Yugoslav Association of Metallurgical Engineers *UDC:669.065-154=20*
YAME

THE INFLUENCE OF THE SOLIDIFICATION RATE ON THE INTERFACE SHAPE AND DISTRIBUTION OF SOLUTE

V. RADOJEVIĆ[1)], S. NIKOLIĆ[2)],
A. VALČIĆ[1)]

[1)]*Faculty of technology and metallurgy, Belgrade, Yugoslavia*
[2)]*Institute of physics, Zemun, Yugoslavia*

ABSTRACT

In this paper investigation of the influence of the solidification conditions on the interface shape and distribution of solute during the solidification of Al-Cu alloy by vertical Bridgman method were investigated.The microstructure of the samples was metallographically investigated. Optical emission spectrometry was used for chemical analysis of distribution of the solute concentration along the specimen. Within experimental range of growth rates the plane-to-cellular and cellular-to-dendrite transition was observed. According to the distribution of the solute along the sample, the effective distribution coefficient k_e was calculated, and by observing its value, the influence of growth rate (R) on the distribution of the solute in solid was investigated.

Key words: Vertical Bridgman, interface shape, effective distribution coefficient, growth rate, Al-Cu alloy

INTRODUCTION

During directional solidification of alloys, the interface morphologies change from planar to cellular to dendritic as the velocity is increased. Extensive research has been done by several authors [1-6] on the evolution of the S-L interface, both in dilute alloys and organic transparent alloys using the linear stability theory where the Constitutional Supercooling (CS) [7] is an important tool in order to predict solid-liquid (S-L) interface instabilities arising during controlled growth from the melt. For a given alloy the decrease of the parameter G_L/R, where G_L is the temperature gradient in liquid in front of the interface and R the solidification rate, controls the evolution of the S-L interface morphology. According to CS criterion the planar interface becomes unstable above a critical growth rate, R_{PC}, given approximately by:

$$\frac{G_L}{R_{PC}} = -\frac{m_L C_0 (1 - k_0)}{k_0 D_L} \qquad (1)$$

where G_L is the temperature gradient in the liquid phase, R_{PC} the critical growth rate for beginning of interface instability, C_0 the initial solute concentration, m_L the liquid line slope in the equilibrium diagram, k_0 the equilibrium coefficient of distribution, D_L the coefficient of diffusion in the liquid phase.

Near the critical rate, R_{PC}, the interface exhibited an irregular morphology. The unstable region lies between stable region for a planar interface (equation 1.) and the stable region of regular cells. So the cellular interface was obtained at appreciable larger rates than R_{PC} [6]. On the other hand, the boundaries of these stable regions are not clearly distinguished. Although the critical rate for beginning of planar interface instability is defined, the precise moment of planar-to-cellular transition is not yet determined. What does the critical microstructure look like, and which is the critical rate for this moment? In our work it was assumed that beginning of connection of cells represents the critical microstructure. This structures is obtained at remarkable higher rate than the calculated one [8-11].

The distribution of solute concentration in the solid phase can be described by the corrected Phann relation [7]:

$$C_S = k_e C_0 (1-g)^{k_e - 1} \qquad (2)$$

where C_S is the concentration of solute in the solid phase, C_0 is the initial concentration of solutes in the liquid phase, k_e is the effective distribution coefficient and g is the fraction of solidified material.

The value of k_e can be determined from experimental results by this equation [12].

EXPERIMENTAL

Solidification of six series of Al-Cu alloy by vertical Bridgman method [8,9] was performed in the inert nitrogen atmosphere: 0.47%Cu, 1.00%Cu, 1.40%Cu, 2.20%Cu, 2.60%Cu and 2.86%Cu. The quartz ampoule containing a graphite vessel was moved downwards. 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 in protective nitrogen atmosphere.

The solidified samples were longitudinally cut, polished, etched and then the metallographic investigation of the microstructure was performed.

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

RESULTS AND DISCUSSION

According to CS criterion, equation (1) was used to calculate R_{PC}, a critical growth rate when the planar interface becomes unstable. The m = -3.4°C/% was calculated from the Al-Cu equilibrium diagram. Values for k_0 =0.153 [13] and D_L= 2.2×10^{-5} cm^2/s [14] were taken from the literature. It has been assumed that temperature gradient in melt and in furnace is equal. Temperature gradient in the furnace is measured and G is estimated to be 14.5°C/cm [15].

As in previous work it is observed that the growth rate at which the connection of cellular structures begins is greatly different from the calculated value for R_{PC} [11-14]. The growth rate when the beginning of connecting of cells has been observed is denoted as R_{PC}^{exp}. The values of the calculated R_{PC} and observed R_{PC}^{exp} for all series are presented in Table I:

Table I -The values of the calculated R_{PC} and observed R_{PC}^{exp}

C_0 ,%	0,47	1,00	1,40	2,20	2,60	2,86
R_{PC} ,m/s	$3{,}59 \times 10^{-7}$	$1{,}71 \times 10^{-7}$	$1{,}21 \times 10^{-7}$	$7{,}72 \times 10^{-8}$	$6{,}55 \times 10^{-8}$	$5{,}90 \times 10^{-8}$
R_{PC}^{exp},m/s	1.75×10^{-5}	$1{,}75 \times 10^{-5}$	8.71×10^{-6}	4.35×10^{-6}	4.35×10^{-6}	4.35×10^{-6}

The existence of convection, as well as difficulties in the experimental metallographic defining the exact moment of planar-to-cellular transition can be the reasons for this deviation. Besides, the definitions of the R_{PC} and R_{PC}^{exp} are different. R_{PC} is the growth rate for the beginning of interface instabilities, while R_{PC}^{exp} is the growth rate at which the connection of cellular structures begins. The critical microstructure corresponding to beginning of connection of cells is obtained at remarkably higher rate than the calculated R_{PC}. In this work it has been proved that R_{PC}^{exp} allows a clear distinction between regions of planar interface and cellular structure.

According to the distribution of the solute along the sample, from the equation (2) [16] the effective distribution coefficient k_e was calculated (Table II).

Table II - The calculated values of k_e

C_0 (%)	0.47	1.00	1.40	2.20	2.60	2.86
R (m/s) ↓	k_e					
1.45×10^{-6}			0.89	0.44	0.71	0.99
2.90×10^{-6}	0.67			0.40		0.88
4.35×10^{-6}	0.69	0.76		0.31		0.85
8.71×10^{-6}			0.77		0.66	0.87
1.75×10^{-5}	0.57	0.90	0.89			
4.35×10^{-5}	0.67	0.90				
8.71×10^{-5}	0.73	0.88	1.00	0.60	0.94	0.98

There is a fall of values of k_e at R_{PC}^{exp} or in its vicinity [17]. The formation of cellular structure and the connection of cells gradually affect the value of k_e. This phenomenon can be used for unambiguous definition of critical rate of plane-to-cellular transition given the relation between the appearance of critical structure and decrease of k_e.

In the real systems the effective distribution coefficient k_e is used instead of the equilibrium one. The CS-criterion was corrected in the same way, but the critical growth rate was R_{PC}^{exp}:

$$\frac{G_L}{R_{PC}^{\exp}} = \frac{m(1-k_e)C_0}{D\,k_e} \qquad (3)$$

From eq. (1) and (3):

$$\frac{R_{PC}^{\exp}}{R_{PC}} = \frac{1-k_0}{k_0}\cdot\frac{k_e}{1-k_e} \qquad (4)$$

Set of experimental data was formed and presented in the Table III, while relation $\frac{R_{PC}^{\exp}}{R_{PC}} = \text{fun}\left(\frac{k_e}{1-k_e}\right)$ is presented in the Figure 1 (There were not data for distribution of solute for the series with 2.2% Cu for $R_{PC}^{\exp}$, so they are not is the Table III and Figure 1).

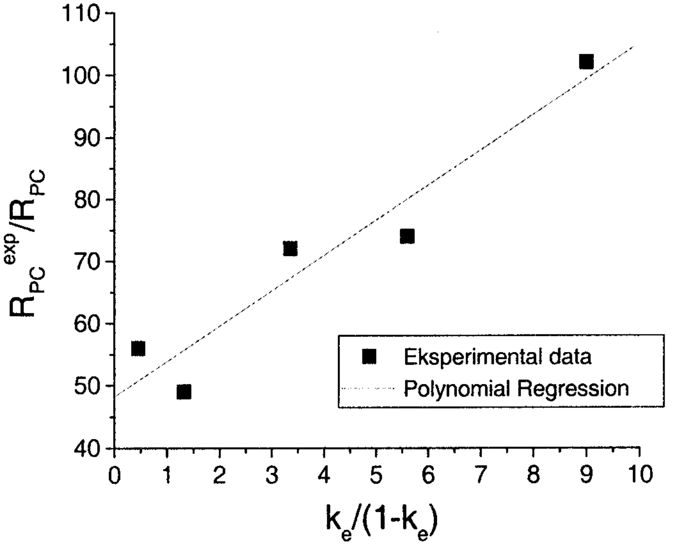

Figure 1 - The correlation of parameters R_{PC}^{exp}/R_{PC} and $k_e/1$-k_e

Table III - The values of parameters $\frac{R_{PC}^{\exp}}{R_{PC}}$ and $\frac{k_e}{1-k_e}$

Co(%)	2,60	0,47	1,40	2,86	1,00
$\frac{k_e}{1-k_e}$	0,45	1,32	3,35	5,6	9

From regression analysis coefficient of correlation was calculated: (R=0,958), and very good linear correlation of these parameters was observed.

Value for k_0 = 0.150 was calculated from the slope n= $(1-k_o/k_o)$. There are values of equilibrium distribution coefficient k_0=0,140 [18] k_0=0,153 [13] in the literature. Our calculated value is very close to these literature data.

CONCLUSION

In this study the solidification of six series of Al-Cu alloy was performed using vertical Bridgman method and influence of the solidification conditions on the microstructure and solute distribution was investigated. Within experimental range of growth rate the plane-to-cellular and cellular-to-dendrite transition was observed.

The critical rate for plane-to-cellular transition (R_{PC}) was calculated, and experimental values (R_{PC}^{exp}) were estimated. The critical microstructure corresponding to beginning of connection of cells (R_{PC}^{exp}) is obtained at remarkably higher rate than the calculated R_{PC}. In this work it has been proved that R_{PC}^{exp} allows a clear distinction between regions of planar interface and cellular structure. This proving has been done by investigation of dependence of k_e on the growth rate and by correlation of R_{PC}^{exp}/R_{PC} and $(1-k_o/k_o)$ parameters.

According to the distribution of the solute along the sample, the effective distribution coefficient k_e was calculated. There is a fall of values of k_e at R_{PC}^{exp} or in its vicinity. According to definition of R_{PC}^{exp} the forming of cellular structure and connecting of cells deform the interface gradually and therefore the regime of distribution of solute is changed. Values of k_e also follow this change and this moment of falling its value is the sign that the cellular growth started.

Correction of the CS-criterion by R_{PC}^{exp} and k_e allowed correlation of R_{PC}^{exp}/R_{PC} and $(1-k_o/k_o)$ parameters.

Very good linear correlation and calculated value of k_0 confirm R_{PC}^{exp} as a border between region of the planar interface and cellular growth.

LITERATURE

[1] T. M. Pollock, W. H. Murphy, *Metal. Mater. Trans.* A, Vol. 27, Iss. 4, (1996) 1081.

[2] D. X. Ma, P. R. Sahm, Z. *Metallk*, Vol. 87, Iss. 8, (1996) 634.

[3] R. Trivedi, Proc. of 1999 TMS Annual Meeting & Exhibition, San Diego, USA, (1999) 36.

[4] J. A. Sarreal, G. J. Abbaschian, *Met. Trans.* A, Vol. 17A, (1986) 2063.

[5] O. Fornaro, H. Palacio, H. Biloni, 1999. TMS Annual Meeting & Exhibition, San Diego, USA, Proceedings TMS, (1999), 119

[6] D. Venugopalan, J. S. Kirkaldy, *Acta. Metall.* Vol. 32, No. 6, (1984) 893.

[7] W. G. Phan, Zone Melting, John Wiley & Sons Inc., New York, (1958)

[8] Valčić, V.Radojević, S. Nikolić, *J. Serb. Chem. Soc.* 60(1), 33-41(1995)

[9] V.Radojević, A. Valčić, S. Nikolić, *Science of Sintering*, Vol. 30,71-76, (1998).

[10] V.Radojević, A. Valčić, S. Nikolić, A. Milutinović-Nikolić, *Materials Congress '98, Book of abstracts, p. 49, Cirencester*, UK, 6-8. April (1998).

[11] V.Radojević, A. Valčić, S. Nikolić, R. Jančić, A. Milutinović-Nikolić, *First International Conference on Inorganic Materials,* 16-19.09.1998. Versailles, France, Proc. of abstracts, C 04.

[12] V.Radojević, A. Valčić, S. Nikolić, *Mat. Lett.* To be published

[13] L. Kuchar, J. Drapala, *Hutnicke listi*, Vol. 7, (1985), 498

[14] A. Valčić, S. Nikolić, B. Radonjić, Proc. of *VII RTC Sintering*, (1988), 156

[15] V.Radojević, The investigation of the influence of crystallization conditions on the liquid-solid interface and solute distribution, Ph. D. Thesis, Faculty of Technology and Metallurgy, Belgrade, (2000)

[16] V.Radojević, A. Valčić, A. Milutinović-Nikolić, *Metalurgija*, Vol.5, Br.3, 195-200, (1999).

[17] V.Radojević, A. Valčić, S. Nikolić, *Mat. Lett.*52, 248-254, (2002)

[18] R. M. Sharp, A. Hellawel, *J. Cryst. Growth* **6**, (1970) 253