Modeling of Cooling Curves in Zn-Al Diluted Alloys

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Abstract—In this paper we analyze the effect of size and the movement of a zone of coexistence of two phases which release latent heat during solidification on the cooling curves of pure Zn and Zn-1wt.%Al; Zn-2wt.%Al; Zn-3.5wt.%Al and Zn-5.0wt.%Al alloys. In samples solidified predominantly unidirectionally it was determined that by the effect of solidification of any portion of the metallic material, either the cooling curves of the alloy in the liquid state or the cooling curves of the solid formed after solidification, a deformation due to thermal effects from mobile sources that release energy occurs. This significantly affects the temperature versus time curves and the form of growth of solids formed during the phase change; hindering the modeling of cooling curves to make them dependent, in addition to time, the properties of the alloy, the particular position in the cylindrical sample, the positions of [(Liquid) / (Solid + Liquid)] and [(Solid + Liquid) / (Solid)] interphases; also, the size of the zone of solid-liquid coexistence, as well as the amount of latent energy released by that zone and segregation of alloying elements, among other factors. From the samples of specified concentrations, the increases in the temperature of cooling liquid due to overheating thereof, ahead of the [(Liquid) / (Solid + Liquid)] interphase were determined. Also, the increases in the solid temperature due to heat buildup behind the [(Solid + Liquid) / (Solid)] interphase as a function of time and position were determined.

Index Terms—Solidification, Zinc-Aluminum alloys, Solid fraction, Modeling.

I. INTRODUCTION

The final properties of castings are determined by the microstructure obtained during the solidification process. Consequently, for researchers and metallurgists it is necessary an accurate understanding of the influence of solidification parameters in order to improve the competence and performance of materials [1-3]. Solidification of metals occurs by a wide variety of structures. The structure is columnar if the growth is preferentially oriented in a direction close to the heat flux, while equiaxed structures can grow in all directions inside the material, leading to a material with more isotropic properties comparing to a columnar structure [4, 5]. Depending on the industrial application, one type of structure will be necessary, e.g. columnar grains in turbine blades and equiaxed grains in structural applications. Hence, it is important to understand the mechanisms which control the directional solidification process and also the transition from columnar to equiaxed structures in the samples [1-10]. In previous studies the authors analyzed the effect of the average cooling rate and alloy composition on the CET in directionally solidified alloys [10-20]. The columnar front position was calculated from experimental cooling curves. Mathematical modeling of unidirectional solidification of alloys has been developed during the last decades due to its importance for metallurgical industries and to the complex interaction of macroscopic phenomena (i.e., fluid flow and heat transfer), and microscopic phenomena (i.e., nucleation and dendritic growth) [1-4, 9, 10]. It has been suggested that the kinetics of solidification and the temperature profile during solidification process can be described by equations of error type [9, 21]. These equations, while they are approximated for pure substances and under very specific conditions, do not permit a very accurate description of the phenomenon of solidification. In particular in the case of binary alloys, showing two interphases of solidification, when the temperature of the metal surface - mould is not constant, the properties of the metal and / or mold are not constants; the liquid is heated locally or there are other effects such as the curvature of solid / liquid interphases. In this work, we determined increases in temperature of a cooling liquid due to overheating of the same, ahead of the (solid-liquid) / (liquid) interphase or liquid interphase. The solid temperature increases due to a global superheating of the solid behind the (solid) / (solid-liquid) interphase as a function of time and position. Regarding interphase velocities, it is necessary to clarify that in the present research we follow the moving of interphases using thermocouple measurements, and did not follow dendrite tips, while temperature measurements are determined from a small volume and not a surface. Temperature measurements were used to track average [liquid/(solid + liquid)] interphases, namely [(L)/(S+L)] (or liquid interphases) and [(solid + liquid)/solid], namely [(S+L)/S] interphases (or solid interphases) but not solid/liquid “interfaces”, so dendrite tip surfaces, or equiaxed grain surfaces may be in any solid + liquid region (see Figure 1 (a) and (b)).
II. EXPERIMENTAL PROCEDURE

Commercially pure Zn and Zn-Al alloys of the following concentrations: Zn-1wt.%Al, Zn-2wt.%Al, Zn-3wt.%Al, Zn-4wt.%Al and Zn-5wt.%Al were unidirectionally solidified into glass cylindrical molds of 2.5 cm-diameter [15, 17]. For the experiments a directional solidification furnace (Figure 2) was used. The temperatures of the alloys were measured at equally spaced intervals (2 cm) from the base of the cylindrical samples with K-type thermocouples, sheathed in glass tubes and placed approximately on the longitudinal axis of the samples; see Figure 2 (a). The temperatures of each of the alloys were recorded by CT 7003 temperature acquiring with eight channels whose RS232 type outlet was connected to a computer obtaining measurements at intervals of one minute during solidification of each alloy [18, 20]. In Figure 2 (b) it is observed the macrostructure of Zn-1wt.%Al obtained by directional solidification process, where it is possible to appreciate the CET zone between columnar and equiaxed structures.

From the experimental data of temperature vs. time curves (see Figure 4) it was possible to determine decreasing exponential functions that simulate those experimentally determined for the material in the liquid and solid state curves, after the disappearance of any thermal transient function, both in function of time and longitudinal position in the sample [4], as can be seen in equations (1) and (2):

\[
T_{\text{liquido}} = (A_{2L} \cdot x^2 + A_{1L} \cdot x + A_{0L}) \cdot \exp(-b_{1L} \cdot x + b_{0L}) \times t
\]  
(1)

\[
T_{\text{sólido}} = (A_{2S} \cdot x^2 + A_{1S} \cdot x + A_{0S}) \cdot \exp(-b_{1S} \cdot x + b_{0S}) \times t
\]  
(2)

where, x is the distance in cm measured from the base of the sample, in contact with the heat removal system, t is the time in minutes, A and b are constant values that are determined from the cooling curves of the solid and liquid experimentally determined [15].

The method to simulate the intermediate zone is based on the following assumptions:
1. It is adopted that the liquid cooling curve can be extrapolated to the intermediate region, which is
equivalent to assuming that the cooling conditions imposed by the cooling system for the alloy in the liquid state is not changed, but the latent heat released at any zone solidifies though they are in solid phase growth.

2. It is assumed that the cooling curve can be extrapolated from the solid to the intermediate region, which is equivalent to assuming that the cooling conditions imposed by the cooling system to the alloy, for the solid, do not change during phase change zone where the thermal evolution is determined or due to overheating caused by other zones.

While the above two scenarios are not entirely accurate, and there may be slight variations of the functions describing the cooling of the liquid and the solid, due to the complex effects involved during the phase change due to the change in size and displacement of the source of latent heat released during solidification, the adoption of such cases does not represent a disadvantage because they allow the accurate simulation of the experimental cooling curve [13]. In Figure 5 shows the exponential functions determined from experimental data, which are extrapolated towards the intermediate zone. In Figure 5 it can be seen that while in the mushy zone the alloy has a single temperature because the thermocouple located in the position in which the registering does not discriminate between the temperature of the liquid phase and the solid phase, it determines the average kinetic energy in the zone. It adopts the temperature of each phase in the solid-liquid zone which is different and should follow the same function of temperature versus time for the phase which applies if the cooling conditions imposed on the system follow the same trend. Thus, in the intermediate zone, the liquid should be cooled to a lower temperature than the recorded and the solid which releases latent heat should be at a temperature higher than that recorded by the thermocouple, which generates heat transmission in the direction from the solid to the liquid due to local temperature gradients [14]. If it is adopted that the extrapolation of the functions into the mushy zone is a valid assumption, the first portion of the solid which forms is initially at a temperature higher than the liquid. The solid which forms is, "overheated" and immersed in a "super cooled" liquid. As solidification progresses, the last portions of liquid should be high "sub cooled" and the final solid must reach the solidus temperature or the eutectic temperature as the case. The average temperature of the mushy zone determined by the temperature sensors does not discriminate between the temperature of the solid and liquid phases which are formed, but an average of both temperatures in this region. From these two functions for cooling the liquid and the solid given by equations (1) and (2) it is possible to determine two functions \( \Phi_L(x,t) \) y \( \Phi_S(x,t) \) defined as in the following equations:

\[
\Phi_L(x,t) = \frac{K}{K_{S-L}} = \frac{T_{sólido}(x,t) - T(x,t)}{T_{sólido}(x,t) - T_{Líquido}(x,t)}
\]

It is verified that:

\[
\Phi_L(x,t) + \Phi_S(x,t) = 1
\]

The expressions in equations (3) and (4) determine a function similar to lever rule of non-equilibrium applied to the cooling curve of a portion of alloying. Figure 5 shows how to determine the functions \( \Phi_L \) and \( \Phi_S \) from the extrapolated functions in the intermediate zone. It is noteworthy that the function \( \Phi_S \) thus determined is a function of the modified hyperbolic tangent type but can be approximated by a polynomial function which is generally of third grade.

![Figure 5](image)

Fig. 5: Rule for determining the functions \( \Phi_L \) and \( \Phi_S \).

Thus, the temperature that will reach the alloy in the intermediate zone, where the phase change occurs, can be readily determined as the sum of the products of the corresponding temperatures per the functions \( \Phi_L \) and \( \Phi_S \) of the liquid and the solid in the concerned zone, as indicate equations (6) and (7):

\[
T_{\text{Sólido-Líquido}}(x,t) = T_{Líquido}(x,t) \times \Phi_L(x,t) + T_{sólido}(x,t) \times \Phi_S(x,t)
\]

or,

\[
T_{\text{Sólido-Líquido}}(x,t) = T_{Líquido}(x,t) \times [1 - \Phi_S(x,t)] + T_{sólido}(x,t) \times \Phi_S(x,t)
\]

Note that \( T_{\text{solid-liquid}} \) represents the temperature of the intermediate zone whether it is constituted by a superheated liquid, an area of two solid-liquid phase or solid formed that is overheated.

### III. RESULTS AND DISCUSSION

The values of \( \Phi_S \) depending on the temperature determined by the method described in the previous paragraph, for commercially pure Zn and Zn-2% Al are shown in the graphs.
of Figure 6. It is worth noting that \( \Phi_3 \) is not in the strict mathematical sense a function of the temperature. Since certain domains exist, more than one image, particularly for the pure elements and where eutectics solidified, make the derivative of \( \Phi_3 \) with respect to temperature take infinite values for \( T = T_{\text{Fusion}} \) and for \( T = T_{\text{Eutectic}} \); however, the representation of \( \Phi_3 \) vs. \( T \) for each concentration and for each \( x \) distance measured from the base is very useful in modeling the cooling curves. This can establish subzones within the intermediate zone (zone II) where the different effects of overheating the fluid occur, phase change zone and solid overheating once it is formed. The thermal effects can be observed directly in the figures as splayed of \( \Phi_3 \) vs. \( T \) curves for values outside the range of solidification at each position. Also, changes in the melting temperatures due to effects such as segregation of alloying, or local variations in concentration may be determined from figures. From the graphs of Figure 6 it can be clearly noted that the thermal effects on the cooling curves affect solids formed to lower temperatures in the areas that are farther from the area of heat extraction, that is, the thermal effects of cooling curves affect liquid to higher temperatures in the areas that are most away from the surface of heat extraction. This results in changes in the cooling rate at higher temperatures- the higher is the distance from the surface where heat is extracted. The \( \Phi_3(x,t) \) function can be very well simulated by a modified hyperbolic tangent function of the type indicate in equation (8):

\[
\Phi_3(t) = \left( \frac{1 + A_0 \cdot \tan(\kappa_0 \cdot t - t_0)}{2} \right) + A_1 \cdot \sec(\kappa_1 \cdot t - t_1)
\]

(8)

where \( A_0, A_1, \kappa_0, \kappa_1 \) are dimensionless constants that depend critically on the distance \( x \) from the surface of heat removal, in addition, depends on the type of elements, alloying concentration in the alloy, among other factors. The graphs of Figure 7 shows the values of \( \Phi_3(x,t) \) versus time considering a starting instant \( t_0 = 0 \) arbitrary. In the graphs of Figure 4 it is shown the variation of the functions \( \Phi_3(x,t) \) with the longitudinal distance \( x \) measured from the base of the samples are plotted as a function of the variable \( (t - t_0/\kappa_0) \). The values of \( t_0/\kappa_0 \) represent the time at which the modified hyperbolic tangent function has the value 1/2 and for different experiments conducted for each concentration of alloying and each distance. \( t_0/\kappa_0 \) can be considered as a characteristic time of solidification of each zone of the test piece or intermediate time during the phase change that occurs in zone II and has the peculiarity that at that moment the derivative of the hyperbolic tangent function modified adopts a maximum value. \( \kappa_0/2 \) is a dimensionless number whose value is the maximum of the derivative of the hyperbolic tangent function with respect to time amended. Higher values of \( \kappa_0 \) indicate faster variations of the hyperbolic tangent function and consequently a shorter duration of the transition zone where

\[
\frac{\partial y}{\partial t} = \frac{1}{\alpha} \left( \frac{\partial^2 y}{\partial x^2} - \beta \frac{\partial y}{\partial x} \right)
\]

represents the instant at which the hyperbolic secant function takes the maximum value of \( y \) for the different experiences made for each concentration of alloying and each distance; \( t_0/\kappa_1 \) can be considered as the instant at which the solid and higher superheat formed in the considered volume (or area of coexistence of two phases even if any) as a result of the latent heat released by other zones of the sample which are in phase transformations.
Values of $\Phi_s(x,t)$ versus time for (a) Zn-3wt.%Al and (b) Zn-5wt.%Al alloys.

**Fig. 6:** Values of $\Phi_s(x,t)$ versus time for (a) Zn-3wt.%Al and (b) Zn-5wt.%Al alloys.

Fig. 7: Values of $\Phi_s(x,t)$ versus $t-(t_0/\kappa_0)$ for Zn-1wt.%Al and Zn-5wt.%Al.

$k_1$ is a dimensionless number whose value is the maximum of the hyperbolic secant function when the constant $A_1$ is equal to unity. Values higher than $k_1$ indicate thermal effects more pronounced at the end of zone II. Figure 8 (a) shows the temperature increase determined from the differences of the functions of temperature versus time for the liquid and the superheated liquid just before the change of phase for each position considered in the sample of Zn-1wt.%Al alloy and which produces the first part of the function $\Phi_s(x,t)$. Temperature differences show a linear dependence on time and both the slope and the intercept are functions of the position $x$ measured from the base. In Figure 8 (b) the temperature increase is determined from the differences of the functions of temperature versus time for the solid and the solid heated just after the change of phase for each position considered in the sample of Zn-1wt.%Al alloy and that produce the final portion of the function $\Phi_s(x,t)$. The temperature differences in this case also show a linear dependence with time but the slope is negative. Both the slope and the intercept are functions of the position $x$ measured from the base.

Fig. 8: (a) Temperature difference between the liquid and the heated liquid to four places from the base of the cylinder. (b) Temperature difference between the solid and the heated solid at the end of the phase shift for the first three positions from the bottom of the beaker. Alloy Zn-1wt.%Al, spacing $d = 2$ cm.

Note in Figure 8 (b) that the temperature difference between the solid and the heated solid is positive, which indicates that the extrapolated solid temperature within zone II is a higher temperature than the heated solid, since the temperature solid assessed a value higher than that corresponding to the temperature of the superheated solid evaluated. This effect is due to the function expressing the temperature of the solid which is displaced in time axis with respect to the function expressing the overheated solid. The heated solid has a slower cooling after the solid thermal transients due to external heat input to the solidifying zone, but that the describe function starts earlier in time than the corresponding solid. In the graphs of Figure 5 it can be noted that while the temperature difference between the cooling curve of the superheated liquid and the curve of normal cooling of the liquid increases, the longer the time in each relevant position, the temperature difference between the cooling curve of the superheated solid and normal cooling curve of the solid decrease the longer the time in each position considered until it is canceled. Furthermore, in the first position ($x = 0$) there is no effect of heating of the liquid, as it is precisely the first portion of alloy in solidified, while
heating effects of solid are almost nil at late positions, there
where solidification ends.

IV. CONCLUSION

The analysis of the effect of size and the movement of a
zone of coexistence of two phases which release latent heat
during solidification on the cooling curves of pure Zn and
Zn-1wt.%Al; Zn-2wt.%Al; Zn-3 wt.%Al; Zn-4wt.%Al and
Zn-5 wt.%Al alloys allowed to conclude that:
1. From experiments carried out on samples of diluted Zn-Al
alloys with concentrations ranging from pure Zn to Zn-5% Al,
\( \Phi(x,t) \) functions were obtained starting from temperature
versus time experimental data and using:
a) Decreasing exponential functions that describe the
evolution of temperature of the liquid alloy when it is cooled
in the absence of transient thermal effects of phase
transformations;
b) Decreasing exponential functions that describe the
evolution of the temperature of the solid alloy which is cooled
in the absence of transient thermal effects and then finishing
the complete solidification of the samples.
2. It simulates \( \Phi_0(x,t) \) functions by adding a modified
hyperbolic tangent function and a function of type hyperbolic
secant type. The temperature difference between the cooling
curves imposed by the system to the liquid and the heated
liquid showed an increased linear dependence with time and is
dependent on the longitudinal position in the cylinder,
returning to zero or negligible value for the surface where heat
is extracted. The temperature difference between the cooling
curves imposed by the system and the heated solid shows a
decreasing linear dependence on time and it is also dependent
on the longitudinal position in the cylinder, returning to zero
or negligible values to the last zones to solidify.
3. These results are very useful for describing the kinetics of
solidification and the temperature profile during
unidirectional solidification process where the
columnar-to-equiaxed transition phenomenon occurs.

REFERENCES

Equiaxed Transition during Diffusion-Controlled Dendritic

the columnar to equiaxed transition in small ingots”, Metall.

Al-Cu alloy ingots”, Acta Metall., vol. 30, pp. 1717-1722,
August 1982.

Macrostructure in Aluminum Castings- Part I: Determination of
Columnar/Equiaxed Transition for Al-4.5%Cu Alloy”, AFS


Columnar to Equiaxed Zone in Ingot", Mater. Sci. Technol.,

transition in tin-lead alloys”, Metall. Trans. B, vol. 18,

October 1989.

[9] J. A. Spittle, “Columnar to Equiaxed Grain Transition in As
Solidified Alloys", International Materials Reviews, vol. 51,

during the Columnar-to-Equiaxed Transition in Lead-Tin
October 2000.

Thermal Parameters Affecting the Columnar-to-Equiaxed
July 2002.

Modeling for Columnar and Equiaxed Growth of Alloys”,

“Analysis of Solidification Parameters during Solidification of
Lead and Aluminum Base Alloys”, Journal of Crystal

Thermal Parameters on the Columnar to Equiaxed Transition

Investigation of the Columnar-to-Equiaxed Grain Transition in
Aluminum-Copper Hypoeutectic Alloys”, Journal of Crystal

Horizontal Directional Solidification of Zn-Al and Zn-Ag
1861-1870, October 2010.

Tensile Properties of Directionally Solidified Zn-base Alloys”,
Journal of Crystal Growth, vol. 318, pp. 59-65,
March 2011.

“Corrosion and Wear Resistance of Hypoeutectic Zn-Al Alloys
as Function of Structural Features”, Materials Chemistry and

“The Influence of Gravity on the CET in Diluted Zn-Al

heat flow during unidirectional solidification of metals”, Int. J.
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