On the subcritical behavior during planar to cellular transition in directional solidification

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Abstract

During directional solidification, the Mullins-Sekerka planar-cellular instability should be subcritical when $k < 0.45$ and latent heat is ignored. However, taking into account both latent heat as thermal conductivities, a change in the behavior of the transition is predicted

Samples of the $Al-0.5wt.\%Cu$ system were directionally grown under controlled conditions, to study the role that plays the instabilities in the process relatives to the microstructure selection for a given values of interface velocity, and thermal gradient. Using an interface quenching technique and metallographic analysis in longitudinal and transversal cuts of the samples, we determine the transition mechanisms between the different stages of growth, and associates them to the stability of the solidification front. We study the planar to a cellular transition in different conditions, found that else the solidification parameters are in a good accord with the perturbations theory, when analyzing the amplitude of the perturbations during the planar to a cellular transition, the same theory is not able to predict certainly the critical wavelength in this case. Also, we found a subcritical behavior during the transition from a planar to a cellular interface for the diluted $Al-Cu$ system, detecting a hysteresis behavior for the amplitude of the perturbations when it is increasing and then decreasing the interface velocity, through the threshold. In addition to that, we analyze mthe change of the microstructure for different initial solidification conditions

I Introduction

When a binary mixture is directionally solidified, a variety of different patterns are revealed [1, 2] in such away, diverse microstructure could appear [3]. Solidifying systems are extremely interesting both for technological and academic reasons, due to (they) represent conceptually an example of self organization systems [4, 5]. However the underlying mechanisms are not fully understood.

In a directional solidification experience, a sample of composition C_0 is located between two thermal sources, one greater and another lesser than the melting point of the mixture, imposing a thermal gradient inside the specimen. Thermal Gradients in solid and liquid, G_S and G_L could differ if thermal conductivities κ_S and κ_L are different. Now, we promote a virtual displacement between the sample and the thermal field, in such a way (so) the interface between solid and liquid follows such movement [6, 7, 8]. Experimentally, it has been found that for fixed G^*

Traditional studies had focused in symmetry, surface anisotropies and near-equilibrium processes.

A linear stability analysis was performed by Mullins and Sekerka [9] which apports some

$$V_C = \frac{2DGk\kappa_L}{|m|\,C_\infty\,(1-k)\,(1+n)\,\kappa_L - kDL} \tag{1}$$

where k is the partition coefficient of the binary alloy, D_L is the diffusion coefficient of the solute in the liquid, m is the liquidus slope in the equilibrium diagram, κ_S and κ_L are the thermal conductivities of solid and liquid and G_L is the temperature gradient in the liquid. For this analisys, the critical wavelength of the first neutrally stable mode is given by [9]:

$$\lambda_C = 2\pi\left(\frac{2\Gamma k D_L^2}{m(k-1)}\right)^{1/3}\frac{1}{C_\infty^{1/3}}\frac{1}{V_C^{2/3}} \tag{2}$$

where $\Gamma = \gamma T_M/L$ is a capillary coefficient with γ the interfacial energy, T_M the melting temperature of the pure material and L the latent heat.

Eq. (1) is a modified form of the Constitutional Supercooling Criterium by Tiller et al. [10] for the low speed range of solidification.

In addition , it was manifest than in organic transparent system the behavior could be different than in thin samples [11].

Wollkind and Segel [12] carried out a weakly non linear extension of of the Mullins-Sekerka analysis neglecting latent heat for one dimensional deformations using a perturbation expansion, which gave a Landau equation of motion for the amplitude ξ_q of a mode with wave number q [13, 14]:

$$\frac{d\xi_q}{dt} = a_0\xi_q - a_1\xi_q^3 - a_2\xi_q^5 + \ldots \tag{3}$$

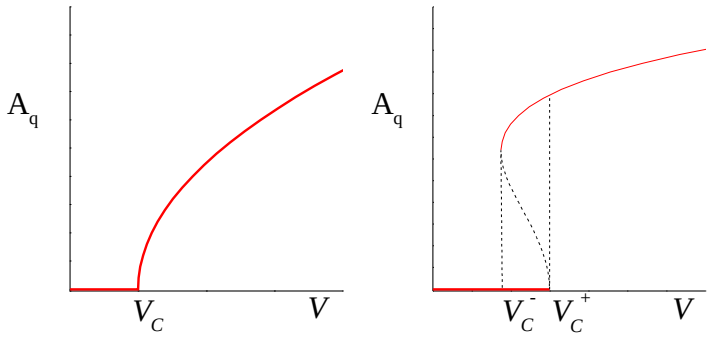


Figure 1: Schematic representation of a a) critical abd b) subcritical bifurcation

In the last equation, the term a_0 is the linear growth rate coefficient and a_1 is known as Landau coefficient. So, Equation (3) predicts different types of bifurcations, depending on the signs of a_0 and a_1: (i) $a_0 < 0; a_1 > 0$: the planar front is stable; (ii) $a_0 > 0; a_1 > 0$: the stationary cellular deformation of amplitude $(a_0/a_1)^{1/2}$ is stable; (iii) $a_0 < 0; a_1 < 0$: the planar front is stable but unstable to finite amplitude deformations, it is the subcritical instability case; (iv) $a_0 > 0; a_1 < 0$: the planar front is completely unstable. In the Figure 1 it is possible to see such different behavior, given us a critical a) or a subcritical b) bifurcation.

The calculation for a_1 was performed by Wollkind and Segel [12] for the one sided model by Langer and Turski [15] and Ungar and Brown [16] for the simetric model and extended by Caroli et al. [17] for the two sided model, neglecting latent heat. Alexander et al. [18] pointed that the inclusion of latent heat results in a positive addition in the value of a_1, and therefore results in supercritical bifurcations even for k values lesser than 0.45 [19]. A modified form for a_1 was given by Merchant and Davis [13, 14]

$$a_1 \approx \frac{1-n+I^{-1}(n-1)}{(n+1)(1+I^{-1})\Gamma} \tag{4}$$

where

$$I^{-1} = \frac{kDL}{(k-1)(1+n)\kappa_L m C_\infty} \tag{5}$$

is a latent heat parameter, and

$$\Gamma = \frac{\gamma T_m k V}{Lm(k-1)C_\infty D} \tag{6}$$

is a scaled surface energy.

The maximum possible hysteresis

$$\Delta V_{max} = \begin{cases} a_1^2/4a_2 s & , \ a_1 < 0 \\ 0 & , \ a_1 > 0 \end{cases} \tag{7}$$

A number of experiences had been developed to test these affirmations

II Experimental

To study the instability of a crystal-melt interface so as the long term microstructures are needed two fundamental factors to be taken account. They are, a very precise linear motion device and a stable temperature gradient. The experimental arragment was explain in extense in [20, 21]

II.1 Device

Directional solidification of the $Al-0.5wt.\%Cu$ samples was carried out in a Bridgman-like apparatus. A schematic view of this equipment can be seen in the Figure 2. The device consists of a mobile vertical chamber furnace of alumina core, where has been located two heating coils with independent temperature controls, maintained at fixed temperatures. This disposition brings a thermal gradient inside the chamber, where we placed the specimens to be directionally growth. Pulling system of the furnace was based in a steeper motor and a gear box, which permitted a translation velocity in the $0-10\,\mu ms^{-1}$ range. The displacement velocity was measured and controlled with a linear variable differential transformer (LVDT) and a signal conditioning interface, and the data was sent to a Personal Computer which drives the motor. This schemes provides a very precise displacement motion, resulting in a precision of $\pm 0.1\,\mu ms^{-1}$

Temperature measurements in the specimen were taken using transverse CrNi-AlNi thermocouples which were made from $0.2\,mm$ diameter wire, isolated by using a ceramic coating. Temperature data was collected by using a data acquisition system, consisting of a 12 bits accuracy analog to digital converter and a multiplexor-low noise differential programmable preamplifier. This assembly also permits the cold junction correction to be carried out. Setting a reader window in $400-1000\,^{\circ}C$ range, the experimental error was estimated in at $\pm 0.5\,^{\circ}C$. In our work, we fixed the thermal gradient at a value of $G_L = 2.5 \pm 0.5\,^{\circ}C\,mm^{-1}$, taking the velocity as the parameter control of the problem. The interface velocity was calculated in each time from the profile temperature vs. time obtained, through heat balance equations.

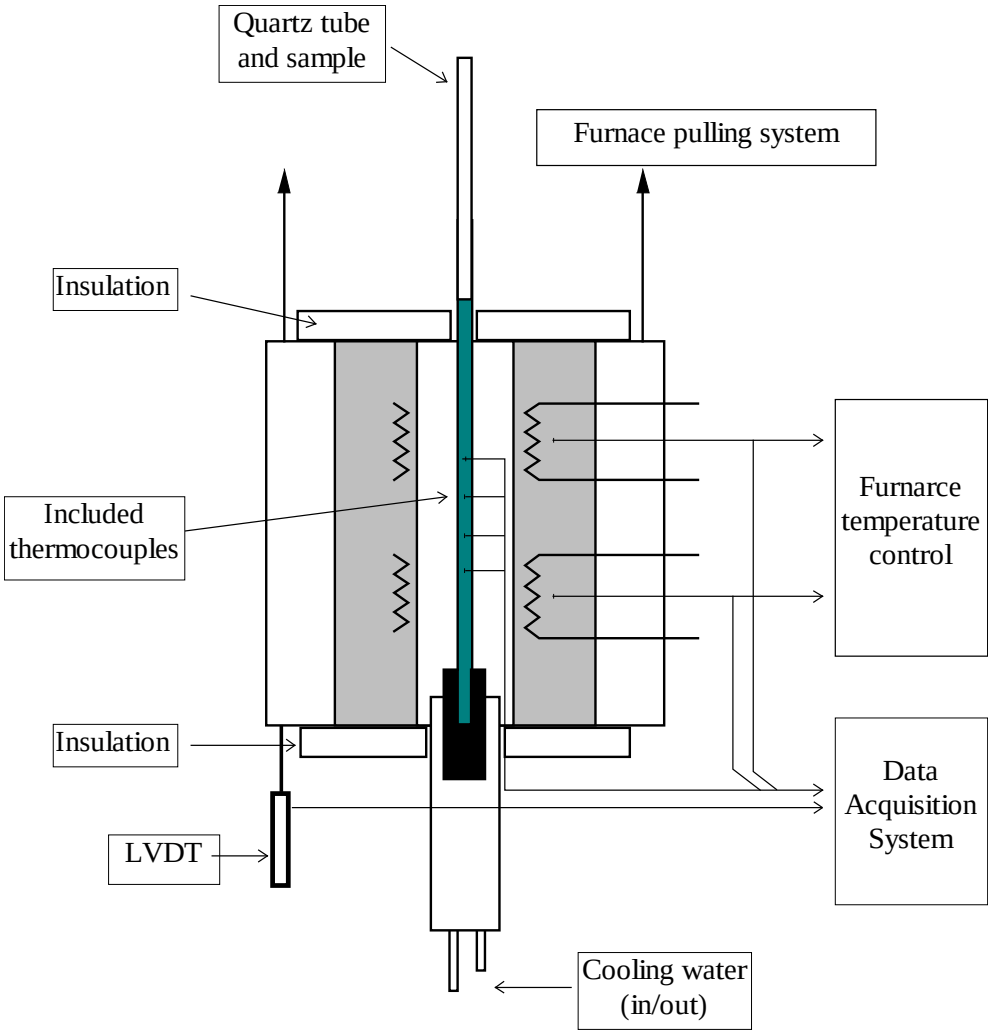
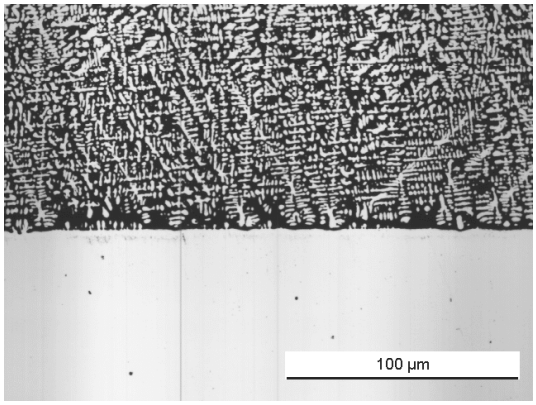


Figure 2: Schematics drawing of the Directional solidification apparatus.

II.2 $Al-0.5\,wt.\%Cu$ Alloy preparation

The alloy was prepared melting purity $99.999\%\,Al$ and adding the required amounts of eutectic $Al-33.2\,wt.\%Cu$, this work was performed under continuous Ar atmosphere. To avoid or minimize the microsegregation the preingots, they were cast in cylindrical quartz tubes of $8\,mm$ internal diameter by $250\,mm$ long, directly from the melt by making use of a depression of $4\,mmHg$. The quartz tubes were internally coated using a based graphite paint. Some samples were sectioned and were chemically analyzed using X ray spectra-photometry. Physical properties of the used system can be seen in Table I

a) 

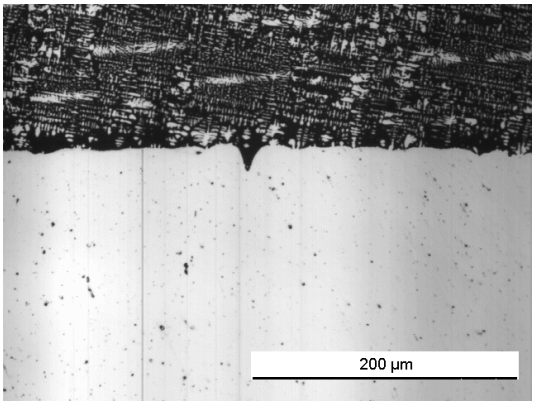
b) 

Figure 3: Samples with planar front of solidification a) Stable situation; b) perturbation which tend to grow at $V_{c,Exp}$.

III Results and Discussion

III.1 Planar interface instability

As an introduction to the problem, were developed several runs around the critical value at which the planar to cellular transition occurs. We found a value of $V_{C,Exp} = 0.5 \pm 0.05\,\mu m s^{-1}$; below this velocity value the microstructure was planar and stable, while above this velocity, the instabilities tend to grow, as can be seen in Figure 3 [8, 20]. In both figures, the crystals were grown from bottom to top, the lower part is the resultant homogenous solid and the upper is the quenched liquid. According to the linear stability theory we expected a theoretical value given by eq. (1). In our case, it brings a threshold velocity of $V_C = 0.58\,[\mu m s^{-1}]$, in such a way the experimental obtained value is in the same order than theoretical one.

III.2 Planar to cellular transition during directional solidification

With this threshold value, we designed experiences which starting with a planar stable front at a velocity lesser than V_C and an increasing velocity, promoting the microstructure change,

Table I: Physical properties of Al-Cu Alloys for use in Numerical Calculations.

m	-2.6	$K\,(wt\%)^{-1}$
k	0.14	- - -
D_L	$3.0\,10^{-9}$	$m^2\,s^{-1}$
Γ	$0.9\,10^{-7}$	$K\,m$
L		
κ_S	210	$W\,(mK)^{-1}$
κ_L	95	$W\,(mK)^{-1}$

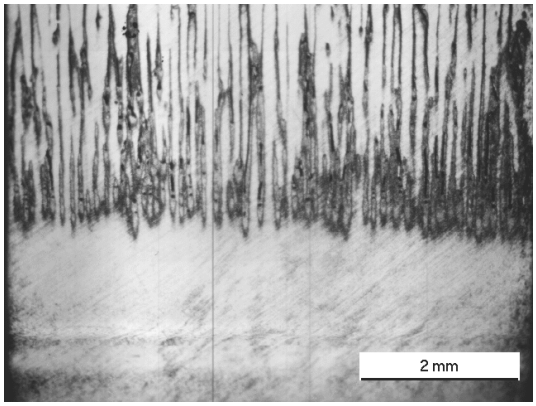


Figure 4: Planar to cellullar Transition at $V^{+}_{C,Exp}$.

ending above the threshold. In this case, the initial velocity was $0.1\ \mu ms^{-1}$, and establishing a final velocity of $3\ \mu ms^{-1}$, the rate of velocity change was estimated in $2 \pm 0.1 \cdot 10^{-4}\ \mu ms^{-2}$. The microstructure evolved from planar to cellular and dendritic at quenching time. In Figure 4 can be seen clearly the planar to cellular transition. For this case, we determined a threshold value given by $V^{+}_{C,Exp} = 0.57 \pm 0.05\ \mu ms^{-1}$, which is a bit greater than the obtained under stable growth conditions.

In the opposite form, were made experiences starting from a velocity value greater than V_C and cellular microstructure with decreasing rate of growth, looking for a planar front of solidification at velocity lesser then V_C. We began starting from a velocity of $3\ \mu ms^{-1}$ and then decreasing the velocity at a rate that was estimated in $3 \pm 0.1 \cdot 10^{-4}\ \mu ms^{-2}$ until a final value of $0.1\ \mu ms^{-1}$. In this first case, the initial microstructure, which was composed by dendritic cells experience a change at a value of $V^{-}_{C,Exp} = 0.3 \pm 0.05\ \mu ms^{-1}$, as can be seen in Figure 5 a). Then we repeat from an initial velocity of $2\ \mu ms^{-1}$ to $0.1\ \mu ms^{-1}$ and a deceleration which was estimated in $1.8 \pm 0.1 \cdot 10^{-4}\ \mu ms^{-2}$. Here, the cellular to planar transition was more notable, as can be seen in Figure 5 b).

a) b)

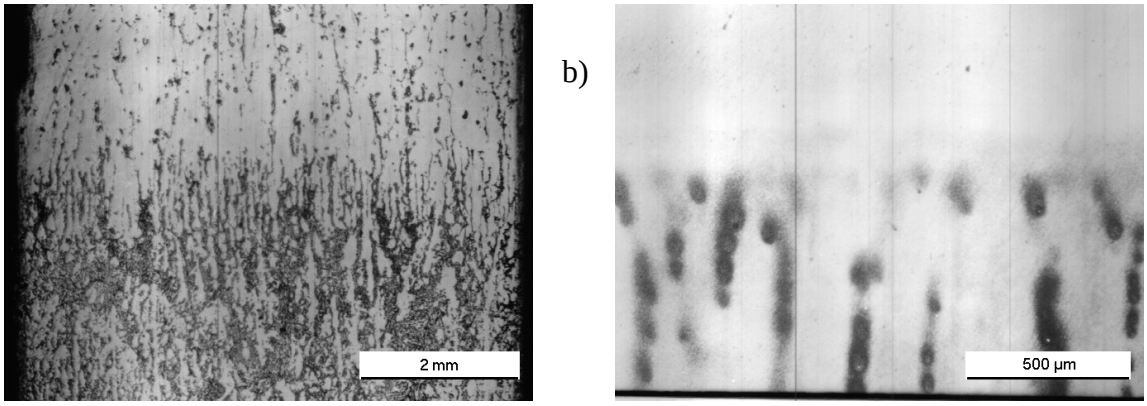


Figure 5: Cellular to planar at $V^{-}_{C,Exp}$ a) from $V \simeq 5V_C$, b) from $V \simeq 2V_C$.

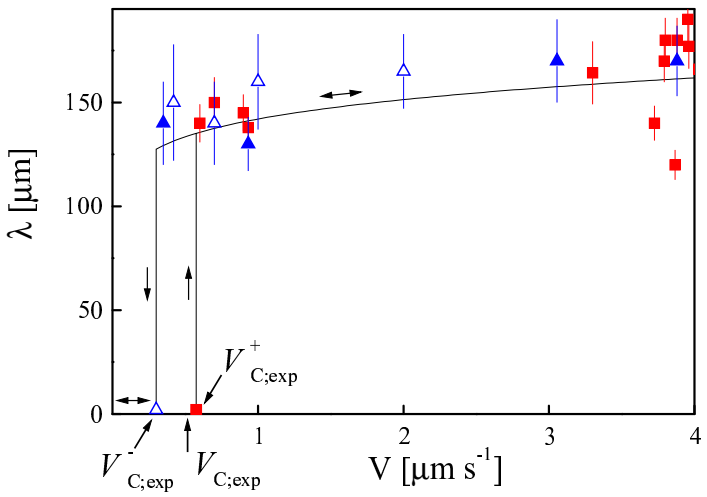


Figure 6: Deformation Amplitude vs. Interface velocity

The results can be summarized by noting that the transition threshold shows a hysteresis behavior if the wavelength of the perturbations are represented against the velocity, if it is increasing and then decreasing through the threshold value V_C, i. e. $V^{-}_{C,Exp} < V_{C,Exp} \lesssim V^{+}_{C,Exp}$, as can be seen in the Figure 6. In the Figure, the arrows show the path of bifurcation, from a planar to a cellular interface as the velocity is increasing and the cellular to a planar interface when the velocity is decreasing, assuming a subcritical transition [8, 20]. The complete behavior could be understood in the following way: when the system start from a planar interface is valid the use of arbitrary small perturbations, in such a way that the threshold is closer to the value given by linear stability theory. Close to V_C there exist a set of wavenumbers which can be grow and define a characteristic spacing. This fact is characteristic of a subcritical transition. When it start from an existing spacing, the hypothesis of small perturbations no longer holds because a cellular state is predicted.

For other side, in accord to the linear stability theory, we expected a critical wavelength given by eq. (2), which in this case is $\lambda_C \approx 520\ \mu m$. The experimental wavelength of the perturbations $\lambda_{C,Exp} \approx 125\ \mu m$, is below in a factor of 4.2. This fact is in accord with the suggestion made by Cheveigné et al. [22] whom predicted a relation in the range 4.5 to 6 for the rate $\lambda_C/\lambda_{C,Exp}$. In addition to that, based in the comparison between the capilarity and composition length, the authors expect a range of variation of approximately $0.1V_C$. In this work, we found a range greater than suggested by the authors [8, 20, 21].

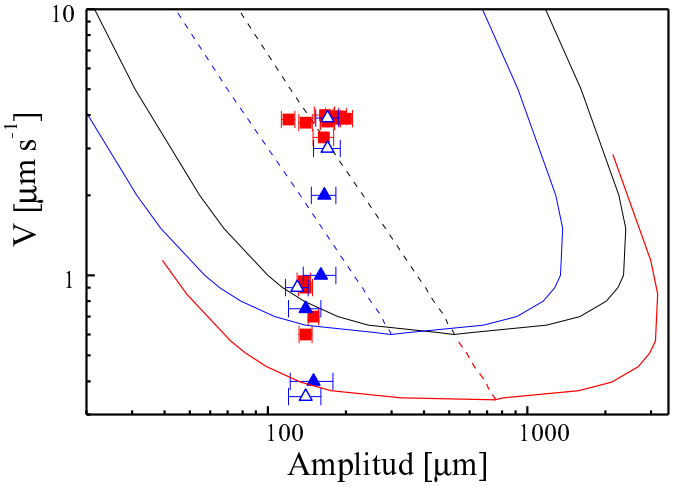


Figure 7: Stability map (Linear and modified non linear)

III.3 Lateral instabilities during the cellular growth

One of the most significative results in the cellular stage of growth are the lateral instabilities. As the cells becomes more deeps with the velocity increasing, the solidification should be completed with the lateral growth of the same. This situation promotes a local unstable condition, due to the interface advances against a greater composition and a lesser thermal gradient than the solidification front. In Figure 8 it can be seen the kind of instabilities that we could observe on the cellular walls. This situation was not present in the case where there been precipated eutectic in the intercellular spacing. It is possible to suppose that the eutectic growth comsumes the higher composition of the remanent liquid, in such a way that the lateral growth becomes stable. This kind of instabilities are very important at time of determine the resultant microsegregation map asociated of the bulk crystaline growth of alloy systems.

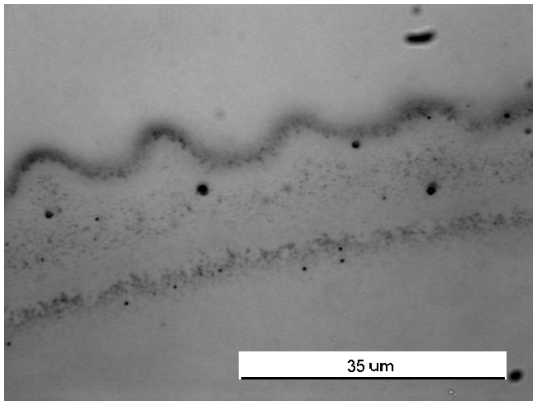


Figure 8: View of a lateral unstability in the cellular wall.

IV Conclusions

We have studied experimentally the system $Al-0.5\,wt.\%Cu$ to determine the behavior of the interface during the transition from a planar to a cellular and from a cellular to a planar morphology. At first, when the velocity is increasing, we determined that the threshold $V^{+}_{C,Exp}$ appears at a value very close to that predicted by the linear stability criterium, V_C. At this value, the instabilities at the interface grow quickly, determining a spacing of the $\lambda_{C,Exp} \approx 125\,\mu m$, approximately 4.2 times below the theoretical value expected. At a decreasing interface velocity, the threshold appears at a value lesser than V_C, determining a hysteresis behavior for the transition [8, 20, 21]. With this evidence we can justify that the transition for this system is subcritical, as expected. The threshold variation found was greater than the $0.1\,V_C$ range proposed theoretically by Cheveigné [22].

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References

[1] J. S. Langer: Rev. Mod. Phys. 52 (1980) 1.

[2] J. S. Kirkaldy: *Metall. Trans.* **24A** (1980) 1969.

[3] H. Biloni and W. J. Boettinger, in Physical Metallurgy, ch. 8: Solidification, edited by R. W. Cahn and P. Haasen, Elsevier Science BV (1996) 669.

[4] Haken

[5] D. Kessler, J. Koplic and H. Levine, *Adv. Phys.* **37** (1988) 255.

[6] W. Kurz and D. J. Fisher: *Fundamentals of Solidification*, Third Ed. Trans Tech Publications (1989).

[7] O. Fornaro and H. Palacio: *Scripta Metall.* **31** (1994) 1265.

[8] O. Fornaro and H. Palacio: *Scripta Mater.* **36** (1997) 439.

[9] W. W. Mullins and R. F. Sekerka: *J. Appl. Phys.* **35** (1964) 444.

[10] W. A. Tiller, K. A. Jackson, J. W. Rutter, and B. Chalmers: *Acta Metall.* **1** (1953) 428.

[11] D. Liu, L. M. Williams, and H. Z. Cummins: *Phys. Rev.* **E50** (1994) 4286.

[12] D. J. Wollkind and. A. Segel: *Philos. Trans. R. Soc.* **A268** (1970) 351.

[13] G. J. Merchant, and S. H. Davis: *Phys. Rev. Let.* **63** (1989) 573.

[14] G. J. Merchant, and S. H. Davis: *Phys. Rev.* **B40** (1989) 11140.

[15] J. S. Langer and L. A. Turski, *Acta Metall.* **25** (1977) 1113.

[16] L. H. Ungar and R. A. Brown, *Phys. Rev.* **B29** (1984) 1367.

[17] B. Caroli, C. Caroli and B. Roulet, *J. Phys. (Paris)* **43** (1982) 1767.

[18] J. I. D. Alexander, D. J. Wollkind and R. F. Sekerka, *J. Crystal Growth* **79** (1986) 849.

[19] B. Billia and R. Trivedi, in Handbook of crystal growth, ch. 14 vol I: "Pattern formation in crystal growth", D. T. J. Hurle eds. (1993) 912.

[20] O. Fornaro, H. Palacio and H. Biloni: Materials Research Society, **481** (1998) ,

[21] O. Fornaro, "Inestabilidades morfológicas en la solidificación unidireccional de aleaciones FCC: Al-Cu diluidas", Doctorate Thesis, Universidad Nacional del Centro de la Provincia de Buenos Aires, Physics Department, 1997.

[22] S. Cheveigné, C. Guthmann, P. Kurowski, E. Vicente and H. Biloni, *J. Crystal Growth* **92** (1988) 616.