



# Nanocrystallization kinetics understood as multiple microprocesses following the classical theory of crystallization



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## ABSTRACT

In this work, we propose a model for using the classical Johnson-Mehl-Avrami-Kolmogorov (JMAK) crystallization theory to analyze nanocrystallization processes as a set of multiple microprocesses. This model is based on the well-known microstructure observations of nanocrystalline systems for which, although the number of crystallites increases along the process, the growth of each crystallite is limited to a much shorter time than the needed one for completing the process. The very low values of the Avrami exponent,  $n \sim 1$ , are well reproduced assuming a set of multiple classical JMAK processes with constant nucleation rate and diffusion controlled growth,  $n_i = 2.5$  for each  $i$  individual microprocess. It is shown that the values of Avrami exponent experimentally observed and lying out of the theoretical range can be assumed as effective values derived from a complex process consisting of multiple microprocesses, which can be individually treated as classical ones.

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## 1. Introduction

The classical theory of crystallization developed by Kolmogorov [1], Johnson and Mehl [2] and Avrami [3–5] (JMAK) takes into account the nucleation and growth processes through the definition of the extended transformed volume fraction:

$$X^* = \frac{4\pi}{3} \int_0^t I(t') \left( \int_{t'}^t G(\tau) d\tau \right)^d dt' = (kt)^n \quad (1)$$

where  $I$  is the nucleation rate,  $d$  is the dimension of growth,  $G(t) = G_0 t^a$  is the growth rate ( $a = 1/2$  for diffusion controlled growth and  $a = 1$  for interface controlled growth, respectively [6]) and  $t$  is the time. Exponent  $n$  is the Avrami exponent and its value gives information about both mechanisms: nucleation and growth. In fact,  $n = b + da$ , being  $b = 1$  for constant nucleation rate and 0 for absence of nucleation [6]. Finally,  $k$  is the frequency factor for which an Arrhenius dependence is generally used and characterized by an activation energy  $Q$  [6]:

$$k = k_0 \exp\left(-\frac{Q}{k_B T}\right) \quad (2)$$

where  $k_0$  is a constant,  $k_B$  is the Boltzmann constant and  $T$  is the temperature.

Expression (1) does not correspond to the actual transformed fraction,  $X$ , as  $X^*$  neglects the geometrical impingement occurring when two transformed regions overlap [7]. This is solved in JMAK theory using statistical arguments assuming that:

$$\frac{dX}{dX^*} = 1 - X \quad (3)$$

Therefore, initially, for low transformed fractions,  $X$  and  $X^*$  almost coincide but as transformation progresses, whereas  $X^*$  can grow without limits,  $X$  is limited to 1.

Integration of expression (3), taking into account expression (1), leads to the well-known JMAK equation relating transformed fraction and time for an isothermal transformation:

$$X = 1 - \exp[-(k(t - t_0))^n] \quad (4)$$

where  $t_0$  is the induction time. This expression was developed for isothermal and polymorphic transformations. The first one assumes a constant temperature and the second one that the initial phase, occupying all the volume, completely transforms to a final phase without compositional change. However, it can be easily extended to describe transformations which do not affect the complete volume of the sample just normalizing the transformed

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volume to its maximum value at the end of the transformation and thus the computed  $X$  runs from 0 to 1 during the transformation. On the other hand, JMAK theory has been also extended to non-isothermal processes [8–11].

JMAK theory was successfully applied to describe many different transformations [12–14]. Experimental values of  $n$  can be obtained even for those systems for which the requirements of JMAK theory are not apparently fulfilled. Particularly, Avrami exponents obtained for nanocrystallization processes, close to 1, are clearly out of the values predicted from the theory as it should imply low dimensionality of the growth process and absence of nucleation, in clear disagreement with the microstructural observations [15]. In fact, nanocrystalline systems, developed during nanocrystallization processes of a precursor amorphous alloy, consist of small dispersed crystallites embedded in a residual amorphous matrix. As the size of the microstructural units in these systems are comparable to (or even lower than) some characteristic interaction lengths, atypical physical properties can be widely found leading to new behaviors with respect to their microcrystalline counterparts. Understanding the kinetics of the nanocrystallization process can help to a better controlling of the microstructure produced to finely tune the desired properties. Particularly, in soft magnetic nanocrystalline systems such as Finemet alloys [16], nanocrystals are much smaller than magnetic domain wall thickness and thus crystal boundaries are no longer pinning centers for the domain wall movement. Moreover, as a magnetic domain contains a large number of crystallites, the large magnetocrystalline anisotropy of Fe ( $K_1 = 10^4$  J/m<sup>3</sup>) is averaged down to almost cancel it [17].

Several attempts have been done to explain the very low values of  $n-1$  reported in the literature, generally based on the non-fulfillment of the JMAK requirements. Some descriptions are based on extra impingement mechanisms [18–20], as the so-called soft impingement [21–23], due to the interaction between the regions surrounding the nanocrystals which are depleted in the elements soluble in the crystalline phase. Using cellular automata simulations, local Avrami exponents were qualitatively reproduced after neglecting the growth process and simplifying the kinetics to that of an instantaneous growth transformation [24], which was further extended to a more realistic limited growth approach [25,26]. In fact, deviations of nanocrystallization kinetics with respect to the classical nucleation and growth model is the limited growth of the nanocrystals. In classical transformations every particle grows continuously, only affected by the geometrical impingement, which equally acts on every crystal independently of its nucleation time. However, in nanocrystallization processes, the growth of nucleated crystal is rapidly blocked due to the accumulation at the boundary of the nanocrystals of those elements insoluble in the crystalline phase (i.e. Nb and B in Finemet alloys). Therefore, those nanocrystals formed in the early stages of the transformation do not contribute to the transformation at later stages, unlike it occurs for classical transformations. This idea is

schematically shown in Fig. 1. Initially the sample is amorphous, after the induction time first set of nanocrystals appear. Later on, these nanocrystals become blocked, whereas, in the meantime, new nanocrystals have nucleated and are growing. The amount of these new nanocrystals should be smaller as the volume available for crystallization decreases as crystallization progresses. This sequence of passive blocked nanocrystals and active growing nanocrystals (shown in yellow and red in Fig. 1, respectively) occurs till the nanocrystallization is finished.

In this work, we have followed this view of the nanocrystallization and we describe the nanocrystallization process as the addition of multiple successive simple JMAK processes corresponding to constant nucleation rate and three dimensional growth controlled by diffusion and thus  $n_i = 2.5$ . In fact, the analysis of a multiple process as a single one has been shown to yield lowers Avrami exponents than the expected ones [27]. As it will be shown below, the Avrami exponents predicted are in agreement with those generally reported for nanocrystallization processes. The prediction of the proposed model will be compared to experimental results derived from isothermal nanocrystallization of an amorphous alloy with Finemet composition.

## 2. Model based on multiple JMAK processes

The proposed model should describe the nanocrystallization process as if the nanocrystals to be formed were grouped in sets sharing their onset of transformation. Assuming that the total transformation consists of a sum of several JMAK transformations, the transformed fraction could be calculated as [27]:

$$X = \sum_i f_i X_i = \sum_i f_i (1 - \exp[-(k_i(t - t_{0i}))^{n_i}]) \quad (5)$$

Where  $X_i$  is the transformed fraction of each individual process normalized to 1 and thus  $\sum f_i = 1$ , being  $f_i$  the maximum transformed fraction of the total volume of the sample corresponding to the  $i$  process and  $k_i$ ,  $t_i$  and  $n_i$ , the frequency factor, the induction time and the Avrami exponent of the  $i$  process, respectively.

As the transformation progresses, the volume able to be transformed,  $1-X$ , decreases and we assume that the maximum transformed fraction of the  $i$  process is proportional to this remnant volume. This volume depends on the addition of the different  $f_j$  values of the previous processes. Therefore, a simple relation among  $f_i$  values is proposed:

$$f_i = f_1 \left( 1 - \sum_{j < i} f_j \right) \quad (6)$$

where  $f_1$  is the maximum transformed fraction achieved by the first process. This expression can also be written as:

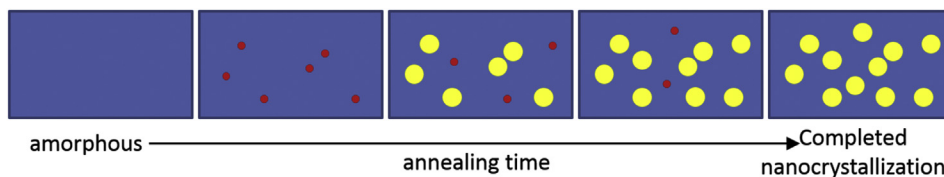


Fig. 1. Schematic view of the progress of the nanocrystallization process with the annealing time. Active growing nanocrystals are shown in red and blocked nanocrystals are shown in yellow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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