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Unidirectional Solidified Zn-Al-Si-Cu Alloys: Columnar-to-Equiaxed Transition (CET)

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Abstract—The present investigation was undertaken to investigate the directional solidification of Zinc-Aluminum alloys with addition of Silicon and Copper, specifically Zn-20%Al-10%Si-3%Cu alloys (weight percent) under different conditions of heat transfer at the metal/mould interface. The columnar-to-equiaxed transition, CET, was observed and related to the solidification thermal parameters such as cooling rates, interphase velocities, thermal gradients and recalescence values which were determined from the temperature versus time curves. The results indicate that there is an increase in the velocity of the liquidus front faster than the solidus front, which increases the size of the mushy zone. The observations indicate that the transition is the result of a competition between columnar grains and finer equiaxed grains.

***Index Terms*—Solidification, Zinc-base alloys, thermal parameters, columnar-to-equiaxed transition.**

I. INTRODUCTION

Solidification of metallic alloys, which begins in the outer equiaxed region (chill) resulting in two main and basic types of structures in the same alloy: columnar and equiaxed, indicating the presence of the phenomenon of the columnar to equiaxed transition (CET) [1-5]. The study of the CET is of immense technological interest for the evaluation and design of mechanical properties of the solidification products. To this end it is necessary to understand the mechanisms by which it is produced. As found in many previous studies [1-15], the CET occurs by competition between columnar and equiaxed growth. It is mainly controlled by the casting parameters, such as alloy composition, density of nuclei present in the liquid, ability to cooling the metal / mold interface, and convection in the liquid [5-15].

In own experiments carried out previously in low melting point alloys (Lead - Tin) [5-7]and taking into account several factors such as, cooling rate, velocities of liquid interphases, v_L, and solid, v_S, alloy composition, gradients and fluid temperature below the interphase liquid, experimental evidence was obtained that suggest that the CET feature occurs when a combination of factors in thermal and dynamics conditions; such as the movement in the liquid, heat transfer, the solidification process and the change of structure [5-15].

This study determined the conditions under which the transition from columnar to equiaxed during directional growth of alloys Zn-20% Al-10% Si-3% Cu (% by weight) occurs, and compared the results of this research with previously obtained in Pb-Sn alloys [5-7], Al-Cu [7, 9], Zn-Al [8, 10-15].

II. EXPERIMENTAL PROCEDURE

The directional solidification was performed in a directional solidification furnace, comprising a heating unit and a control and acquisition systems of temperatures to which a system of directional heat extraction was added [4-12]. A total of five experiences of directional growth with Zn-20% Al-10%Si-3%Cu alloy were conducted. Temperatures were measured at regular intervals of 0.2 seconds, using a set of six type K thermocouples calibrated, (see Figure 1).

Tthermocouples were precoated with refractory ceramic and were introduced in holes with a depth of 0.7 cm, which coincide with the center of the diameter of the sample. The distance between thermocouples used in the test samples was 2 cm approximately. Figure 1 shows a sketch of the experimental set-up.

After the directional solidification process, Zn-20%Al-10%Si-3%Cu alloys samples were cut in longitudinal direction were polished with sandpaper of different grits (#60 to #1500). In order to reveal the macrostructure the samples were chemically attacked with concentrated hydrochloric acid, during approximately 3 seconds, at room temperature, followed by the removal and cleaning of the tank blacks. The CET position was located by visual observation and optical microscopy, and the distance from the base of the samples was measured with a ruler [10-15]. Figure 2 shows one macrograph directionally solidified of Zn-20%Al-10%Si-3%Cu alloy. For the CET the columnar growth front needs to be arrested by equiaxed grains.

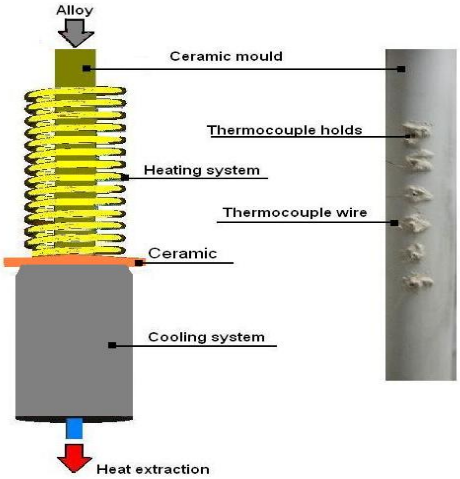


Fig. 1: Schematic of experimental setup.

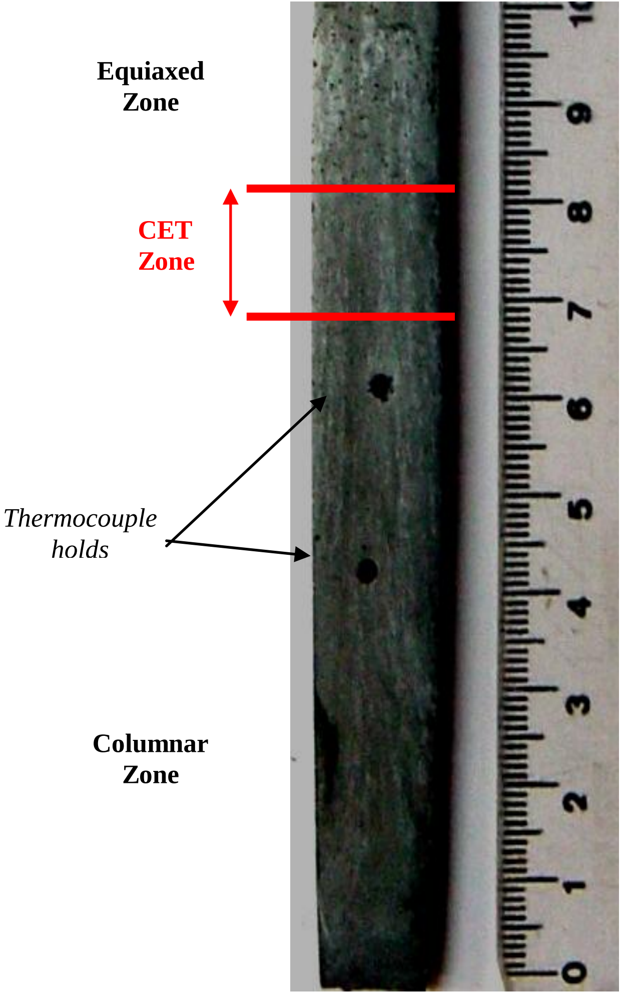


Fig. 2: Macrograph of Zn-20%Al-10%Si-3%Cu alloy.

III. RESULTS

The liquidus and solidus temperatures for each alloy were determined by Differential Thermal Analysis (DTA) using the NETZSCH STA 449 C Standard system, with calibrated cell as with pure elements. These measurements involved the pre-cast of 200 milligrams of samples in alumina crucibles. For analysis, the samples were heated and cooled at a rate of 10 °C/min under Argon atmosphere [7, 9]. Multiple cycles were performed to ensure reproducibility of results. The liquidus temperature, T_L, was obtained from the cooling curves. The determined values can be observed in Figure 3. The results are consistent with which is predicted in the phase diagram [16].

Cooling rates of alloys in liquid state were determined on the average values of the slopes of temperature versus time curves for each thermocouple position. Figure 3 shows the temperature versus time variation recorded for each thermocouple during the experiments.

A summary of the cooling rates calculated in different experiments and the average length of columnar regions, measured from the base of the samples, for each one of the experiments are presented in Table 1. Comparing the values of cooling rates in the liquid and the maximum and minimum lengths of the CET for each experiment, with the same alloy concentration, it can be appreciated that as increasing the cooling rates in the liquid increases the length of the columnar zones.

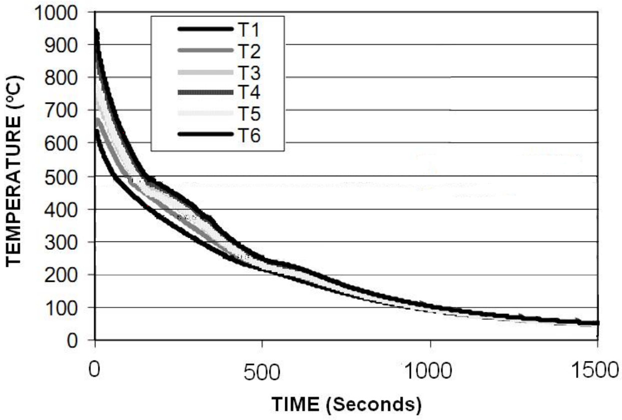


Fig. 3: Temperature versus time curve of Zn-20%Al-10%Si-3%Cu alloy.

In the temperature versus time curves for each experiment was possible identify a period of a cooling of liquid, a second period of solidification and a final period of cooling of solid to room temperature. In some cases it was possible to identify a short period of recalescence at the position of the thermocouple where the CET occurs [7, 9, 10-15]. The necessary overheating for restored the heat flow between the equiaxed nuclei formed was measured. The mean values obtained for each experiment are listed in Table 1.

The equiaxed nuclei start to grow adjacent to the solidus interphase, but separated from there. These nuclei are overheated and the liquid is cooled. The reheating continue when solidifying small equiaxed grains and the liquid is also overheats. When the whole zone is overheat due to latent heat accumulated evenly and more extent that in the solidus interphase can produce the recalescence, reaching a positive ΔT [7,9, 10-15].

This thermal condition causes a larger number of small nuclei that grow adjacent to the solid interphase and some nuclei disappear at higher distances of this interphase, producing the growth of equiaxed nuclei at larger distances of the solid interphase, as it can be seen in the macrograph of Figure 2.

The positions of the solidification fronts versus time were determined at the beginning and the end of the solidification of each thermocouple and correspond to the liquidus and solidus temperatures, respectively. Both points were detected by the changes in the slopes of the cooling curves at the beginning and end of solidification.

The velocities of the solidification fronts were calculated as the relation between the distance of thermocouples and the time taken for any of the liquidus or solidus temperatures to move from the lower to the upper thermocouple. These velocities are called velocity of the liquidus interphase, V_L, and the velocity of the solidus interphase, V_S, respectively. Furthermore, the velocities of the liquidus interphase at the instant of the CET are called "critical liquidus interphase velocity", V_{LC}. This critical velocity is detailed in Table 2 for different experiments (grey values in Table 2).

Table 1. Liquid cooling rates ($\dot{T}_{LIQ.}$) and solid cooling rates ($\dot{T}_{SOL.}$),minimum CET ($CET_{MIN.}$), and maximum CET position ($CET_{MAX.}$), critical temperature gradients (G_C), i.e. at the time that the CET occurs; and values of recalescence (REC.), obtained from the temperature versus time curves of the Zn-20% Al-10% Si-3% Cu alloys.

#	$\dot{T}_{LIQ.}$ (°C/S)	$\dot{T}_{SOL.}$ (°C/S)	$CET_{MIN.}$ (cm)	$CET_{MAX.}$ (cm)	G_c (°C/ cm)	REC. (°C)
1	2.28	1.38	4.9	5.2	1.18	1.74
2	1.98	1.29	2.8	4.1	-1.52	2.21
3	2.09	1.24	3.6	4.8	-0.66	2.53
4	2.33	1.41	5.2	7.9	-2.40	3.12
5	2.38	1.78	6.8	8.2	1.25	1.58

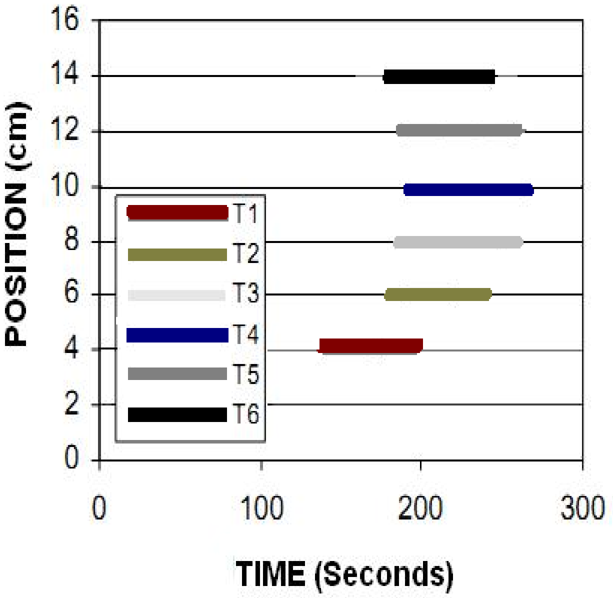
A typical results of the position of the liquidus and solidus fronts as a function of time is represented in Figure 4 for Zn-20%Al-10%Si-3%Cu alloy. In the particular case of Figure 4 (b), it can be noted that after 180 seconds, the liquidus front advances rapidly. The solidus front moves behind the liquidus front at a velocity that after the CET is similar to the liquidus velocity, but it accelerates less than after the transition. The position of the liquidus interphase can be represented by a potential function.

Table 2. Velocities of liquid, V_L and solid, V_S interphase velocities.

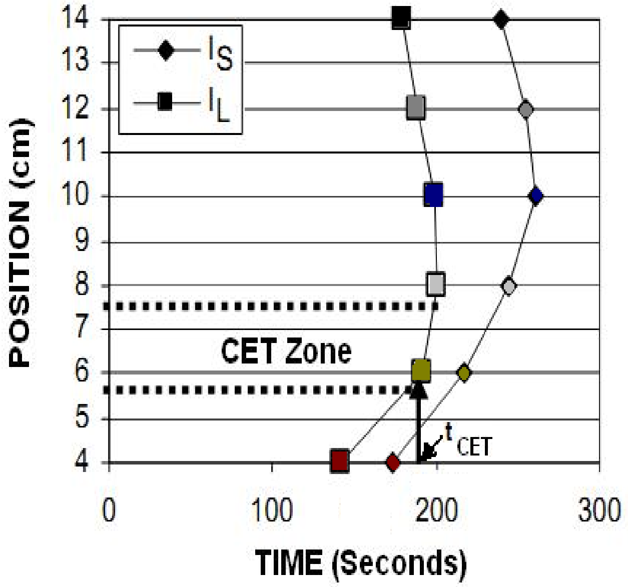
#	Liquid Interphase Velocity, V_L (cm/S)				Solid Interphase Velocity, V_S (cm/S)			
	V_L1	V_L2	V_L3	V_L4	V_S1	V_S2	V_S3	V_S4
1	0.15	0.19	0.27	0.43	0.06	0.09	0.12	0.17
2	0.16	0.20	0.26	0.34	0.09	0.13	0.17	0.22
3	0.11	0.19	0.25	0.38	0.08	0.12	0.15	0.18
4	0.14	0.21	0.30	0.41	0.05	0.08	0.11	0.14
5	0.12	0.21	0.27	0.32	0.07	0.13	0.16	0.20

The rate can be derivative of this potential function, depending on the time or position. For example, for Zn-20%Al-10%Si-3%Cu alloy sample, the liquidus interphase velocity can be represented by the function expressed in Figure 5. One can see in Figure 5 that the velocity of solidus front remains lower. As a result, the mushy zone increases very quickly. Furthermore, a specific direction of movement of the interphases, which is upward, indicating that heat extraction, is from the base and that the nucleation of new equiaxed grains ahead of the columnar front is in cascaded.

This behavior has been observed in other experiments with different concentrations. The numerical values of both velocities of interphases for different experiences can be seen in Table 2. Grey values of V_L in this table are the values of liquidus interphase velocity, V_{LC}, this is when the CET occur, the values are greater than those obtained in Pb- Sn alloys [2-5], which were around 0.01 cm/s [1-5] and the values obtained in the present research are the same order of magnitude as those obtained in Al-Cu alloys [12], Al-Si-Cu [13] and Zn -Al [14, 15].



(a)



(b)

Fig. 4: Positions of liquidus and solidus interphases, I_L and I_S, versus time. (a) The period of solidification time in each thermocouple position. (b) Liquidus and solidus interphases.

Temperature gradients for each pair of adjacent thermocouples were calculated as the relation between the temperature difference at the unlike distances between thermocouples (2-5). Figure 6 shows the graph of gradient variation with time for one experiment with Zn-20%Al-10%Si-3%Cu alloy. It is observed that when the CET occurs, the temperature gradient ahead of the interphase reaches a minimum and critical value of 1.28 °C/cm. In Table 1 are presented the critical temperature gradients values of all experiments. These results agree with those obtained previously in other alloy systems (Pb-Sn [5-7], Al-Cu [7, 9], Zn-Al [8, 10-15] and those obtained by Gandin in Al-Si alloys [4]).

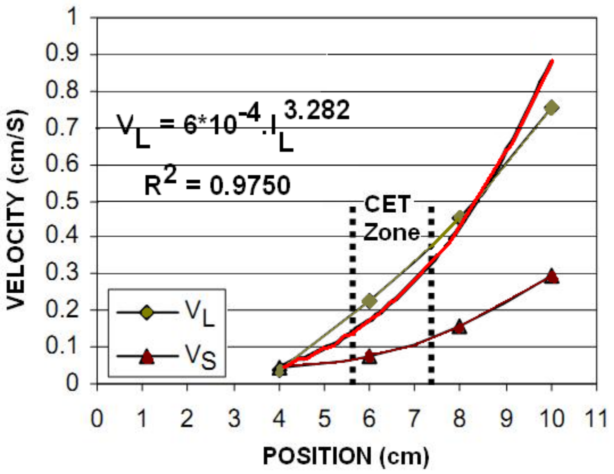


Fig. 5: Velocity of liquidus and solidus front. Zn-20%Al-10%Si-3%Cu alloy.

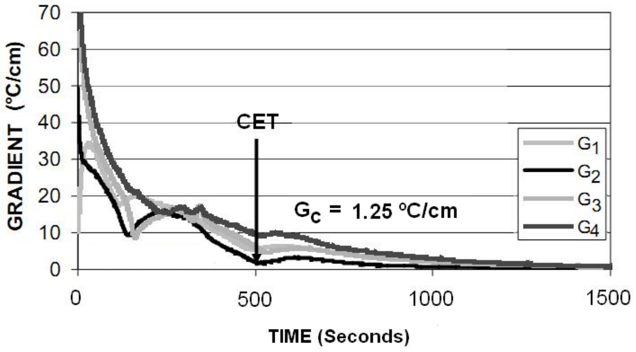


Fig. 6: Temperature gradient versus time. Zn-20%Al-10%Si-3%Cu alloy.

IV. CONCLUSIONS

In summary, the main results of the present research can state as follows:

1. The transition occurs in a region of the order of 1 cm or greater, where both types of grains, columnar and equiaxed coexists.
2. When the CET occurs, the temperature gradient ahead of the interphase reaches the minimum values between -0.66 °C/cm and 1.25 °C/cm for the Zn-20%Al-10%Si-3%Cu alloy.
3. The length of the columnar zone increases with cooling rate.
4. The velocity of the interphases reaches critical values that are on the order of 0.20 to 0.27 cm/s.
5. In the experiments noted the effect of recalescence in the positions of the thermocouples located in the CET and equiaxed zones of the samples. The values are in the range between 1.58 °C to 3.12 °C.
6. The results are consistent with those found previously in other alloy systems (Zn-Al, Pb-Sn, Al-Cu).

REFERENCES

[1] J. A. Spittle, "Columnar to Equiaxed Grain Transition in As Solidified Alloys", International Materials Reviews, vol. 51, pp. 247-269, August 2006.

[2] S.C. Flood and J.D. Hunt, Metals Handbook, **v**ol. 15**,** ASM International, Materials Park, OH (1988) pp. 130-138.

[3] W. Kurz and D. J. Fisher, "Fundamentals of Solidification", Chapter 2, Trans Tech Publications. Switzerland, p. 8, June 1986.

[4] Ch-A. Gandin, "From Constrained to Unconstrained Growth during Directional Solidification", Acta Mater. vol. 48**,** pp. 2483-2501., March 2000.

[5] A.E. Ares and C.E. Schvezov, "Solidification Parameters during the Columnar-to-Equiaxed Transition in Lead-Tin Alloys", Metall. Mater. Trans A,. vol. 31 pp. 1611-1625, October 2000.

[6] A.E. Ares, S.F. Gueijman, C.E. Schvezov, "Semi-Empirical Modeling for Columnar and Equiaxed Growth of Alloys", Journal of Crystal Growth, vol. 241, pp. 235-240, May 2002.

[7] A. E. Ares, S. F. Gueijman, R. Caram, C.E. Schvezov, "Analysis of Solidification Parameters during Solidification of Lead and Aluminium Base Alloys", Journal of Crystal Growth, vol. 275, pp. e319-e327, February 2005.

[8] A.E. Ares and C.E. Schvezov, "Influence of Solidification Thermal Parameters on the Columnar to Equiaxed Transition of Al-Zn and Zn-Al Alloys", Metall. Mater. Trans. A, vol. 38, pp. 1485-1499, July 2007.

[9] A. E. Ares, S. F. Gueijman, C.E. Schvezov, "An Experimental Investigation of the Columnar-to-Equiaxed Grain Transition in Aluminium-Copper Hypoeutectic Alloys", Journal of Crystal Growth, vol. 312, pp. 2154–2170, July 2010.

[10] S.F. Gueijman, C.E. Schvezov, A.E. Ares, "Vertical and Horizontal Directional Solidification of Zn-Al and Zn-Ag Diluted Alloys", Materials Transactions, vol 51, pp. 1861-1870, October 2010.

[11] A.E. Ares and C.E. Schvezov, "The Effect of Structure on Tensile Properties of Directionally Solidified Zn-base Alloys", Journal of Crystal Growth, vol. 318, pp. 59-65, March 2011.

[12] A.E. Ares, L.M. Gassa, C.E. Schvezov, M.R. Rosenberger, "Corrosion and Wear Resistance of Hypoeutectic Zn-Al Alloys as Function of Structural Features", Materials Chemistry and Physics. vol. 136, pp. 394-414, October 2012.

[13] M.V. Okseniuk, S.F. Gueijman, C.E. Schvezov, A.E. Ares, "The Influence of Gravity on the CET in Diluted Zn-Al Alloys", Procedia Materials Science, vol. 1, pp. 64-71.

[14] S.F. Gueijman, A. E. Ares, “Modelling of Cooling Curves in Zn-Al Diluted Alloys”, International Journal of Engineering and Innovative Technology (IJEIT), vol. 3, p.p. 293-299, November 2013.

[15] S.F. Gueijman, A. E. Ares, “Estimation of the Evolution of Solid Fractions in Constant Volumes of Cylindrical Samples Unidirectionally Solidified”, International Journal of Engineering and Innovative Technology (IJEIT), vol. 3, p.p. 133-138, December 2013.

[16] H. Okamoto, “Phase Diagrams for Binary Alloys”, ASM International, p. 49, September 2000.

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