The kinetics of heterogeneous nucleation and growth: an approach based on a grain explicit model

B Rouet-Leduc\textsuperscript{1,2}, J-B Maillet\textsuperscript{1} and C Denoual\textsuperscript{1}

\textsuperscript{1} CEA, DAM, DIF, F-91297 Arpajon, France
\textsuperscript{2} Département de Chimie, Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris cedex 05, France

E-mail: jean-bernard.maillet@cea.fr

Received 21 October 2013, revised 31 December 2013
Accepted for publication 20 January 2014
Published 28 March 2014

Abstract

A model for phase transitions initiated on grain boundaries is proposed and tested against numerical simulations: this approach, based on a grain explicit model, allows us to consider the granular structure, resulting in accurate predictions for a wide span of nucleation processes. Comparisons are made with classical models of homogeneous (JMAK: Johnson and Mehl 1939 \textit{Trans. Am. Inst. Min. Eng.} \textbf{135} 416; Avrami 1939 \textit{J. Chem. Phys.} \textbf{7} 1103; Kolmogorov 1937 \textit{Bull. Acad. Sci. USSR, Mat. Ser.} \textbf{1} 335) as well as heterogeneous (Cahn 1996 \textit{Thermodynamics and Kinetics of Phase Transformations} (Pittsburgh: Materials Research Society)) nucleation. A transition scale based on material properties is proposed, allowing us to discriminate between random and site-saturated regimes. Finally, we discuss the relationship between an Avrami-type exponent and the transition regime, establishing conditions for its extraction from experiments.

Keywords: microstructure, analytical methods, phase transformations, recrystallization, kinetics

Online supplementary data available from stacks.iop.org/MSMSE/22/035018/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Recrystallization is a mechanism of great scientific and technological importance, widely studied and modeled [3], encountered during the thermomechanical processing of various materials including metals [4, 5]. The first model that efficiently captured the main features...
of crystallization, namely, the JMAK model, states that grains nucleate from random locations and that the grains grow until they are impinging other neighboring growing grains. Thanks to its straightforwardness, this model has also been used in many other situations, provided that the hypotheses of random nuclei and an independent growing zone are met: temperature dependent crystallization [6], combustion [7], particle physics [8], crystallization in amorphous materials [9], evolution of damage under dynamic tensile loadings [10] and solid state phase transitions in general [11], making the JMAK model a much-encountered approach.

Random distribution of nuclei is, however, a rather crude hypothesis. For example, material failure can occur from cracks nucleating preferably on grain boundaries [12, 13], combustion of solid energetic materials starts at preferred sites [14], nucleation of grains during recrystallization appears at a prior grains frontier [15], microstructuring nanocomposites enhances the kinetics of physisorption [16] and crystallization can be influenced by impurities [17], confinement in a porous media [18] or contact with grain boundaries of another material [19]. Thus, the problem of nucleation from interfaces is encountered in a variety of fields [20–26] and the importance of structured nucleation sites—in inner nucleation-free volumes bounded by interfaces—as well as grain-size dependence is commonly witnessed [2, 27].

In this regard, extensions of the JMAK model have been proposed over the years to account for the specificities of structured nucleation. Most derivations still consider random distribution of nuclei, improving the model by fitting the so-called Avrami parameters [28, 29].

One of the major improvements of the JMAK model, which considers the problem of nucleation heterogeneity, was proposed by Cahn and considers nuclei distributed on planar interfaces [2, 30] and was further generalized by Villa and Rios [31]. Cahn’s main assumption is that the superimposing planes are randomly located. However, an accurate modeling for higher nucleation densities requires capturing the deterministic nature of the location of nucleation—the grains boundaries—excluding grain volume from possible nuclei sources. In other words, an assembly of random planes is a coarse description of interfaces in a granular material.

In this paper, we propose an accurate modeling of the kinetics of grain nucleation and growth that explicitly accounts for grain boundaries as preferred sites for nuclei. A characteristic length \( L_t \) is introduced and compared with the average grain size, which allows for a detailed analysis of the influence of the microstructure on the kinetics of transformation. It is shown that for high nucleation rates, the kinetics are controlled by the granular structure, leading to a deterministic behavior. On the other hand, for a decreasing nucleation rate the effect of microstructure progressively vanishes. We predict the transition between these two regimes. The validity of this modeling is supported by simulations of transformations initiated by random nucleation on the interfaces of a Voronoi tessellation. Finally, we revisit the relationship between an Avrami-type exponent and the transition from homogeneous to heterogeneous nucleation.

2. Model

Once nucleated at time \( t' \), a transformation zone expands from the nucleation site over a maximum travel distance given by \( h_T(t) = \int_{t'}^t c(s) \, ds \), with \( c(s) \) being the expansion celerity and \( t \) the present time. All potential nucleation sites in this expansion zone then become inhibited. Thus, a nucleation point \( q' \) is inhibiting all nucleation in a time-growing transformed zone of radius \( h_T(t) \).
Considering a random point \( q \), a nucleation event taking place at time \( t' \) at a distance smaller than \( h_{t'}(t) \) will transform \( q \) before \( t \). Therefore, the probability that \( q \) is transformed at \( t \) is given by the probability that at least one nucleation occurred in its horizon \( H(q, t) = \{(x, t'), \|x - q\| \leq h_{t'}(t)\} \) (see figure 1(a)).

Using the time-cone method (see [32] for a demonstration), the transformed volume fraction is expressed as

\[
\Phi(t) = \Phi(q, t) = 1 - \exp \left(-\int_{H(q, t)} \alpha(q', t') \, dq \, dt'\right)
\]

\[
= 1 - \exp \left(-N(q, t)\right),
\]

where \( \alpha(t) \) is the nucleation rate density and \( N(q, t) \) is therefore the average number of nucleation events over the horizon \( H(q, t) \). This model, as the JMAK and Cahn’s model, assumes hard impingement.

In what follows, we give an expression for \( N \) in the general case of heterogeneous nucleation, focusing on nucleation on grain boundaries. Our model is grounded on a simplified representation of a polycrystal as a spherical grain surrounded by an averaged and homogeneous
material. In this grain explicit model (GEM), nucleation can occur on the grain surface (with intensity \( \alpha(t) \)) or beyond with an intensity approximated by the average nucleation rate over the whole volume, \( \alpha(t)(S/V) \), as depicted in the lower panel of figure 1.

The spherical symmetry allows us to reduce the integration over the grain radius \( r \) only. Considering a point \( q_a \) at a distance \( a \) from the grain boundary, we define the average number of nucleation events \( N_r(a, t) \) inside the horizon \( H(a, t) \) as a function of \( a \) and \( r \).

By noting that nucleation is not possible inside the grain, the volume integral in equation (1) can be split into two terms, accounting for nucleation at its surface and denoted as \( S_r \), and from the outside material denoted as \( V_r \):

\[
N_r(a, t) = \int_{S_r \cap H(a, t)} \alpha(t') \, ds \, dt' + \int_{V_r \cap H(a, t)} \frac{S}{V} \alpha(t') \, dv \, dt',
\]

where \( S_r \cap H(a, t) \) is the intersection of the horizon with the grain surface, \( V_r \cap H(a, t) \) is the intersection of the horizon with the outside material and \( ds \) and \( dv \) are elementary surface and volume elements. The fraction of grain surface \( w_S(r, a, \tau) = \frac{S_r \cap H(a, t)}{S} \) is a function of the propagation time \( \tau = t - t' \) between a past event occurring at \( t' \) and the current time \( t \):

\[
w_S(r, a, \tau) = \begin{cases} 
0 & \text{if } c \tau < a, \\
\pi \left[ c^2 \tau^2 - a^2 \right] \left( \frac{r}{r-a} \right) & \text{if } a \leq c \tau \leq 2r - a, \\
4\pi r^2 & \text{if } c \tau > 2r - a,
\end{cases}
\]

where \( c \) is considered constant for the sake of simplicity. Similarly, the fraction of the averaged volume \( w_V(r, a, \tau) = \frac{V_r \cap H(a, t)}{V} \) (a lens) is given by

\[
w_V(r, a, \tau) = \begin{cases} 
0 & \text{if } b < 0, \\
\frac{4}{3} \pi c^3 r^3 - \frac{\pi}{3} (c\tau + a - b)^2 (2c\tau - a + b) & \text{if } 0 \leq b \leq 2r, \\
-\frac{\pi}{3} b^2 (3r - b) & \text{if } b > 2r,
\end{cases}
\]

with \( b = ((c^2 \tau^2 - a^2)/2(r - a)) \). Finally, the investigated integral \( N_r(a, t) \) becomes a simple time convolution:

\[
N_r(a, t) = \int_0^t \left[ w_S(r, a, t - t') + w_V(r, a, t - t') \right] \frac{S}{V} \alpha(t') \, dt'.
\]

We can now express the transformed fraction of a grain \( \Phi(t, r) \) as an integration of the probability of transformation \( [1 - \exp(-N_r(a, t))] \) toward its center following a homothetic path:

\[
\Phi(t, r) = \frac{3}{r} \int_0^r \left[ 1 - \exp(-N_r(a, t)) \right] \left( \frac{r-a}{r} \right)^2 \, da.
\]

This closed-form solution is numerically integrated (see supplementary material for a detailed implementation), and allows for an instantaneous evaluation (less than 1s) of \( \Phi(t, r) \). Taking into account a realistic grain-size distribution, e.g. as in [33], would require an additional integral.

In what follows, we will show that the model presented here is accurate over a wide range of situations, and is exact for the limit cases of homogeneous and site-saturated nucleation.
point is most likely to be caused by a nucleation outside of the grain. The transformed fraction \( \Phi(t) \) then reduces to the classical solution of the JMAK model:

\[
\Phi(t) = 1 - \exp\left(-\frac{4\pi}{3} \int_0^t \alpha(t') |c(t - t')|^3 dt'\right),
\]

(7)

On the other hand, a sufficiently high nucleation rate ensures that \( 1 - \exp(-N_r(a, t)) = 1 \) for \( ct \geq a \) (and 0 otherwise), yielding the exact expression of the homothetic transformation of a grain, similar to the model proposed in [34], once injected into equation (6):

\[
\Phi(t, r) = \frac{3}{r} \int_0^{ct} \left(\frac{r - a}{r}\right)^2 da = 1 - \left(\frac{r - ct}{r}\right)^3,
\]

(8)

with \( ct \leq r \). In figure 2, model predictions are presented compared with grid-based simulation results with Voronoi tessellations accounting for the granular microstructure and nucleation events being randomly generated on grain surface voxels, with a spherical expansion of transformed zones from nucleation sites.

The grain centers are randomly distributed within the volume and each simulation voxel is attributed to the nearest grain center, generating a Poisson Voronoi tessellation. Grain surfaces are described by voxels in the vicinity of grain boundaries, i.e. voxels at equal distance from two grain centers, \( \pm \delta_g/2 \), with \( \delta_g \) being the thickness of the grain boundary. While noting \( (S/V) \) the fraction of voxels attributed to surfaces, we calculate the nucleation rate \( \alpha \) of these voxels by stating the product \( \alpha(S/V) \) to be equal to a volume nucleation rate. Once a nucleation has occurred, it propagates isotropically for each subsequent step. The transformed fraction at each time step is then the fraction of transformed voxels. The numerical parameters of the grid-based simulation we used for figure 2 are as follows: the microstructure was generated by a voronoi tessellation of density \( 5 \times 10^{-6} \), giving an average grain radius \( L_g = 28.8 \) units of length, the propagation speed of the transformation was \( c = 0.5 \) units of length per unit of time and the nucleation rate averaged over the whole simulation volume was set to \( \alpha(S/V) = 0.002 \) 75 nucleation events per voxel and per unit of time. The simulations were performed on \( 10^6 \) voxels with periodic boundary conditions.

The very good agreement of the GEM model with the voronoi-based simulations validates the spherical grain approximation as well as the representation of the heterogeneous material as a surrounding equivalent media, with Voronoi tessellations being considered as a relevant model for the microstructure of real materials [35]. As the JMAK model contains no structural information about the nucleation sites, differences from the structured models (Cahn and GEM) become significant very early. Up to intermediate time steps, the absence of grain-size scale correlations between nucleation sites makes the random planes (Cahn) and grain explicit (GEM) models indiscernable. However, when approaching complete transformation, the increasing difference between the Cahn and GEM models highlights the importance of having an explicit grain description.

3. Transition scale

We will now show that the transition between homogeneous nucleation (from the 3D averaged volume) and heterogeneous nucleation (from the 2D grain surface) is associated with a characteristic scale. With the intent of distinguishing these two extreme behaviors, we will define a characteristic length for dimensions \( D = 2 \) and \( D = 3 \). With this goal in mind, we consider the horizon that contains one nucleation event on average at a characteristic time \( t_c \) [36]:

\[
\int_0^{t_c} \alpha |D(t_c - t')| k c^D(t_c - t')^D dt' = 1,
\]

(9)
Figure 2. Fraction of transformed material plotted against time. We see a comparison between analytical models (JMAK, Cahn, GEM) and numerical simulations of transformation propagating from grain boundaries (see the text for simulation details). The Mathematica program computing GEM is supplied as online supplemental material (stacks.iop.org/MSMSE/22/035018/mmedia).

where \( k \) is a shape parameter (\( k = \pi \) in 2D and \( k = 4\pi/3 \) in 3D). For a constant \( \alpha \), \( t_c \) is given by

\[
t_c = \left( \frac{D + 1}{\alpha D k c \alpha} \right)^{1/(D+1)},
\]

with \( \alpha_2 = \alpha \) and \( \alpha_3 = \alpha S/V \). The radius of the horizon at \( t_c \) defines the characteristic length \( L_D \) representing half of the average distance between nucleation sites:

\[
L_D = \left( \frac{c(D + 1)}{k \alpha D} \right)^{1/(D+1)}.
\]

For \( D = 2 \), \( L_2 \) should be orders of magnitude smaller than the grain radius \( L_g \) in order to guarantee the 2D nucleation hypothesis. On the other hand, for \( D = 3 \), homogeneous nucleation can only hold when \( L_3 \) is compatible with an averaging over numerous grains, that is, for \( L_3 \gg L_g \). A simple transition definition is to consider the frontier between the two domains, at \( L_2 = L_3 = L_t \), which leads to

\[
L_t = \left( \frac{3c}{\pi \alpha} \right)^{1/7}.
\]

Nucleation can thus be defined as homogeneous or heterogeneous depending on how \( L_t \) compares with the average volume-to-surface ratio \( V/S \). If \( L_t \) is larger than \( V/S \), then the horizon containing one event covers many grains, thus making the dynamics of nucleation homogeneous. On the other hand, if \( L_t \) is smaller than \( V/S \), then the horizon containing one event is smaller than the grain, and the kinetics are that of a heterogeneous nucleation.

4. Discussion

The transition from homogeneous to heterogeneous nucleation is investigated through the use of a wide range of nucleation rates \( \alpha \). Recalling that the Cahn and GEM models diverge
Figure 3. Time to reach 80% transformation is plotted against the proposed scale \( L_t/(V/S) \). The numerical parameters are identical to those used for figure 2, except for the nucleation rate \( \alpha \), which varies in order to cover a wide range of nucleation regimes, according to equation (12).

when approaching complete transformation, we arbitrarily choose the time to reach 80% transformation \( t_{80} \) as a criterium for subsequent evaluation, and compare in figure 3 the various models and the simulation across the transition. As anticipated, the GEM and Cahn models exhibit a JMAK asymptotic behavior for low \( \alpha \left( L_t \gg (V/S) \right) \). For very high nucleation rates \( \left( L_t \ll (V/S) \right) \) the GEM \( t_{80} \) becomes proportional to the grain size \( L_g \), and the Cahn model exhibits a horizontal asymptote as well. However, its limit is different from that of the simulations and does not explicitly depend on the grain size, but rather on the volume-to-surface ratio. The evolution between these two asymptotic behaviors, reproduced by numerical simulations, demonstrates the transition occurring over approximately one decade of \( L_t/(V/S) \). Since the transition takes place around \( L_t = V/S \), the initial assumption of a transition scale of \( L_2 = L_3 \) is confirmed to be relevant.

In addition, a criterium frequently proposed to characterize this transition is

\[
    n = \frac{dA(t)}{d \ln(t)},
\]

with \( A(t) = \ln(-\ln(1 - \Phi(t))) \), which is often referred to as the Avrami exponent. This exponent varies from 4 in the case of 3D homogeneous nucleation to 1 in the limit of site-saturated grain boundary nucleation. Therefore, it is considered to be a reliable signature of the nucleation regime (heterogeneous versus homogeneous). With the aim of providing an unbiased method to determine the Avrami exponent, we propose to define it as the minimum of \( n(\Phi) \) (equation (13)) and compare it with the commonly used \( n \) at fixed transformed fractions.

In figure 4, \( \min(n(\Phi)) \) (extracted from the GEM model) ranges from 1 to 4, with most of its variation taking place across the previously observed transition \( 0.1 < L_t/(V/S) < 1 \). Surprisingly, none of the \( n \) determined at the fixed transformed fraction are able to reproduce both the transition at \( L_t/(V/S) \approx 1 \) and the asymptotic value of \( n = 1 \). Hence, \( \min(n(\Phi)) \) is the only definition of the Avrami exponent that carries reliable information about the transition between homogeneous and heterogeneous nucleation.

In conclusion, we have proposed a grain explicit model (GEM) for the kinetics of phase transformation initiated at interfaces that reconciles heterogeneous and homogeneous
nucleation. The GEM model exhibits exact limits (JMAK and site saturated), and is validated against numerical simulations spanning all nucleation regimes. Furthermore, we proposed a reliable transition scale $L_t$, based on material properties, which enables the prediction of the nucleation regime once compared with the characteristic length $V/S$ of the granular structure. Finally, we revisited the determination method of the Avrami-type exponent, commonly derived from experimental data, and showed that once defined as the minimum slope of Avrami-type plots, it offers a second and independent way to retrieve information about the nucleation regime.

Acknowledgment

The authors thank N Desbiens and C Matignon for their useful points of view. D Hassine is also thanked for his helpful review.

References

[1] Johnson W A and Mehl R. F. 1939 Trans. Am. Inst. Min. Eng. 135 416
Avrami M 1939 J. Chem. Phys. 7 1103
Kolmogorov A N 1937 Bull. Acad. Sci. USSR, Phys. Ser. 1 335
[2] Cahn J W 1996 The Time Cone Method for Nucleation and Growth Kinetics on a Finite Domain Proc. MRS Symp. on Thermodynamics and Kinetics of Phase Transformations ed J S Im et al (Pittsburgh: Materials Research Society) 425–38
[3] Rollett A D 1997 Prog. Mater. Sci. 42 79
[4] Doherty R D, Hughes D A, Humphreys F J, Jonas J J, Juul Jensen D, Kassner M E, King W E, McNelley T R, McQueen H J and Rollett A D 1997 Mater. Sci. Eng. A 238 219
[5] Christian J W 1970 Physical Metallurgy 2nd edn ed R W Cahn (Amsterdam: North-Holland)
[6] Farjas J and Roura P 2007 Phys. Rev. B 75 184112
[7] Karttunen M, Provatas N, Ala-Nissila T and Grant M 1998 J. Stat. Phys. 90 1401
[8] Csermai L P and Kapusta J I 1992 Phys. Rev. Lett. 69 737
[9] Spinella C, Lombardo S and Priolo F 1998 J. Appl. Phys. 84 5383
[10] Trumel H, Roy G, Pellegrini V-P and Denoual C 2009 J. Mech. Phys. Solids 57 1980
[11] Liu F, Sommer F and Mittemeijer E 2007 Int. Mater. Rev. 52 193
[12] Kobayashi S, Inomata T, Kobayashi H, Tsurekawa S and Watanabe T 2008 J. Mater. Sci. 43 3792
[13] Cserna L P and Kapusta J I 1992 Phys. Rev. Lett. 69 737
[14] Spinella C, Lombardo S and Priolo F 1998 J. Appl. Phys. 84 5383
[15] Trumel H, Roy G, Pellegrini V-P and Denoual C 2009 J. Mech. Phys. Solids 57 1980
[16] Liu F, Sommer F and Mittemeijer E 2007 Int. Mater. Rev. 52 193
[17] Karttunen M, Provatas N, Ala-Nissila T and Grant M 1998 J. Stat. Phys. 90 1401
[18] Csermai L P and Kapusta J I 1992 Phys. Rev. Lett. 69 737
[19] Spinella C, Lombardo S and Priolo F 1998 J. Appl. Phys. 84 5383
[20] Trumel H, Roy G, Pellegrini V-P and Denoual C 2009 J. Mech. Phys. Solids 57 1980
[21] Liu F, Sommer F and Mittemeijer E 2007 Int. Mater. Rev. 52 193
[22] Karttunen M, Provatas N, Ala-Nissila T and Grant M 1998 J. Stat. Phys. 90 1401
[23] Csermai L P and Kapusta J I 1992 Phys. Rev. Lett. 69 737
[24] Spinella C, Lombardo S and Priolo F 1998 J. Appl. Phys. 84 5383
[25] Trumel H, Roy G, Pellegrini V-P and Denoual C 2009 J. Mech. Phys. Solids 57 1980
[26] Liu F, Sommer F and Mittemeijer E 2007 Int. Mater. Rev. 52 193
[27] Karttunen M, Provatas N, Ala-Nissila T and Grant M 1998 J. Stat. Phys. 90 1401
[28] Csermai L P and Kapusta J I 1992 Phys. Rev. Lett. 69 737
[29] Spinella C, Lombardo S and Priolo F 1998 J. Appl. Phys. 84 5383
[30] Trumel H, Roy G, Pellegrini V-P and Denoual C 2009 J. Mech. Phys. Solids 57 1980
[31] Liu F, Sommer F and Mittemeijer E 2007 Int. Mater. Rev. 52 193
[32] Karttunen M, Provatas N, Ala-Nissila T and Grant M 1998 J. Stat. Phys. 90 1401
[33] Csermai L P and Kapusta J I 1992 Phys. Rev. Lett. 69 737
[34] Spinella C, Lombardo S and Priolo F 1998 J. Appl. Phys. 84 5383
[35] Trumel H, Roy G, Pellegrini V-P and Denoual C 2009 J. Mech. Phys. Solids 57 1980