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SIZE DISTRIBUTION OF NUCLEATION SUBSTRATES FOR Al-Cu ALLOY: THEORETICAL CALCULATION AND SIMULATION OF CRYSTALIZATION PROCESS

Janusz LELITO, Beata GRACZ, Paweł L. ŻAK, Michał SZUCKI, Paweł MALINOWSKI, Józef Sz. SUCHY

AGH University of Science and Technology, Faculty of Foundry Engineering, Department of Foundry Processes Engineering, 23 Reymonta Street, 30-059 Krakow, Poland.

Abstract - The free-growth model was introduced by Greer et al. in 2000. This model bases on hypothetical size distribution of nucleation substrates. The aim of this work is to develop a log-normal distribution of heterogeneous nucleation substrates for the Al-Cu alloy. The computational algorithm allowing to restore the nucleation substrates distribution was created. The input data for algorithm, that is grains density of aluminum primary phase and supercooling, were taken from literature. These data are important for inverse modelling which is based on the numerical optimization methods that allows to identify parameters of substrate distribution. The distribution described in this way may be then applied in simulation based on the free-growth model. Numerical simulations based on the free-growth model can predict the grains density of the examined Al-Cu alloy. These predictions are compared with the experimental data.

Résumé – Distribution de la taille de substrats de nucléation pour des alliages Al-Cu: calcul théorique et simulation d'un processus de cristallisation. Le modèle de croissance libre a été introduit par Greer et al. en 2000. Ce modèle est basé sur une distribution hypothétique de taille de substrats de nucléation. Le but de ce travail est de développer la distribution log-normale des substrats de nucléation hétérogènes pour alliage Al-Cu. L'algorithme qui a été créé qui permet de restaurer la distribution de substrats de nucléation. Les données utilisées sont issues de la littérature. Ces données, importantes pour la modélisation inverse basée sur les méthodes d'optimisation numérique, permettent de déterminer les paramètres de la distribution du substrat. La distribution décrite de cette façon peut être ensuite appliquée à une simulation basée sur le modèle de croissance libre qui permet de prédire la densité de grain de l'alliage Al-Cu étudié. Ces prédictions ont été comparées aux données expérimentales.

1. INTRODUCTION

Software which is designed for casting and metallurgical processes, including commercial, can simulate the formation of microstructure and microsegregation [5-12]. The mathematical description of a process and the initial parameters are necessary to predict the nucleation and growth of grains. One of the nucleation models which is often used recently is the free-growth model (f-g model) proposed by Greer et al. [1-3]. In the free growth model, temperature field is

Tirés-à-part: J. LELITO, AGH University of Science and Technology, Faculty of Foundry Engineering, Department of Foundry Processes Engineering, 23 Reymonta Street, 30-059 Krakow, Poland.

described by Fourier-Kirchhoff equation. The nucleation and growth of grains from the melt was modelled using the hemispherical cap model. In this model it is assumed that a barrier for heterogeneous nucleation depends only on the radius of the nucleation substrate. Growth of nuclei on top of a nucleation substrate with diameter d takes place as long as the curvature $1/r$ of the growing spherical cap satisfies the condition [13]:

$$\Delta T \geq \frac{2\gamma_{s/l}}{\Delta S_V \cdot r}, \tag{1}$$

where ΔT is the supercooling, K; $\gamma_{s/l}$ is the solid–liquid interfacial energy, J m^{-2} and ΔS_V is the entropy of fusion per unit volume, J m^{-3} K^{-1}. Upon further supercooling, free growth will start if the spherical cap of the nuclei becomes hemispherical and the curvature $1/r$ reaches the value $2/d$. The supercooling at which a nucleation substrate becomes active is that at which free growth of the nucleated grain from the substrate begins. Greer et al. suggested that this critical supercooling is inversely proportional to the nucleation substrate diameter [1, 13]:

$$\Delta T_{fg} = \frac{4\gamma_{s/l}}{\Delta S_V \cdot d}, \tag{2}$$

where: ΔT_{fg} – free growth supercooling, K.

Günther, Hartig and Bormann [13] modified the free-growth model. They presented equation, where the free growth velocity of an existing crystal is controlled by the diffusion balance of the solute between melt and solid. This equation is based on the assumption that the driving force of the crystallization process is dimensionless supersaturation of the alloy, which is related by a growth restriction factor of Q [1-3]:

$$\Omega = \frac{S}{2} = \frac{C_o - C_L^*}{C_S^* - C_L^*} \approx \frac{\Delta T_S}{Q}, \tag{3}$$

where: Q – growth restriction factor described by: $Q = m_L\,(k\text{-}1)\,C_o$; m_L – the liquidus slope in the phase diagram of the solute with aluminium, K wt.%$^{-1}$, k – the equlibrium partition coefficient, C_o – the solute content in the melt, wt. %, C^*_L , C^*_S – liquid and solid solute content, wt%.

Therefore, the grain growth rate (dr/dt) of successful nucleation substrate in the free growth model is described by [8]:

$$\frac{dr}{dt} \propto \frac{D_S \Delta T_S}{Q \cdot r}, \tag{4}$$

where: D_S is the diffusion constant of the solutes in the melt, m^2 s^{-1} and ΔT_S is the solutal supercooling, the difference between the observed supercooling $T_m - T$ and the free growth supercooling ΔT_{fg} [13].

$$\Delta T_S = T_m - T - \Delta T_{fg}, \tag{5}$$

where: T_m - melting temperature, K, T - observed temperature, K.

That means that free growth of the grain will start on nucleation substrate under the following conditions [1-3, 13]:

$$\Delta T_S \geq 0; \quad 2r \geq d = \frac{4\gamma_{s/l}}{\Delta S_V \cdot (T_m - T)}. \tag{6}$$

The size distribution of nucleation substrate is given as a log-normal distribution function $N(d)$ [1-3]:

$$N(d) = \frac{N_0}{\sigma \cdot d \cdot \sqrt{2\pi}} \exp\left(- \frac{(\ln(d) - \ln(d_0))^2}{2 \cdot \sigma^2} \right), \tag{7}$$

where: N_0 – total population of nucleation substrate (both active and inactive), m^{-3}; d_0 – the geometric mean of the log-normal distribution, m; σ – geometric standard deviation of log-normal distribution; d – mean diameter of nucleation substrate, m.

The evolution of the grains size distribution is governed by Fourier-Kirchhoff equation and distribution of the substrates sizes.

Nowadays aluminum alloys usage in industry increased significantly. This is caused by the global obligation of carbon emission reduction and fuel efficiency in transportation. Because of those global processes more and more research on the Al-based alloys is performed [14,15].

The aim of this work was to approximate a real size distribution of substrates of the heterogeneous nucleation of primary α(Al) phase in Al-Cu alloy. The assumed distribution was of log-normal shape. Additionally, this distribution was used in the free growth model to simulate the Al-Cu alloy crystallization process.

2. RESEARCH METHODOLOGY

To achieve the aim of this work a calculation algorithm was developed by the means of inverse modeling. The elaborated algorithm allows obtaining the actual substrates size distribution (SSD) of the Al-Cu alloy heterogeneous nucleation. After determining the actual SSD the simulation of the Al-Cu alloy crystallization process was elaborated.

3. COMPUTATIONAL ALGORITHM

The developed algorithm bases on the following input data: experimental values characterizing the Al-Cu alloy (maximal supercooling, grain densities) taken from the literature [4]. The other parameters are: thermodynamic parameters of the Al-Cu alloy (volumetric entropy of fusion and interfacial energy at the boundary liquid/crystallite) and assumed total number of nucleation substrates (N_0), interval of substrate size ($D_{\min} - D_{\max}$), within which a value of geometric mean will be searched, interval of a standard deviation, integration step, maximal number of integration steps and the assumed tolerance for integral calculations accuracy.

During cooling of an alloy which contains nucleation substrates, nucleation occurs first on the largest substrates. The equation (2) allows determining the minimal dimension of the active substrate $d_{min}^{\ i}$ and can be described by:

$$d_{min}^{i} = \frac{4\gamma_{s/l}}{\Delta S_V \Delta T_{max}^{i}} . \tag{8}$$

Basing on eq. (7), value of misfit function $J(\sigma^j, d_0^k)$ can be calculated:

$$J(\sigma^j, d_0^k) = \sum_{i=1}^{n} \left[N_V^i - N_{Vt}^i(\sigma^j, d_0^k) \right]^2 , \tag{9}$$

where: $N^{\ i}_V$ – experimental grain density, m^{-3}, $N^{\ i}_{Vt}$ – theoretical substrate density calculated by numerical integration of eq. (7), m^{-3}:

$$N_{Vt}^i(\sigma^i, d_0^k) = \int_{d_{\min}^i}^{+\infty} N(d, \sigma^i, d_0^k, N_0)\, \delta d . \tag{10}$$

In other words, the computational algorithm generates a sequence of distribution depended on the distribution geometrical mean, on the standard deviation and on the previously assumed N_0, and then allows to determine the theoretical density of active nucleation substrates (integral of lower limit d_{min}). The misfit functional (9), enabling the selection of the distribution the best resembling the actual distribution of the heterogeneous nucleation substrate in the given alloy. The graphical diagram of the developed algorithm was presented by Gracz [5] and is shown in Fig. 1.

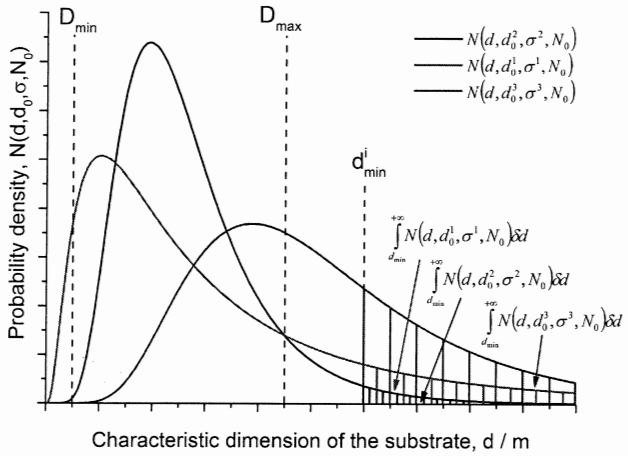

Figure 1. Diagram of the computational algorithm [5]

4. RESULTS

The input data for presented computational algorithm are $\gamma_{s/l} = 0.169$ Jm^{-2} [14] and $\Delta S_V = 9.125 \cdot 10^5$ Jm^{-3}K^{-1}. The ΔS_V value was calculated using ThermoCalc software for the chemical composition of the examined Al-Cu alloy (*Table I*) and for results obtained in the experimental investigation (*Table II*).

Table I. Chemical composition of the examined Al-Cu alloy [4]

Chemical composition (wt. %)					
Si	**Fe**	**Cu**	**Mn**	**B**	**Ti**
0.05	0.11	4.90	0.4	0.0013	0.07

Table II. The volumetric grain density and maximal supercooling of Al-Cu alloy [4]

Plate thicknes (mm)	Maximal supercooling (K)	Grain density (cm^{-3})
3	11.80	17.16
5	10.93	10.094
13	8.71	7.832
25	8.26	6.503

The above data allowed to determine by equation (11) the nucleation substrate size distribution for the Al-Cu alloy:

$$N(d) = \frac{1 \cdot 10^{11}}{1.580 \cdot d\sqrt{2\pi}} \cdot \exp\left(- \frac{(\ln(d) - \ln(2.165 \cdot 10^{-10}))^2}{2 \cdot 1.580^2} \right). \tag{11}$$

The graphical illustration of the formula (11) is shown in *figure 2* and *figure 3*.

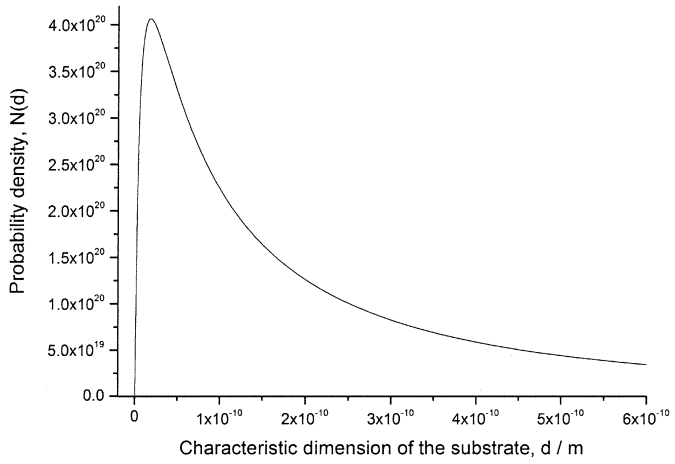

Figure 2. Diagram of nucleation substrate size distribution for the Al-Cu alloy after equation (11)

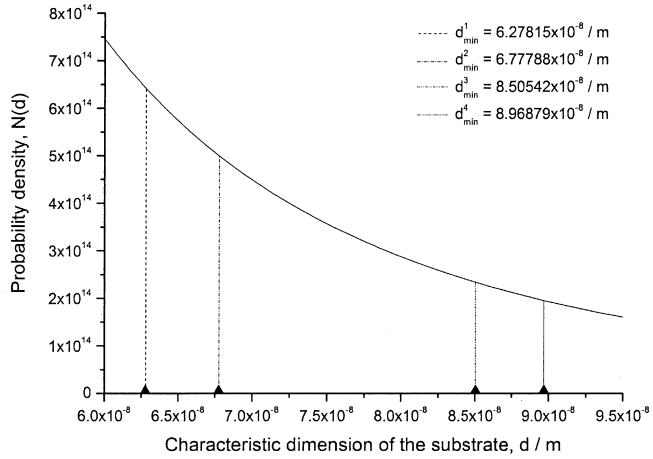

Figure 3. Diagram of nucleation substrates size distribution for the Al-Cu alloy on base of equation (11) with minimal substrate dimensions for experimental data

Basing on equation (4) the minimal active nucleation substrate, which took part in heterogeneous nucleation process, was calculated for different conditions (*Table I*) and showed in *figure 4*.

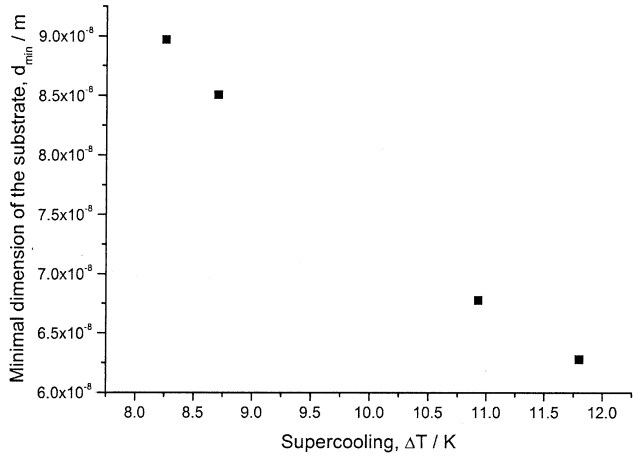

Figure 4. The minimal dimension of the active substrate as a function of supercooling

The relationship: grain density vs. supercooling obtained from the experimental investigation reported in [4] were compared with computational results and are shown in the *figure 5*. There can be seen a good fit of the computational results with the experimental ones [4]. Only one point from the computational calculations (for supercooling of 11) shows difference in comparison with the experimental value *figure 5*.

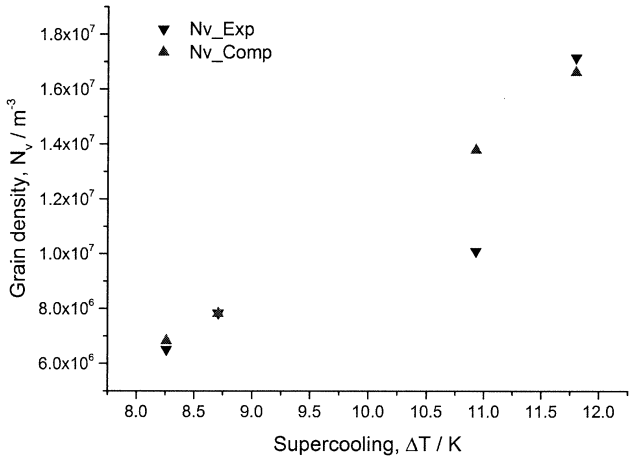

Figure 5. The grain density of aluminium primary phase as a function of supercooling obtained from simulation and compared with results of the experimental investigation [4]

The input data for simulation of nucleation using free-growth model based on the free-growth model explained above, a computer program in the C++ language was written to simulate the nucleation and growth of α(Al) phase in the Al-Cu alloy. As in the analyses of Greer et al. [1-3] the liquid is taken to be isothermal. The computations are performed on the base of micro model. The input data in the simulation are shown in *Table III*.

Table III. Materials properties used in the modelling

Symbol	Definition	Value	Units	Ref.
c_V	Volumetric heat capacity	$2.58x10^6$	$J\,m^{-3}K^{-1}$	[2]
ΔH_V	Volumetric enthalpy of fusion	$1.088x10^9$	$J\,m^{-3}$	Thermo-Calc
ΔS_V	Volumetric entropy of fusion	9.125	$J\,m^{-3}K^{-1}$	Thermo-Calc
$\gamma_{s/l}$	Solid/liquid interfacial energy	0.169	$J\,m^{-2}$	[14]
D_S	Diffusivity of solute in liquid	$2.52x10^{-9}$	$m^2\,s^{-1}$	[2]
m_L	Liquidus slope of Cu in Al	-2.5	$K\,wt.\%^{-1}$	Thermo-Calc
k	Partition coefficient of Cu in Al	0.1	-	Thermo-Calc
dT/dt	Cooling rate	0.68	$K\,s^{-1}$	From cooling curve
C_0	The solute content in the melt	11.7	wt.%	Calculate on the base [1]

Figure 6 shows the calculated and measured cooling curves of the alloys studied in this work. There can be seen a good fit of curves. The aim of the free-growth model was to calculate the volumetric grain density. Therefore the calculations continue only until the end of nucleation process and as well as cooling curve.

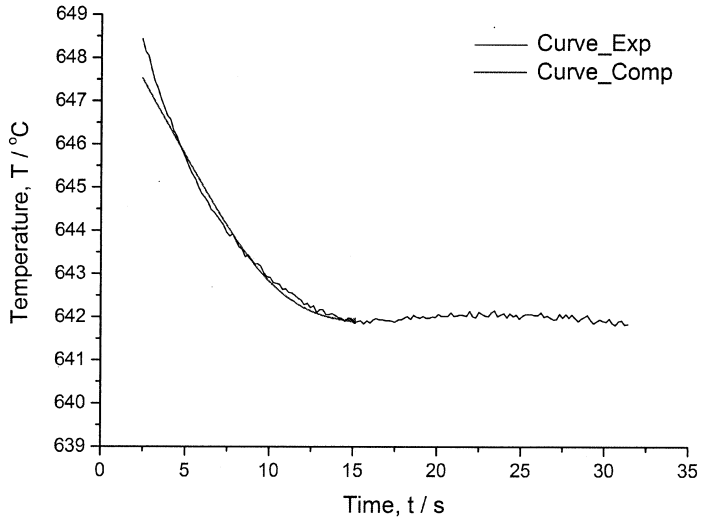

Figure 6. The cooling curve obtained from experimental [4] and simulation based on the free growth model

Given the assumptions made in this model and associated limitations, the predicted grain densities ($N_V = 4.94239 \cdot 10^7 m^{-3}$) are reasonably close to the measured values ($N_V = 6.50300 \cdot 10^6 m^{-3}$).

5. CONCLUSION

The implemented algorithm, described by equation (11), allowed to determine the nucleation substrate size distribution for the Al-Cu alloy. The equation (11) allowed to calculate grain density of aluminum primary phase in the Al-Cu alloy.
Using the inverse modelling results in performed simulation allowed to predict grain density of aluminium primary phase in Al-Cu alloy under different cooling rate.

6. ACKNOWLEDGEMENTS

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