}{dt} + \frac{E_a}{RT} \tag{23}$$

where the parameter k_o only involves a shift in the direction of the ordinate axis, while retaining the shape of these master curves.

More recently [32,33], the $y(\alpha)$ function (which can easily be obtained from the observed data) has been defined as

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right) \exp(E/RT) \tag{24}$$

The values of $y(\alpha)$ are then proportional to the $f(\alpha)$ function. Thus, the use of a modified version of $y(\alpha)$ normalized within the interval $\langle 0, 1 \rangle$ allows us to get a picture of $f(\alpha)$. Further advantages of the $y(\alpha)$ representation, as well as some mathematical properties of this function useful for kinetic analysis, are considered in Ref. [33]. However, a problem must be noted in that the shape of $y(\alpha)$ is strongly dependent on E. Hence, the foregoing application needs a reliable previous determination of the activation energy.

In relation to the master curves of the second group the characteristic function has been proposed [24]

$$w(\alpha) = \frac{d^2\alpha/dt^2}{(d\alpha/dt)^2} = \frac{1}{f(\alpha)}\left[f'(\alpha) + \frac{x\pi(x)}{g(\alpha)}\right] \tag{25}$$

At first sight, this seems a suitable choice as a master plot because the $w(\alpha)$ function is independent of the heating rate (unlike the $z(\alpha)$ representation) and its values can easily be calculated from the experimental data. A closer examination, however, leads us to advise against this method since $w(\alpha)$ is dependent on the value of x (as is evident from Eq. (25)). Criado et al. [23] have shown that under these circumstances it is very difficult to draw any conclusion without a very precise knowledge of x_m (the value of x related to the maximum of $d\alpha/dt$).

5. Non-isothermal description of JMAYK kinetics

We will now discuss the interpretation of non-isothermal transformations. In fact, is industrial practice, the kinetic behaviour of a system at constant temperature is frequently of less interest than its behaviour during constant heating or cooling through a transformation range. As a starting point, many researchers [34–38] have applied the JMAYK equation, as derived for the isothermal case, to non-isothermal conditions. However, this indiscriminate use of isothermal laws under non-isothermal conditions is a practice not generally recognized [39,40]. Ref. [9] discusses this at great length. The difficulties in treating non-isothermal transformations are mainly due to the independent variations of the nucleation and growth rate with temperature. According to Christian [7], this problem can only be resolved when the instantaneous transformation rate can be shown to be a function solely of temperature and the degree

of transformation. Moreover, the 'separation of variables' principle expressed in is universally accepted (14). The isokinetic hypothesis states that the transformation rate as described in Eq. (14) is independent of its thermal history. Under these circumstances, the transformed fraction α is calculated by integration of the rate equation

$$g(\alpha) = \int_0^t K[T(t')] \, dt' \tag{26}$$

where α is clearly dependent on the whole $T(t)$ path. Under isothermal conditions, Eq. (26) can be rewritten as

$$[-\ln(1-\alpha)]^{1/n} = kt \tag{27}$$

which corresponds to the classical formulation of the JMAYK equation. It is clear from Eq. (26) that the correct non-isothermal equivalent of the widely used isothermal Eq. (27) is

$$[-\ln(1-\alpha)]^{1/n} = \int_0^t K[T(t')] \, dt' \tag{28}$$

An alternative formalism was suggested by McCallum and Tanner [34], rejecting Eq. (14) under non-isothermal conditions. Then it is claimed that the actual rate under non-isothermal conditions is

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T + \left(\frac{\partial \alpha}{\partial T}\right)_t \frac{dT}{dt} \tag{29}$$

where the use of partial derivatives requires the existence of an $\alpha = \hat{\alpha}(t, T)$ function on account of which a unique vlaue of α is determined for any point (t, T) independent of previous thermal history. However, because the point (t, T) can also be reached along an isothermal route, the transformed fraction must be similar to that calculated isothermally. Therefore, a significant modification of the rate equation is obtained

$$\frac{d\alpha}{dt} = f(\alpha) K(T) \left\{ 1 + \frac{E_a t}{RT^2} \frac{dT}{dt} \right\} \tag{30}$$

Nevertheless, some examples have been proposed to point out that this formalism is a fallacy [16, 41], even by experimental comparisons [42]. Kemény [40] emphasizes the correct steps: Eqn. (14) is to be used as the actual rate equation; the appropriate mathematical approximations of Eq. (28) predict the transformed fraction α.

The reminder of this section will be devoted to discussion of the recent work of Woldt [43]. This author has performed an original approach to the problem of non-isothermal kinetics for the case of a constant heating rate $\beta = dT/dt$. Here, the amazing result is that under the JMAYK kinetics the transformed fraction for isothermal conditions and for constant heating rate can be described with equations of identical form and a slightly different definition of the kinetic parameters. The Woldt approach is based on the recognition that Eq. (5) is still valid during linear heating except that its integration now becomes much more difficult. After the achievement of a number of approximations whose accuracy is meticulously checked, the following results are

obtained for the transformed fraction

$$\alpha(t, T) \simeq 1 - \exp(-K'(T)t^{2m+2}) \tag{31}$$

with $K'(T) = k'_o \exp(-E'_a/RT)$, and for the rate equation

$$\frac{d\alpha}{dt} = k_1(1-\alpha)[-\ln(1-\alpha)]\frac{1}{Tt} \tag{32}$$

where k_1 is a constant and the activation energy E'_a is identical to the isothermal activation energy. Table 3 summarizes the meaning of the parameters of the non-isothermal JMAYK description in the cases of continuous nucleation and fixed number nucleation.

It may be remarked that this rate equation obtained by Woldt differs considerably from that generally used in the literature for isothermal transformations.

6. Critical considerations concerning the extended-volume concept

It has been observed [13] that JMAYK plots for recrystallization in cold-worked metals frequently show a severe negative curvature. In fact, some problems in the application of JMAYK kinetics have been suspected to be related to the extended volume concept, V_e, and more particularly with the well-known Avrami Eqs. (2) and (3). Some earlier criticisms concerning this equation are due to Rozovskii [44]. Recently, Urbanovici and segal [45] have pointed out in an excellent work that there is not adequate theoretical sanction for Eq. (3) from the formal theory of nucleation and growth transformations.

In spite of this criticism, computer simulations due to Price [21] demonstrate that the JMAYK extended volume concept does provide a reasonable compensation for grain impingement (with the possible exception of dispersion-strengthened metals). In the opinion of Price, the major limitation of the JMAYK relation is the assumption of linear growth. However, in a recent work Rollet et al. [46] presented their results on the computer simulation of recrystallization in non-uniformly deformed metals. For this

Table 3
Meaning of the parameters of the non-isothermal JMAYK description for continuous and fixed number nucleation

Continuous nucleation	Isothermal	Non-isothermal
E_a	$E_N + mE_G$	$E_N + mE_G$
k_o	$gI_o Y_o^m/(m+1)$	$gI_o Y_o^m C a^{m+1}$
n	$m+1$	$2m+2$

Fixed number	Isothermal	Non-isothermal
E_a	mE_G	mE_G
k_o	$gI_o^* Y_o^m$	$gI_o^* Y_o^m D a^m$
n	m	$2m$

purpose they performed Monte Carlo simulations to model grain growth and recrystallization. It was found that Eq. (3) is correct under conditions of uniform stored energy of plastic deformation. With non-uniform stored energy, however, the results proved that the Avrami equation underestimated the effect of impingement. In this case, therefore, the JMAYK kinetic law would not be appropriate because of the failure of its key assumption: spatially random nucleation and uniform growth. On second thoughts, it has been emphasized [21] that these observed deviations do not necessarily constitute a true failure of the JMAYK kinetic relation; in fact they only signify that the actual growth dependence must be coupled with the Avrami extended-volume to obtain the proper kinetic relation.

From the foregoing considerations it can be concluded that the Avrami interpretation of V_e does not cause severe deviation from linear JMAYK behaviour in spite of the formal inconveniences underlined in Refs. [45, 46]. In fact, according to Urbanovici and Segal [45], the search for an adequate relationship between α and α_e is a fairly complicated problem which is not worth considering from the point of view of the current practical applications.

7. Deviations from the ideal JMAYK kinetics

In the preceding section, it was remarked how the majority of the published recrystallization studies show a significant deviation from the ideal JMAYK kinetics. A similar situation [47] occurs for the crystallization kinetics of many amorphous alloys, e.g. the conventional JMAYK plot of $Ni_{24.1}Zr_{74.7}Si_{1.1}$ in Ref. [47] showed marked deviations from linearity from the beginning of crystallization. Sometimes, this spread in the Avrami exponent n over the full range of transformations has lead to determination of a mean value for n. Nevertheless, Calka and Radlinski [48, 49] demonstrated that this practice may be inappropriate and, perhaps, misleading. They proposed an alternative method of examining the JMAYK plot: a local value n_{loc} is defined as

$$n_{loc} = \frac{\partial \ln [-\ln(1-\alpha)]}{\partial \ln t} \tag{33}$$

being a function of the transformed fraction. In this analysis the variations in n_{loc} are attributed to real changes in the transformation process, i.e. changes in growth morphology, growth velocity, nucleation rate, etc; in fact, in a recent paper Shepilov and Baik [50] suggest high anisotropy in the growing crystalline phases as a possible alternative explanation for non-linear effects. Let us now consider two likely explanations of such non-linearity effects. Although several different causes have been pointed out and will be considered as a whole in the following section, we highlight and analyse two significant and crucial shortcomings which have been seldom recognized, namely: (a) The large uncertainty associated in determining the effective time lag τ; (b) The loss of early-time data.

(a) The parameter τ indicates the incubation time necessary for obtaining a population of critical-size nuclei characteristic of the annealing temperature. In fact, according to the non-steady theory of nucleation [47, 51], the experimentally observed incuba-

tion time τ can be expressed as

$$\tau = \tau_{o} + \tau_{\beta} \tag{34}$$

where τ_{o} is the time for non-steady state nucleation and τ_{β} is the time required to attain an experimentally observable degree of transformation. Therefore, the experimentally observed incubation periods will be larger than the theoretically estimated one. Within these considerations, the JMAYK kinetic equation (9) is frequently rewritten as

$$\alpha = 1 - \exp\{- K(t - \tau)^{n}\} \tag{35}$$

In this way, Thompson et al. [52] linearized the JMAYK plot by treating τ as an adjustable parameter for a given value of n. In our opinion this method suffers on two important drawbacks: it assumes an a priori knowledge of n; and no further changes are allowed in n throughout the transformation process.

Recently, Mao and Altounian [53] proposed an original and simple method for the accurate determination of n, for which an exact knowledge of τ is not necessary. They called their method the modified Avrami (MA) plot. The subtle procedure consists of eliminating the explicit form $(t - \tau)$, which appears in Eqn. (35), by substitution of the rate equation (11). Then, instead of Eq. (10), the new fitting equation is

$$\ln\left[-\ln(1 - \alpha)\right] = \frac{-1}{n-1}\ln(nK) + \frac{n}{n-1}\ln\left(\frac{d\alpha/dt}{1-\alpha}\right) \tag{36}$$

From this MA plot, the Avrami exponent and the activation energy can be easily deduced.

(b) In a very recent publication Smith [54] emphasized the problems which can occur in using the JMAYK equation if values of $\alpha(t)$ for early times are either not valid or unavailable. This situation may arise in many experimental circumstances, e.g. the sample is out of equilibrium because of a rapid warm-up. Thus, Smith investigated, by means of two alternative methods, the effect of missing or invalid initial data from isothermal experiments.

The first method (interesting but exceedingly tedious) consists of replotting the experimental data for successive shifts, Δt, of the time origin; then, the corresponding curves $\alpha(t)$ versus t are calculated for each time shift, Δt; next, the JMAYK plot allows us to derive the kinetic parameters n and E_a; finally, extrapolation to $\Delta t = 0$ lead us to the best values. Smith [54] has found that the method is particularly effective when n values are not too far from unity or when the time interval over which data are missing or invalid is small compared to $K(T)^{-1}$, the inverse of the rate constant at temperature T.

A second method (faster than the first) uses a 2-exponential simulation approximating the DSC data from zero to infinity; then, $\alpha(t)$ is calculated and a JMAYK fit allows us to determine n and E_a.

8. Superposition of local JMAYK processes: the use of an activation energy distribution (AED)

According to the previous sections, the JMAYK relation cannot be safely applied to describe the recrystallization kinetics of metals unless the assumption of random

nucleation can be verified or guaranteed. A new approach addressing the problem was due to Rollett [55] who was the first to incorporate a superposition of local JMAYK processes into an analytical model of the recrystallization. A little later, Krüger and Woldt [56] revived the old basic idea of Primak [57] concerning the distribution of activation energies into a more general model, which is shown in Ref. [56] to work very well with data for the recrystallization of copper. The new approach is based on abandoning the assumption of global homogeneity and isotropy. Thus, for the isothermal case we can write

$$\alpha(t) = \int_0^\infty \Lambda(t, E) f(E) \, dE \tag{37}$$

where

$$\Lambda(t, E) = 1 - \exp\left\{ -\left[K(E, T)t \right]^n \right\} \tag{38}$$

and $f(E)$ is the normalized AED

$$\int_0^\infty f(E) \, dE = 1 \tag{39}$$

and $K(E, T)$ has the usual Arrhenius form (Eq. 11)).

After the application of the Laplace-transformation and rescaling time as $z = t^n$, the following kth order approximation of $f(E)$ is obtained

$$f_k(E) = \frac{n}{RT} \frac{1}{(k-1)!} \left(\frac{-k}{\mu(E)} \right)^k \left[\frac{d^k}{dz^k} (1 - \alpha(z^{1/n})) \right]_{z = k/\mu(E)} \tag{40}$$

where $\mu(E) = [K(E, T)]^n$.

Here a difficulty is thought to arise from the instability of the preceeding equation which requires the evaluation of a kth derivative of a function derived from experimental data. Then, Krüger and Woldt [56] suggest two alternative numerical approximations to this problem:

(a) The experimental data are fitted with a suitable analytical function which can be subsequently differentiated by current algebraic program packages [58].

(b) Eq. (37) can be regarded as a Fredholm integral equation of the first kind. It can be approached, with the help of a quardrature formula, by a system of linear equations of the form

$$\bar{\alpha} = \bar{\Lambda} \bar{f} \tag{41}$$

where α and f correspond to a discrete representation of $\alpha(t)$ and $f(E)$ with a constant step, and the coefficients of matrix $\bar{\Lambda}$ can be obtained by means of a Simpson quardrature.

From a computational standpoint, the inversion of such an integral equation represents an 'ill-posed' problem and the regularization method is the traditional way to convert it into a related well-posed problem by the introduction of some condition of

smoothness within the field of admissible solutions. In this way, the minimization of the so-called Tikhonov functional leads to the following system of equations

$$(\bar{\Lambda}^t \bar{\Lambda} + \lambda I)\bar{f} = \bar{\Lambda}^t \bar{\alpha} \tag{42}$$

I being the identity matrix and λ a parameter controlling the balance between the smoothness of the solution and the accuracy of the stabilized solution (indicated by the residual $\| \Lambda \bar{f} - \bar{\alpha} \|$). Unlike the original problem, Eq. (42) can be solved by a simple inversion matrix.

Under a minor modification, this model can work satisfactorily with data of either isothermal or non-isothermal transformations.

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