

Nucleation of Crystals in Undercooled Molten Aluminium

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Experimental progress in the study of solidification nucleation has significantly increased our understanding of homogeneous nucleation. A metallic system has been studied according to two mathematical models of homogeneous nucleation able to describe grain growth in metals: free boundary model (FBM) and interacting boundary model (IBM). The predictions of two nucleation models compared in terms of kinetic parameters revealed the limits of FBM and the correct predictions of IBM. Moreover, the validity of two models assumption has been checked up through the solidification kinetic curves.

Keywords: homogeneous nucleation, nucleation rate, linear growth rate

A large number of studies on solidification have been carried out to characterize microstructural evolution. Grain growth inhibition in aluminium continuously cooled from melt was studied. The grain growth inhibiting effect has been studied by a large number of investigators [1,2] who have refined Zener's original calculation [3]. Although the validity of Zener's assumption has been a challenge on theoretical grounds based on experimental studies, the experimental verification of Zener's prediction is very limited due to the difficulties in accurately analyzing the mean size and volume fraction of the dispersed particles. Mullis [4] has recently used a free-boundary model (FBM) for dendritic solidification to study the effect of fluid flow on growth morphology. He shows that dendritic arms bend into the flow due to thermal advection. Studies regarding various models for grain growth inhibition have been provided by Ryum et al [5]. All these investigations are helpful in understanding the microstructural evolution of solidification structures. However, there still remain several features of the solidification process that call for further investigations.

This study concerning solidification is focused on an analysis of the steady-state regime. Experimental data of solidification are analyzed and correlated according to two models: free boundary model (FBM) and interacting boundary model (IBM). These are able to describe simultaneous crystallization and grain growth in metals and are valid for isothermal transformations.

The aim of the present work is to analyze the application of two nucleation models in order to estimate idealized micro-structural evolution processes and to predict the external cooling conditions of the solidification process.

Characterization of the solidification parameters

In the classical nucleation theory, the nucleus and undercooled melt are separated by a sharp interface with positive interfacial free energy. For the steady-state regime, the temperature gradient is held approximately constant. The densities of the phases are assumed equal and therefore, heat is transferred by conduction only. The other thermophysical properties describing the system - thermal conductivity, thermal diffusivity, heat capacity and heat of fusion - are also treated as averages and constants. The model kinetic parameters are independent of temperature and accurate for nucleation and growths reactions with

linear growth. These parameters can be used to estimate the type of structures resulting from the various solidification conditions: crystals size, shape and pattern of phase dispersion into the resulting material.

In FBM, the nuclei interaction during growth is neglected when these grow enough to come into contact [6, 7]. If at moment t_1 a nucleus has been formed, in the time range $t_2 - t_1$ it will grow by $R \cdot (t_2 - t_1)$ so that, if a spherical shape is assumed, its volume becomes

$$V_0 = \frac{4\pi}{3} R^3 (t_2 - t_1)^3. \text{ In } dt_1 \text{ time range, } v_G \cdot u(t_1) dt_1$$

nuclei will be formed where v_G denotes the non-crystallized fraction of the volume unit at time t_1 . At moment t_2 the nuclei volume is

$$V = v_G u(t_1) \frac{4\pi}{3} R^3 (t_2 - t_1)^3 dt_1. \text{ The crystal fraction generated since the initial moment of crystallization is:}$$

$$1 - u(t_2) = v_G \frac{4\pi}{3} R^3 \int_0^{t_2} u(t_1) (t_2 - t_1)^3 dt_1 \quad (1)$$

The relation (1) is a Volterra equation. The solution for $u(t_r) = 0$ leads to $t_r = \frac{\pi}{2a}$ which physically means the solidification process is complete. It denotes $a^4 = 2\pi R^3 v_G$. R is the linear growth rate and v_G the nucleation rate.

The number of crystallites in volume unit will be

$$N_r = v_G \int_0^{t_r} u(t) dt \text{ and the relation calculating the crystallite size is } d_m = R t_r.$$

Within this model, the kinetic parameters are:

- Solidification time (the time after crystallization is finished and the whole melt volume is crystallized) is:

$$t_r = \frac{\pi}{2a} = \frac{1}{2} \left(\frac{\pi^3}{2 v_G R^3} \right)^{1/4} \quad (2)$$

- Number of crystallites in volume unit is:

$$N_r = 1.25 \left(\frac{1}{2\pi} \frac{v_G^3}{R^3} \right)^{1/4} \quad (3)$$

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- Crystallite size is expressed as:

$$d_m = \left(\frac{\pi^3 R}{32 v_G} \right)^{1/4} \quad (4)$$

The IBM predicts the grain-growth inhibition due to pinning by particles and limiting the grain size [8]. The nuclei linear increase is considered over the distance $R(t_2 - t_1)$. The "dangerous" volume representing the growth limit is $V(t_1) = \frac{4\pi}{3} R^3 (t_2 - t_1)^3$. At any point of this

volume crystal germs are growing. By considering a time interval small enough Δt_1 , the nuclei formation probability is $v_G V(t_1) \Delta t_1$. If the time interval $[0, t_2]$ is divided into equal and small enough segments, so that $t_j = j \Delta t_1$, $j = \overline{1, n}$ the probability that the considered unit volume of the germ to be left outside the crystal after time is:

$$P(t) = \prod_{j=1}^n [1 - v_G V(j \cdot \Delta t_1) \cdot \Delta t_1]$$

The mathematical computations lead to the expression of the melt non-crystallized fraction:

$$u(t) = \exp\left(-\frac{a^4 t^4}{6}\right) \quad (5)$$

To complete the crystallization process according to relation (5), an infinitely long time is needed. If we consider the same time t_r taken by crystallization to finish, then according to this model, the above-mentioned kinetic parameters are expressed as:

$$t_r = \frac{1.6}{(v_G R^3)^{1/4}} \quad (6)$$

$$N_r = 0.065 \left(\frac{1}{2\pi} \frac{v_G^3}{R^3} \right)^{1/4} \quad (7)$$

$$d_m = 0.508 \left(\frac{R}{2\pi v_G} \right)^{1/4} \quad (8)$$

The crystallization kinetic curves characterize the variation of solidification matter ratio. Using the two models above mentioned, the ratio of the whole volume solidification matter V and the initial volume V_0 of the melt is:

$$\frac{V}{V_0} = 1 - \exp\left(-\frac{\pi}{3} R^3 v_G \tau^4\right) \quad (9)$$

The product $R^3 v_G$ characterizes the crystallization process conditions and τ is the solidification time.

Experimental part

Aluminium of industrial purity (> 99.7 wt. pct.) is used. The molten metal was kept in a graphite crucible at a predetermined temperature usually overheated by 23°C. The crucible was contained within a concentric thermal shield made of stainless steel. The solidification process was performed under continuously controlled cooling conditions, using variable airflow rates to cool the external surface of the mould. The external cooling rate of the crucible decreased from sample 1 to sample 9. For reliable results, the temperature distribution in the melt should be accurately known throughout the solidification process. The temperature of the melt is detected by a chromel-alumel thermocouple placed at the center of the melt. The errors in measuring the absolute temperature inside the crucible are small and do not affect the measured

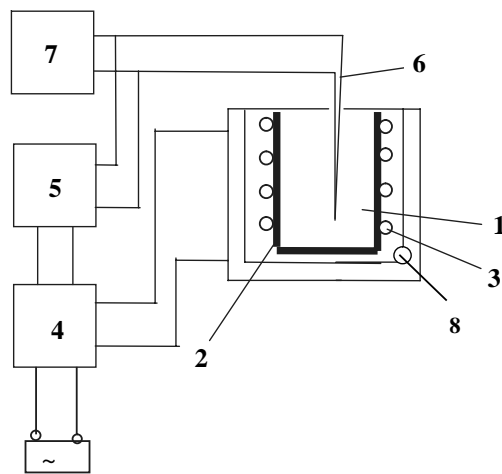


Fig. 1 Schematic drawing of experimental setup
1-liquid metal sample; 2-crucible; 3-electric furnace; 4-power supplier; 5- thermostat; 6-chromel-alumel thermocouple; 7- registering apparatus for solidification curves; 8-cool-air admission

temperature (the accuracy of temperature measurements is of ± 0.1 K).

The reliability of the experimental values has been well established. The standard deviation of each temperature measurement has been found to be 4%.

The undercooling degree is determined using the registered solidification curve at various controlled cooling speed and the reference solidification curve obtained for natural cooling speed. Figure 1 shows the experimental setup.

Results and discussion

The primary solidifying phase is exclusively determined by the onset temperature of nucleation, which depends on the cooling rate and the number of nucleation sites.

The relation between measured undercooling ΔT and the nucleation rate v_G and the linear growth rate R characterize the melting kinetics. In order to take into account the solidification with melt, undercooling, a kinetic relationship between the interface velocity and the interface undercooling is incorporated in the model [9].

Once a nucleus emerges from the melt it can grow as long as it receives atoms from the melt by two processes: i) thermal concentration fluctuation when new nuclei are formed; ii) atoms diffusion from the liquid zone to the new nuclei when the increase in the viscosity is really important and the temperature decreases. The nucleation rate of the crystallization germs in the condensate phase will be proportional with the total formation probability due to the two processes $v_G \propto P_1 \cdot P_2$.

The nucleation rate v_G depends on undercooling ΔT and interfacial effects and it can be determined provided that the solidification conditions (solidification temperature T_s , solidification heat Q_s) and the volume V of liquid metal are known [10, 11]. From experimental solidification curves the values of the metastability range τ and the degree of undercooling are determined. Figure 2 shows the solidification curves.

From the thermodynamic grounds and based on the kinetic-molecular analysis of the melt crystallization process, the nucleation rate is proportional with the probability [12-13]:

$$P_1 = C_1 \exp\left[-\frac{16\pi\sigma^3 T_s^2}{3k_B Q_s^2 (\Delta T)^3}\right] \quad (10)$$

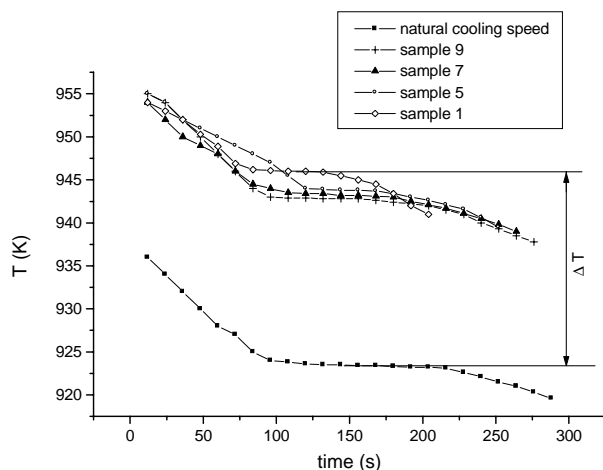


Fig. 2. Solidification curves of 99,7 wt % Al for various controlled cooling speed and the undercooling degree ΔT

Table 1
PARAMETERS OF SOLIDIFICATION PROCESS:
UNDERCOOLING ΔT AND NUCLEATION RATE v_G

Nr. Crt.	ΔT (K)	$v_G \cdot 10^7$ (s ⁻¹ cm ⁻³)
1.	22.9	4.48
2.	22.3	4.34
3.	21.4	4.11
4.	20.9	3.97
5.	20.5	3.85
6.	20.0	3.70
7.	19.9	3.66
8.	19.0	3.36
9.	18.8	3.28

where σ is the surface tension at melt-solid phase interface and k_B the Boltzmann's constant. The experimental values of the surface tension at melt-solid phase interface and

experimental procedure are all described in a previous report [15].

The probability of the nuclei formation through diffusion processes is:

$$P_2 = C_2 \exp\left(-\frac{Q}{k_B T}\right) \quad (11)$$

where Q is the diffusion energy.

Near the solidification temperature $T \cong T_s$, diffusion is negligible and the nucleation rate strongly depends on the thermal fluctuation. The present approach makes use of the max value of the nucleation rate as calculated by means of probability P_1 , relation (10), and using the physical constants and experimental values of the surface tension and the kinetic constant at melt-solid phase interface $\sigma=0.098 \text{ J m}^{-2}$ and $C1=6.57 \cdot 10^7 \text{ s}^{-2} \text{ cm}^{-3}$ the current temperature of the melting T [15].

The values of the nucleation rate v_G and undercooling degree are given in table I. All experimental parameters listed in table I have shown that under high external cool air flow the undercooling degree and nucleation rate are higher. According to Tammann's predictions the nucleation rate and the linear growth rate could give information about solidification structure obtained under various external experimental conditions.

Table 2 presents the kinetic parameters of the crystallization.

At slower cooling rates (characteristic for samples 7-9) the nucleation rate is low while the linear growth rate is

Table 2
KINETIC PARAMETERS IN FRAME OF FBM AND IBM

Sample no	$R \cdot 10^{-6}$ [cms ⁻¹]		$N_r \cdot 10^9$ [cm ⁻³]		$d_m \cdot 10^{-3}$ [cm]	
	FBM	IBM	FBM	IBM	FBM	IBM
1.	0.506	1.007	22.79	0.704	0.323	0.233
2.	0.547	1.089	20.97	0.647	0.332	0.240
3.	0.737	1.468	16.11	0.497	0.362	0.262
4.	1.031	2.053	12.20	0.376	0.397	0.287
5.	1.803	3.591	7.84	0.242	0.460	0.333
6.	1.995	3.974	7.05	0.217	0.477	0.345
7.	3.326	6.625	4.77	0.147	0.543	0.393
8.	6.617	13.181	2.67	0.082	0.660	0.477
9.	7.308	14.557	2.43	0.075	0.680	0.492

higher. A small number of nucleation sites are formed. The crystal growth prevails and the coarse structure is obtained.

At higher cooling rates (samples 1-3), the nucleation rate is higher and linear growth rate is lower. A lot of nucleation sites are formed and there is no possibility to reach big grain sizes. A fine structure will be obtained.

The FBM accurately describes only the early stage of the crystallization process when both the number and size of the nuclei are small and their volume does not exceed 15-20 % of the volume of the entire crystal. This model does not consider the inhibition of the crystallization process by the crystallites growth that enables them to come into contact and thus eliminate them from the crystallization process. If there are coarse crystals and newly formed crystallization germs, the probability for the latter to grow is extremely small in comparison with the coarse crystals. The amount of crystallized substance will be relatively small, as the dimensions of the growth interface are larger accordingly.

In the case of FBM the following conclusions can be drawn concerning the correlation between solidification and obtained grain structure. When the columnar dendrite zone is significantly larger than the area of equiaxed dendrites and globular microsegregation cells, the fraction of coarse columnar grains become larger than that of fine equiaxed grains. This result is in abnormal grain growth and no limiting size is obtained.

Consequently, the role played by the new germs is quite insignificant in FBM.

According to IBM of grain growth inhibition, the pinned grain size tended to be much smaller than those predicted by FBM. Smaller values of d_m are due to the fact that reference is no longer made to the entire crystal volume but only to that region where the nucleation and growth process is inhibited as soon as the grains come into contact. It should be pointed out, on the basis of IBM analysis that the limiting grain size depends only on the size and volume fraction of particles, not on the content of a dissolved element. Nonetheless, this is not always true, since the dissolved element segregates to grain boundaries, thus leading to a much stronger influence on the interaction between the grain boundary and particles.

Figures 3 and 4 present the crystallization kinetic curves (9), in the limits of the two models above mentioned, for sample no 1 (with higher external cooling rate), samples solidified in intermediate external cooling rate (sample no 5 and 7) and the sample no 9 (with lower external cooling rate).

Analyzing the crystallization kinetic curves, it can be noteworthy the followings:

i) The solidification starts by heterogeneous nucleation at the crucible wall through the so-called "big-bang" mechanism. Only a fraction of the nuclei formed at this

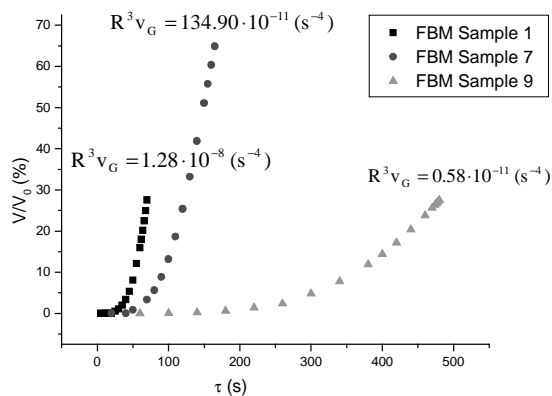


Fig. 3 Kinetic curves for solidified samples in the limits of FBM

stage contributed to the formation of the chilled zone and the majority of the nuclei are transferred into the hotter bulk liquid and remelted. At this early stage of the crystallizations process, there is an “initial stage” of the process, when the solidification matter ratio slowly increases. It is the so called “incubation stage” when the number and the size of the nuclei is very small (almost undetectable);

ii) The final solidified microstructure largely depends on the amount of nuclei surviving after the big-bang nucleation. At the final stage of the crystallization process it appears the same slowly increase of solidification matter ratio due to grain pinning. The ratio of the grains is about (80-90)% of the whole volume and the growth process is inhibited on this contact surface. This inhibition process is evident as shown by kinetic curves draw using the characteristic parameters of IBM. At the end of metastability solidifying range, the ratio $V/V_0 = 100\%$, namely the whole molten has been solidified. In the FBM, the final stage of solidification process cannot be put into evidence. The relative ratio of solidification bulk matter is $V/V_0 = 60\%$ and the final stage of crystallization related with the slowly increase of crystalline phase, is not found again in kinetic curves;

iii) In the intermediate stage, the rate of the crystallization process is higher than those specific to early and final stages. In the real solidification conditions, the kinetic of the solidification process is more complicated, due to the heat transferred by the thermal conductivity between liquid and solid phases and the temperature gradient in liquid phase. The size of the crystals, shape and pattern of the phase dispersion into the solidification material depend on the undercooling degree.

Our experimental data are reasonable despite of several items that might affect these results. These items are as follows:

-The heat flow equations are one-dimensional and the temperature-dependent thermophysical properties describing them are considered as constant;

-The conditions for convective fluid flow that are very important in solidification processes differ from horizontal and vertical arrangement.

Conclusions

1) This paper presents the study of the nucleation phenomena in solidifying metallic system and its correlation with the free boundary model (classical nucleation theory) and interacting boundary model. The results obtained differ especially in terms of crystallite

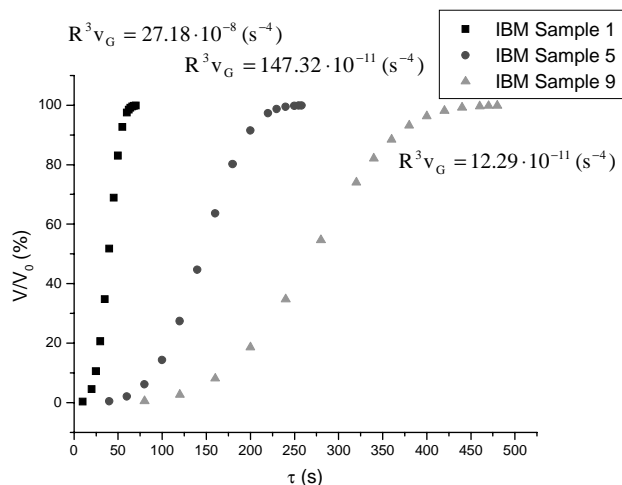


Fig. 4 Kinetic curves for solidified samples in the limits of IBM

number and crystallite size. The FBM are not suitable to correlate the solidification process. This model does not consider inhibition as soon as the crystallites come into contact. On the other hand, the IBM predicts the end of the nucleation when boundaries of nuclei are contacting. A lot of nucleation sites are found and there is no possibility to reach big grain sizes.

2) Experimental investigations determining the microstructural features as a function of the melt undercooling and cooling rate, prior to solidification, will be of vital interest for testing the predictions of different nucleation models and answer questions which arise from engineering goals.

3) Prediction of the evolution of crystallographic structure is required in order to identify and confirm the controlling solidification mechanisms underlying model predictions of structure evolution.

4) In our opinion, according to experimental data, IBM is the model that correctly describes the solidification processes and makes a good choice of the external cooling conditions. Also, using the IBM estimation can be made concerning the solidification structure via crystallite size and number of crystallite in unit volume values.

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