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## Extension of the classical theory of crystallization to non-isothermal regimes: Application to nanocrystallization processes

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#### ABSTRACT

The non-isothermal kinetics of primary crystallization processes is studied from numerically generated curves and their predictions have been tested in several nanocrystallization processes. Single processes and transformations involving two overlapped processes in a non-isothermal regime have been generated and deviations from isokinetic behavior are found when the overlapped processes have different activation energies. In the case of overlapped processes competing for the same type of atoms, the heating rate dependence of the obtained Avrami exponent can supply information on the activation energies of each individual processes. The application to experimental data of nanocrystallization processes is consistent with a limited growth approximation. In the case of preexisting crystallites in the as-cast samples, predictions on the heating rate dependence of the obtained Avrami exponents of multiple processes have been confirmed.

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#### 1. Introduction

The study of the devitrification kinetics in glassy metals has received attention since their discovery [1-3]. The application of the classical theory of crystallization (based on nucleation and growth processes) to this process was also early adapted [2,3]. This theory was developed independently by Kolmogorov [4,5], Jhonson and Mehl [6], and Avrami [7] (JMAK theory) in the late 1930s of the last century to be applied to isothermal polymorphic transformations. However, it can be appropriately extended to transformations implying compositional changes [8,9] and to non-isothermal processes [10-19].

In this work, a direct extension of the classical theory of isothermal crystallization to non-isothermal processes, previously proposed by the authors [16], is revised in order to solve deviations observed for low transformed fractions. In the frame of this approach, the kinetic analysis of the primary crystallization of several metallic glasses including the development of single or multiple phases is evaluated. Nanocrystallization processes fulfill most of the five postulates of Kolmogorov (listed in Ref. [5]). In the case of nanocrystallization processes, the crystallites can be considered spherical (isotropic growth) and non-random nucleation is claimed to occur (due to non-homogeneity of the matrix [20], nucleation enhancement by Cu clustering phenomena [21–23] or formation of agglomerates in Hitperm alloys [24]). However, random nucleation can be assumed as an approximation for a global view of the transformation.

#### 2. Kinetics of crystallization

#### 2.1. Isothermal processes

In JMAK theory, the extended transformed fraction,  $X^*$  [5] corresponds to the fraction of the system that should be transformed if any growing crystal could freely grow without impinging with another growing crystal (i.e., if no geometrical impingement occurred). It is obtained from the nucleation rate, I = dN/dt (N being the number of nuclei formed per unit volume, and t, the time), and the rate of linear growth, G = dR/dt (R being the average radius of the crystals). For isotropic growth in three dimensions:

$$X^{*} = \frac{4\pi}{3} \int_{0}^{t} I(t') \left( \int_{t'}^{t} G(\tau) d\tau \right)^{3} dt'$$
(1)

where crystals are considered to be spherical. Assuming power laws for nucleation rate  $I = I_0 t^b$  and linear growth  $G = G_0 t^a$ , results:

$$X^* = \frac{4\pi}{3} \frac{I_0 G_0^3}{C} t^{3(a+1)+b+1} = K t^n = (kt)^n$$
(2)

with *C* a constant,  $k = K^{1/n}$ , the frequency factor, and *n*, the Avrami exponent. The value of this exponent can be decomposed as  $n = n_l + 3n_G$ , where  $n_l = 1 + b$  corresponds to nucleation (with a nucleation rate constant if b = 0 ( $n_l = 1$ ), increasing l(t) if b > 0 and decreasing l(t) if b < 0); and  $n_G = a + 1$  corresponds to growth





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( $n_G = 1/2$ , for diffusion controlled growth,  $G = G_0/t^{1/2}$ , and  $n_G = 1$  for interface controlled growth,  $G = G_0$ ).

The relationship between  $X^*$  and the actual transformed fraction, X, is obtained considering a statistical geometrical impingement:

$$\frac{dX}{dX^*} = 1 - X \tag{3}$$

The JMAK equation results when Eqs. (2) and (3) are combined:

$$X = I - \exp\left(-(kt)^n\right) \tag{4}$$

#### 2.2. Extension to non-isothermal processes

Nakamura et al. [25] proposed a general expression of the transformation equation to extend JMAK equation to non-isothermal processes, which for a constant heating rate  $\beta$  results:

$$X = 1 - \exp\left\{-(1/\beta^n) \left[\int_{T_o}^T k(T) dT\right]^n\right\}$$
(5)

where *T* is the temperature,  $T_O$  is the onset temperature and  $k(T) = k_0 \exp(-Q/k_B T)$  is a temperature dependent frequency factor, which is assumed to follow an Arrhenius law with *Q*, the activation energy, and  $k_B$ , the Boltzmann constant.

Later on, some of the present authors simplified Nakamura's expression considering the following approximation [16]:

$$K'_{0}\exp[-Q/k_{B}T](T-T'_{0}) = \int_{T_{0}}^{T} k(T)dT$$
(6)

In previous works [16,26–30], it was implicitly assumed  $T'_{O} = T_{O}$  (the onset temperature of the process). However, a deeper insight into this relationship is required to appreciate the effect of  $T'_{O}$  on the estimated values.

If we divide the two terms of Eq. (6) by k(T) we obtain a function A(T):

$$\frac{k'_0}{k_0}(T - T'_0) = \frac{\beta \int_0^t k(T)dt}{k(T)} = A(T)$$
(7)

which, according to Eq. (6), can be approximated to a straight line for a certain temperature range and, thus:

$$\frac{dA(T)}{dT} = \frac{k_0}{k_0} = D(T) \tag{8}$$

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The value of  $T'_{o}$  which leads to the best fitting depends on the value of the temperature *T* at which the approximation will be performed:

$$T'_{0} = T - \frac{A(T)}{D(T)}$$
 (9)

Fig. 1a shows the value of  $T'_o$  as a function of the temperature, *T*, at which the approximation of Nakamura's expression is performed for activation energies in the range 0.5–10 eV. Except for Q < 2 eV, a very good linear behavior can be found in a wide temperature range (from ~100 K to >1000 K), which extends far beyond the temperature range of interest for practical uses in the analysis of devitrification processes of amorphous alloys. As an example, for Q = 4 eV (typical value for primary crystallization processes of Fe-based amorphous alloys [3]) the fitting gives  $T'_o = [0.48993(2)T + 2.43(1)]$  K.

As Q changes from 3 to 10 eV, the slope of the straight line increases 2% and the value of the intercept with the Y-axis decreases from  $\sim$ 3 K to 0.3 K. These results allow us to propose an approximated value of  $T'_o$  for practical applications:

$$T'_0 = T_P/2$$
 (10)



**Fig. 1.** (a) Values of  $T'_o$  as a function of the temperature at which the approximation of Nakamura expression is performed for different values of activation energy. The dashed red line is a linear fitting to the curve corresponding to Q = 4 eV. (b) Left axis: comparison between A(T) (symbols) and the proposed approximation  $\frac{V_b}{k_0}(T - \frac{T_b}{2})$  (red line). Right axis: corresponding dX/dt curve generated using Nakamura kinetic equation at 10 K/min (Q = 4 eV; n = 4) (black line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

where  $T_P$  is the crystallization peak temperature and thus, the temperature around which it is found the thermal range of interest to perform the simplification of Nakamura's expression. It is worth mentioning that the present result is independent of the values of  $\beta$ ,  $k_0$  and  $k'_0$ . Moreover, as this approximation affects  $X^*$ , it is also independent of whether the kinetics of transformation follows JMAK equation or an expression considering a generalized impingement parameter [31,32].

In order to appreciate the goodness of the proposed approximation, Fig. 1b shows the two terms of Eq. (7) using  $T'_0 = T_P/2$  along with the corresponding curve of the transformation rate generated using Nakamura's equation ( $k_0 = 10^{25} \text{ s}^{-1}$ , n = 4, Q = 4 eV,  $\beta = 10 \text{ K/}$ min) as will be explained below. Only one free parameter,  $k'_0/k_0$ , has been used to fit A(T) function in the temperature range from 730 to 760 K resulting  $k'_0 k_0 = 5.314(3)$ .

## 3. Results. Validity of the approximation using numerically generated curves

#### 3.1. Crystallization processes implying the formation of a single phase

In order to appreciate the effect of  $T'_o$  on the Avrami exponent obtained applying the approximation of a direct extension to nonisothermal processes of Avrami equation, a systematic procedure was followed. Kinetic curves of X(t) were generated using Eq. (5) for different values of  $\beta$  (from 10 to 60 K/min), Q and n; and Kissinger method [33] was applied to recalculate the activation Download English Version:

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