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Spatial distribution of nuclei in progressive nucleation: Modeling and application

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HIGHLIGHTS

- An analytical model for pair-correlation function of actual nuclei is developed.
- The nearest-neighbor distribution function of nuclei is computed for electrochemical nucleation.
- The approach describes the transition from Poissonian to non-random spatial distribution of nuclei.
- The model is in good agreement with experimental data and computer simulations.

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ABSTRACT

Phase transformations ruled by non-simultaneous nucleation and growth do not lead to random distribution of nuclei. Since nucleation is only allowed in the untransformed portion of space, positions of nuclei are correlated. In this article an analytical approach is presented for computing pair-correlation function of nuclei in progressive nucleation. This quantity is further employed for characterizing the spatial distribution of nuclei through the nearest neighbor distribution function. The modeling is developed for nucleation in 2D space with power growth law and it is applied to describe electrochemical nucleation where correlation effects are significant. Comparison with both computer simulations and experimental data lends support to the model which gives insights into the transition from Poissonian to correlated nearest neighbor probability density.

1. Introduction

Phase transformations ruled by nucleation and growth represent an important topic in Materials Science because of the effect these processes have on the microscopic structure of the materials. In modeling phase transformations, nucleation is assumed to occur at seeds, randomly distributed throughout the space, which become nuclei once they start growing. Nucleation can be either simultaneous or progressive; in the first case nuclei are all formed at the same instant while in the second are generated continuously as the transformation proceeds. The transformation can be analyzed by the theory of nucleation and growth developed, independently, by Kolmogorov, Johnson and Mehl and Avrami (KJMA) [1–3]. Progressive nucleation rises some issues at the level of modeling; the most celebrated one is related to the "phantom overgrowth" which limits the applicability of the KJMA approach to a particular class of growth laws [4]. The term phantom, as originally introduced in Ref. [3], is referred to a seed that was swallowed by the new phase before it starts growing. Such a seed will not contribute to the phase transformation. Nevertheless, in the framework of Poisson dot process both actual and phantom nuclei have to be included in the mathematical formulation, since seeds are randomly distributed throughout the space [4].

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The presence of phantom nuclei put in evidence another difference between simultaneous and progressive nucleation, that is related to the spatial distribution of actual nuclei. In fact, from the previous considerations it follows that in the former case nuclei are randomly distributed throughout the space while in the latter non-Poissonian distribution is expected.

On one hand several studies have been devoted to model the *size*-distribution function of nuclei in phase transformations which are compliant with the KJMA approach. These modelings are aimed at determining the time dependence of the distribution function for both simultaneous and progressive nucleation [5–7]. In the case of simultaneous nucleation the distribution function at the end of the transformation matches the Gamma distribution which well describes Poisson–Voronoi tessellation even in non-Euclidean metrics [5,8,9]. Progressive nucleation is more involved as it implies fragmentation of Voronoi cells during nucleation; yet a good description of the distribution function has been achieved through superposition of Gamma distribution functions [7]. Insights into macroscopic properties of materials can also be gained through the study of correlation functions among transformed and/or untransformed points of the system [10–12]. On the other hand, modelings devoted to characterize the spatial distribution of the actual nuclei in KJMA-type phase transformations are scarce in the literature. This is due to the fact that a comprehensive description of the microscopic structure of the system is achieved by means of the quantities above mentioned, linked to size and shape of the grains of the product phase. Nevertheless, the study of spatial arrangement of actual nuclei in KJMA compliant transformations ruled by progressive nucleation is of great interest in view of its application to electrodeposition. At large overpotentials the diffusion of the active species in the liquid phase becomes rate determining and diffusion fields are established around growing nuclei. As the deposition proceeds, overlap among diffusion fields leads the transition from a spherical to a planar regime of diffusion [13,14]. In order to describe this complex transition, modeling based on the concept of "diffusion zones" has been developed which is suitable for describing experimental kinetics [15–18]. This approach exploits the analogy between the diffusion current at the surface of a hemispherical nucleus and that at a planar surface [19]. The complex problem of describing mass transport for overlapping 3D diffusion-fields is reduced to study the planar diffusion across overlapping disks [13,14]. In the planar diffusion zones approach a 1:1 correspondence is assumed between actual nuclei and disks, the growth of each nucleus is modeled by diffusion through its own disk (or a part of it). It follows that during progressive nucleation an exclusion zone for nucleation develops around each actual nucleus [13]. The radius of the exclusion disk (r_d) is computed to be greater than the nucleus radius (r_n) [14] where the area of the diffusion zone is computed by means of the KJMA model. Owing to the large r_d/r_n ratio, when nucleation is exhausted the fraction of electrode surface covered by nuclei is small, nuclei are well separated and their distribution is, in general, non-Poissonian [20,21]. It is also in this ambit that the modeling of the distribution of actual nuclei in KJMA-type transitions finds its justification.

Characterization of the spatial distribution of actual nuclei in electrodeposition is performed through the nearest neighbor probability density and pair correlation functions. Experimental data on a variety of electrochemical systems [22–25] are successfully interpreted on the basis of the "exclusion zone" model for nucleation. Computer simulations also show that the spatial arrangement is ruled by the most influential neighbor, so supporting the exclusion zone hypothesis above reported [26]. Studies on the possibility to get long-range order in electrodeposition have been carried out in Ref. [24] and distribution function for nth-neighbors determined by computer simulations in Ref. [27]. On one hand, computer simulations of progressive nucleation with exclusion zones show that the displacement of the nearest neighbor distribution (nnd) from the Poissonian distribution depends upon number density of nucleation sites [21,27]. On the other hand, analytical approaches of the nnd in electrodeposition are limited to the hard-core correlation between disks equal in size [20].

The purpose of the present work is twofold: Firstly, to develop an analytical model of the pair-correlation function and nearest neighbor probability density of actual nuclei in KJMA transformations with progressive nucleation. Secondly, to apply the modeling for describing nnd in electrodeposition and to compare it with computer simulations and experimental data. In view of this application the theory is developed for transformations in 2D space, although its extension to other dimensions is straightforward.

The paper is organized as follows. The first two sections are devoted to the computation of the pair-correlation function and nearest neighbor probability density. The purpose of the third section is to bridge the gap between computer simulations and analytical approach for nnd in electrochemical nucleation. To this end, the last section provides application of the model to describe nnd obtained from experiments and computer simulations.

2. Results and discussion

2.1. Pair-correlation function of actual nuclei

In this section we determine the pair-correlation function of actual nuclei in 2D transformations occurring by progressive nucleation and growth. Throughout the paper, we distinguish between actual and phantom (or virtual) nuclei since they are both considered in the formulation of the theory. As anticipated in the introduction, the present work also focuses on modeling the spatial distribution of actual nuclei in electrodeposition. To this end, upon nucleation a disk of radius r_d, centered on each nucleus starts growing, that is the disk where further nucleation is prevented. In the following the term "exclusion zone" is referred to the region unavailable to the formation of actual nuclei. The area of the exclusion zone is computed through the KJMA theory for nucleation and growth of disks of radius r_d, where r_d is greater than nucleus radius. Clearly, if the radius of the exclusion disk coincides with the nucleus radius the "exclusion zone" is the "natural region"