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The plane-to-cellular-to-dendrite transition of the shape of the crystallization front during the crystallization of Al–Cu alloys

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Abstract: The evolution of the crystallization front from a planar to a dendritic one as a function of the $G_L/(Rc_0)$ parameter was investigated during the crystallization of Al–Cu alloys by the vertical Bridgman method. Six series of alloys with different initial compositions of Cu were solidified at different growth rates. A mathematical model for the heat transfer during vertical Bridgmen crystal growth was developed. The model was solved using the finite element method. The temperature gradient in the melt at the beginning of crystal growth was calculated using the obtained model. Discrete stages of the crystallization front were identified in the experiments, as the ratio $G_L/(Rc_0)$ decreased.

Keywords: vertical Bridgman, interface shape, crystallization, Cu–Al alloy.

INTRODUCTION

The growth rate and the initial concentration have been identified as important factors in the crystallization process. These parameters considerably influence the shape of the crystallization front, as well as the distribution of solute in the crystal. The classical theory of constitutional supercooling (CS)[1] is an important tool for predicting instabilities of the crystallization front arising during controlled growth from the melt. According to the CS criterion, the planar interface becomes unstable above a critical growth rate, R_{PC}, given approximately by:

$$\frac{G_L}{R_{PC}} = -\frac{m_L c_0 (1-k_0)}{k_0 D_L} \quad (1)$$

where G_L is the temperature gradient in the liquid phase, R_{PC} the critical growth rate for the beginning of instability of the crystallization front, c_0 the initial solute concentration, m_L the liquid line slope in the equilibrium diagram, k_0 the equilib-

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rium distribution coefficient, and D_L the diffusion coefficient in the liquid phase.

As the growth rate increases above R_{PC}, the morphology of the crystallization front becomes oscillatorily unstable, then, at appreciably higher growth rates, cellular and, finally, at large velocities, dendritic. In this evolution of the shape of the crystallization front, it is possible to recognise discrete stages of the substructures.[2] Near the critical rate, R_{PC}, the crystallization front exhibits irregular morphology.

Considering the CS criteria (Eq. (1)), two different groups of process parameters may be correlated. On the one hand, there are crystal growth conditions (G_L, R, c_0) and on the other, system properties (m, k_0, D_L). As a result of the correlation between these two groups of properties, a specific microstructure of the solid phase is obtained. Since the system properties are constant for a defined alloy, it is obvious that the microstructure is defined by other group-crystal growth conditions. The influence of the parameter $G_L/(Rc_0)$ on the microstructure of Al–Cu alloys was investigated in this study, based on the work of Biloni *et al.*[3,4]

EXPERIMENTAL

The crystallization of six series of Al–Cu alloys with different initial solute concentrations: 0.47 % Cu, 1.00 % Cu, 1.40 % Cu, 2.20 % Cu, 2.60 % Cu and 2.86 % Cu was performed according to the vertical Bridgman method[5] (Fig. 1). A quartz ampoule containing a graphite vessel was moved downwards. The experiments were performed in an apparatus consisting of a resistance furnace

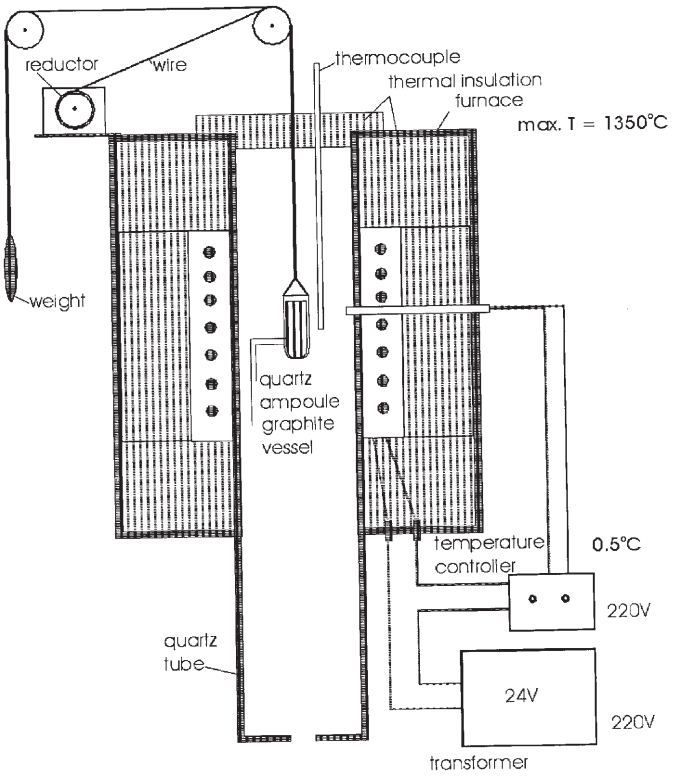

Fig. 1. A schematic view of the apparatus and the possition of the sample in the furnace.

equipped with a synchronized motor with a speed reduction gear. The furnace itself contained two thermo-couples, one in the heater that maintains the temperature constant, the other measuring the temperature in the zone where the ampoule is placed. The experiments were carried out within a range of growth rates from 1.45×10^{-6} m/s to 8.71×10^{-5} m/s, under a protective nitrogen atmosphere.

The solidified samples were longitudinally cut, polished and etched. The microstructure was then metallographically investigated.

Optical emission spectrometry was used for the chemical analysis of the distribution of the solute concentration along the specimen.

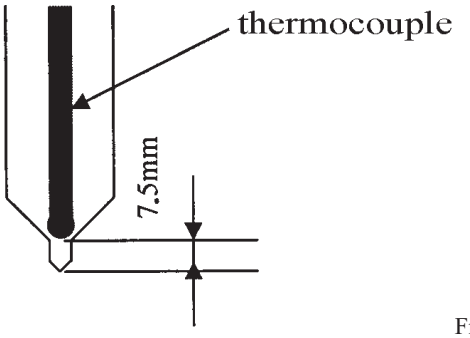

Fig. 2. The position of the thermocouple in the sample.

During the process of crystal growth, the temperature was measured in the sample and in the furnace in order to establish a mathematical model and calculate the temperature gradient in the melt. For this purpose, two Ni–Cr–Ni thermocouples were placed in a modified vertical Bridgman apparatus connected to a data acquisition system. In this way, the temperature changes in both the melt and the furnace could be simultaneously monitored. One thermocouple was mounted inside the furnace (Fig. 1), while another one was positioned on the sample (Fig. 2). A crystallized sample (c_0 = 2.2 % Cu) with a defined shape from a previous experiment was used as a charge to exactly define the position of the thermocouple. The sample was drilled to a considerable depth and the thermocouple was mounted inside (Fig. 2). This thermocouple was continually moved through the furnace at a rate of $R = 8.71\times10^{-5}$ m/s. The other thermocouple, which measured the temperature in the furnace, was moved discontinually – it was moved 10 mm every 2 min following the lowering of the samples (the equivalent rate was 8.33×10^{-5} m/s).

MATHEMATICAL MODEL

In order for solidification to begin, it was necessary to attain conditions of supercooling. The equilibrium temperature of solidification, T_0, was determined from the equilibrium diagram of Al–Cu for c_0 = 2.2 %. Burden and Hunt[6] determined that the interface temperature for the Al–Cu system varied with the growth rate from 653–655 ºC. From the data on the measured temperatures of the sample, these temperature values were reached at a depth $z \approx 200$ mm from the middle of the furnace. At this depth, the temperature gradient in the furnace was 14.5 ºC/cm, according to the measured temperatures. This value was used to calculate the supercooling of the interfacial front from Eq. (2), according to the investigations of Burden and Hunt.[6]

$$\Delta T = \frac{G_L D_L}{R} + 2^{3/2}\left[-\frac{m(1-k_0)c_0K}{D_L}\right]^{1/2} R^{1/2} \qquad (2)$$

The data used in the calculation are given in Table I. From the presented values, m was calculated from the Al–Cu equilibrium diagram, while the values for K,[6] D_L,[7] and k_0[8] were taken from the literature.

TABLE I. Data used in the calculation of ΔT

G_L/(°C/cm)	D_L/(cm^2/s)	R/(m/s)	m/(°C/%)	k_0	c_0/(%)	K/(°C cm)
14.5	2.2×10^{-5}	1.45×10^{-6}	– 3.4	0.153	2.20	1.04×10^{-7}
14.5	2.2×10^{-5}	8.71×10^{-5}	– 3.4	0.153	2.20	1.04×10^{-7}

According to Eq. (2), values for supercooling of 0.6 ºC and 0.077 ºC were obtained for the maximum and minimum values of the growth rate, respectively. In the case of these small supercoolings (this is heterogenic nucleation) and by the determined "field" of equilibrium of solidification (653–655 ºC), a solidification temperature of 653 ºC was assumed. It could be stated that the equilibrium temperature of solidification was equal to 655 ºC, and the supposed supercooling was 2 ºC.

Solidification mainly depends on the manner in which heat is conducted within a sample. A model of heat conduction was proposed for the directional solidification of an aluminium alloy sample. Heat conduction inside the sample, as well as heat exchange to the environment was observed. Axial conduction could be neglected compared to radial conduction. A general differential equation which describes heat transfer can be given as:

$$\frac{\partial T}{\partial \tau} + (R\nabla)T = \alpha \nabla^2 T \tag{3}$$

where R is the rate of crystal growth, τ time, T temperature and α heat diffusivity. If it is assumed that the heat flux of the interface is equal to the vessel-air flux, the equation could then be written as:

$$Q_{r_s} = Q_{r_c}\left(\frac{r_c}{r_s}\right) \tag{4}$$

where Q_{rc} is the sum contribution of radiation and conduction-convection through the air boundary, r_c the outer radius of the vessel, and r_s the inner radius of the vessel

$$Q_{r_c} = q_{r_c}\ p_{r_c} \tag{5}$$

The heat flux of radiation is given by:

$$p_{r_c} = \sigma(a_c \varepsilon_E T_E^4 - a_E \varepsilon_c T_c^4)\frac{r_E}{r_s} \tag{6}$$

where σ is the Stefan–Boltzman constant, a the coefficient of absorption, ε the emissivity. The indices s, c and E are related to the sample, the vessel and the environment, respectively, while r_E is the inner radius of the furnace.

The heat exchange of conduction and convection through an air boundary is described by the following equation:

$$q_{r_c} = \frac{K_a \cdot f \cdot (T_E - T_c)}{r_c \cdot \ln\left(\frac{r_E}{r_c}\right)} \quad (7)$$

where f is a factor related to the distribution of convection. The distribution of convection and conduction can be estimated in a satisfactory way and this factor is usually equal to 2.

The differences between the temperatures inside the furnace and inside the samples were measured, and they are presented by polynomials which were obtained by regessional analysis of the measured temperature changes. The measurements were carried out at a lower speed of 8.71×10^{-5} m/s. The polynomial depndencies are given by the equations:

$$T_p = 766.6869 - 0.14909z - 0.02199z^2 + 3.92989\times10^{-5}z^3 + 3.86778\times10^{-8}z^4 \quad (8)$$

$$T_u = 824.8249 - 0.26392z + 0.0112z^2 - 1.13145\times10^{-4}z^3 + 2.10979\times10^{-7}z^4 \quad (9)$$

where T_p is the temperature in the furnace and T_u the temperature in the sample.

SIMULATION RESULTS

Changes in the temperature field of the sample during solidification were determined by solving the defined differential equations. If there is a temperature change in the centre of the sample for a sufficient period, a value comparable with that from the experiment is obtained. The comparison of the experimentally obtained temperature at the top of the sample and that calculated by the model is a crucial comparison between the experimental data and the results of the model. Some modifications of the presented mathematical model needed to be made. As the model implies only heat transfer, but does not describe phase transformations, it was assumed that the phase transformation was another heat source. Also, a delay coefficient of 1.07 was included in the calculation, which enabled a better interpretation of the results (Fig. 3).[9]

These improvements enabled the application of the model with satisfactory accuracy to estimate the temperature changes in the sample. The temperature gra-

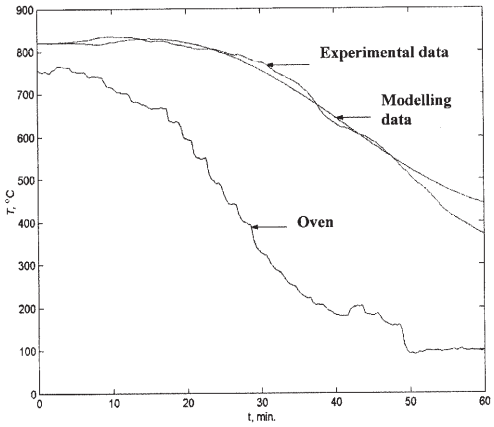

Fig. 3. The measured and calculated temperatures after the sample was introduced into the heat source and the coefficient of delay of the temperature measurements.

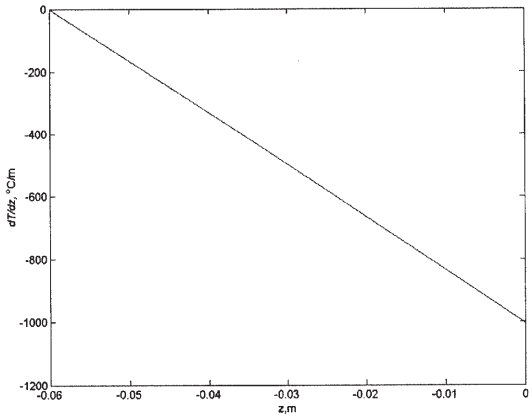

Fig. 4. The temperature gradient in the sample at the moment solidification commences.

dient in the sample at the beginning of solidification, G_L = 10 ºC/cm, was calculated using the improved model. The changes of the temperature gradient in the sample at the beginning of solidification are presented in Fig. 4.

The temperature profile along the sample during the experiment could also be calculated, as shown in Fig. 5.

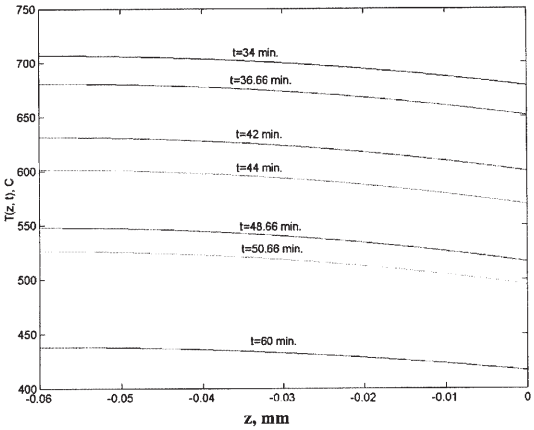

Fig. 5. The calculated changes of temperature along the sample for the chosen period from the moment of lowering the sample into the furnace.

RESULTS AND DISCUSSION OF THE INVESTIGATION OF THE MICROSTRUCTURE OF THE SAMPLES

The critical growth rate for the beginning of instability of the crystallization front (R_{PC}) was calculated using Eq. (1) with the new G_L calculated by mathematical modelling. The results are presented in Table II for each of the six series. The data used in the calculation are presented in Table III.

The published experimental data[10–14] indicate that the shape of the crystallization front changed at higher growth rates than the calculated R_{PC}. One of the reasons for these difference is real convection, which was not considered in the theoretical CS criterion. The calculated R_{PC} is the critical rate for the beginning of oscillatory instabilities of the shape of the crystallization front. This phenomenon

was very difficult to observe by metallography. The connection of cells was assumed as the beginning of cellular growth in this study. This assumption was proven[15] at the experimentally obtained growth rates R_{PC}^{exp} by investigating solute segregation. R_{PC}^{exp} is also presented in Table II.

TABLE II. Calculated (R_{PC}) and experimental (R_{PC}^{exp}) values of the growth rate (m/s)

c_0 (%)	0.47	1.00	1.40	2.20	2.60	2.86
R_{PC}/(cm/s)	2.48×10^{-5}	1.18×10^{-5}	8.34×10^{-6}	5.33×10^{-6}	4.52×10^{-6}	4.07×10^{-6}
R_{PC}^{exp}/(cm/s)	1.75×10^{-3}	1.75×10^{-3}	8.71×10^{-4}	4.35×10^{-4}	4.35×10^{-4}	4.35×10^{-4}

TABLE III. Data used in the calculation of R_{PC}

m/(ºC/%)	D_L/(cm/s^2)[7]	k_0[8]	G_L/(ºC/cm)
– 3.4	2.2×10^{-5}	0.153	10

The parameter $G_L/(Rc_0)$ was derived for the all experiments and is presented in Table IV. The same values are presented in Fig. 6 with the corresponding microstructures. It is obvious that the crystallization front changed from a planar-to-cellular-to-dendritic structure as the $G_L/(Rc_0)$ parameter decreased. For this Al–Cu alloy, the crystallization front is planar until the $G_L(Rc_0)$ parameter reaches a value of 35000. Morphological instabilities were obtained at lower values. A similar microstructure corresponds to certain ranges of $G_L/(Rc_0)$ values. R_{PC}^{exp} values in the range of 12000 – 5500 were determined for all series.

TABLE IV. Values of the parameter $G/(Rc_0)$ expressed in (s ºC/cm^2 %)

c_0/% → R/(cm/s)	0.47	1.00	1.40	2.20	2.60	2.86
1.45×10^{-4}	146808		49285	31380	26538	24126
2.90×10^{-4}	73403			15690		12062
4.35×10^{-4}	48935	2300		10460	8846	8041
8.71×10^{-4}			8.204		4417	4003
1.75×10^{-3}	11892	5589	3.991			
3.48×10^{-3}			2.053			
4.35×10^{-3}	4893	2300				
8.71×10^{-3}	2443	1148	820	521	442	401

It is possible to observe the gradual transition of the shape of the interface from planar to dendritic in Fig. 6. These results are in agreement with the investigation of Audero and Biloni.[3,4] It is now possible to correct and govern the process of crystal growth by the interaction of the parameters growth rate, temperature gradient and initial solute concentation.

CONCLUSION

The results presented in this paper contribute to the investigation of the influ-

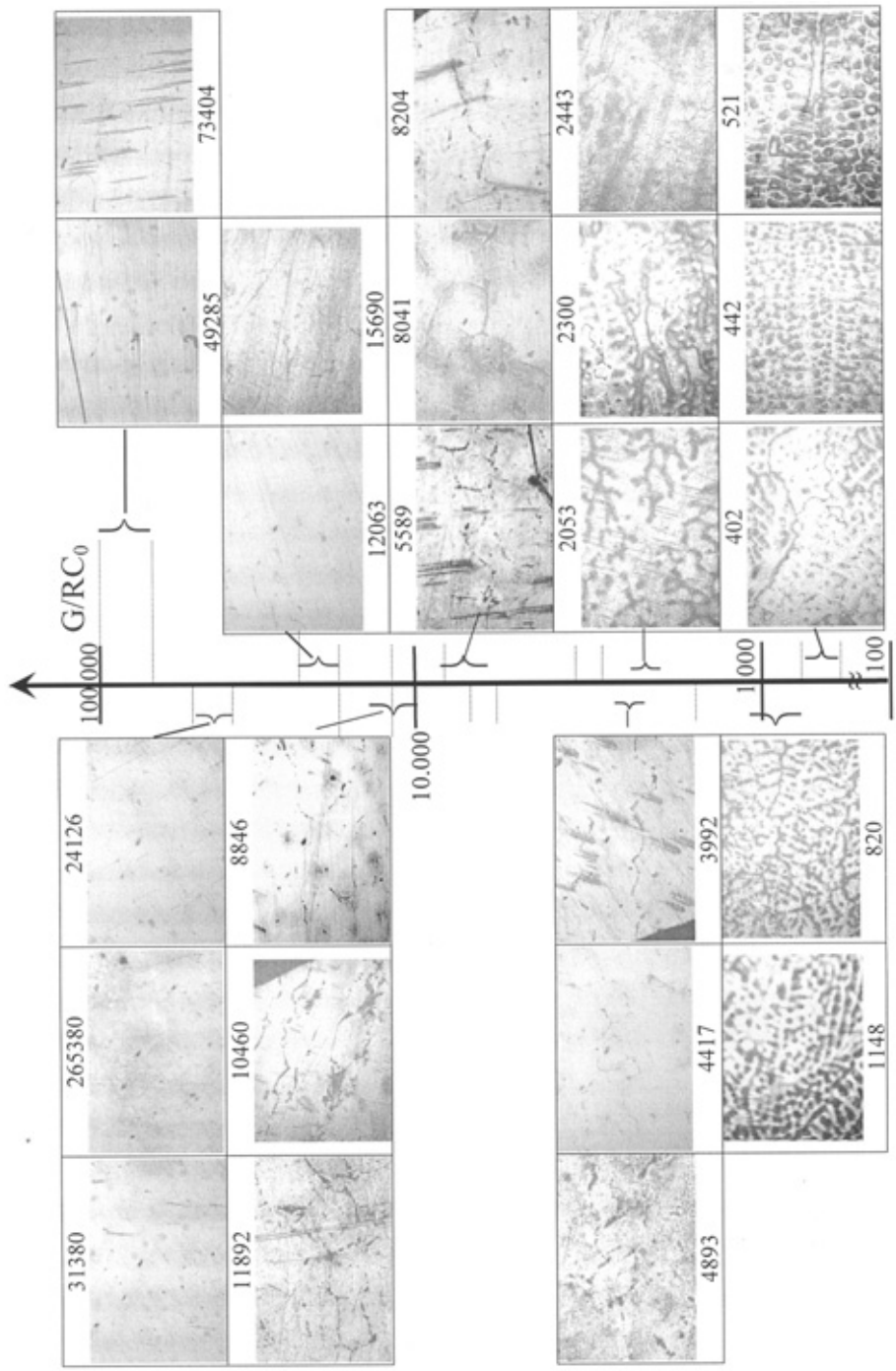

Fig. 6. The dependence of the microstructure of the sample on the $G_L/(Rc_0)$ parameter (micro photos of all samples).

ence of the solidification rate (R), temperature gradient (G_L) and initial solute concentration (c_0) on the shape of the interface. The crystallization of six series of Al–Cu alloys at different crystal growth rates was analyzed by the vertical Bridgman method.

A mathematical model for calculating the temperature profile inside the sample using the results of the vertical Bridgman method is shown. The mathematical model was solved by introducing appropriate assumptions which enabled the defined equations to be solved by the finite element method. The heat of emission due to phase transformations was taken into account by introducing a heat source in the sample. Also, a correction which took into account the delay in the measurement during the experiment was introduced.

The $G_L/(Rc_0)$ parameter was created for all the experiments and the dependence of the shape of the crystallization front on this parameter was investigated. It was observed that the crystallization front changed from a planar-to-cellular-to-dendritic structure as the value of the $G_L/(Rc_0)$ parameter decreased. A similar microstructure was observed for similar values of the $G_L/(Rc_0)$ parameter. That means that it is possible to create the desired microstructure by combining the growth parameters within the $G_L/(Rc_0)$ factor.

ИЗВОД

ПРЕЛАЗ СА РАВНОГ ФРОНТА КРИСТАЛИЗАЦИЈЕ НА ЋЕЛИЈСКИ И ДЕНДРИТНИ РАСТ КОД КРИСТАЛИЗАЦИЈЕ ЛЕГУРЕ Al–Cu

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У оквиру овог рада испитивана је трансформација фронта кристализације од равног ка дендритној структури као функција параметра $G_L/(Rc_0)$ при кристализацији легуре Al–Cu методом вертикални Bridgman. У том циљу изведени су експерименти са шест серија узорака различитих почетних концентрација и различитим брзинама раста. Изведен је и математички модел процеса раста кристала методом вертикални Bridgman коришћењем методе коначних елемената. На основу математичког модела израчунат је температурни градијент у растопу у тренутку када започиње раст кристала. У оквиру експерименталног опсега са снижењем вредности параметра $G_L/(Rc_0)$ долази до постепеног развоја фронта кристализације по етапама.

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