

Estimation of the Evolution of Solid Fractions in Constant Volumes of Cylindrical Samples Unidirectionally Solidified

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Abstract— *An estimation of the evolution of solid fractions in cylindrical samples with predominantly lower heat extraction have been performed, considering approximately constant finite volume constituting the alloy samples of Zn commercial grade and Zn - Al diluted alloys, with concentrations ranging from Zn-1wt.%Al to Zn-5wt.%Al. From decreasing exponential functions that simulate the experimentally determined temperature versus time curves, for materials in the liquid state, in a state of superheated liquid, superheated solid state, solid state and after the disappearance of the thermal transient, typically determines the evolving of solid fractions as functions depending on time and position. We concluded that the variation with time of solid fraction between zero and unity, during the phase change, was not linear and was estimated by hyperbolic tangent functions such as modified or approximated by third degree polynomials in the intervals of local solidification. Also, the form that presented the variation of the solid fraction depends on the position considered along the sample, exhibiting different behaviors conditional on the distance from the base of the sample, and depending on cooling rates imposed, thermal effects of heating of liquid and solid due to the release of latent energy of the movable and resizable region where liquid and solid coexists during solidification.*

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

I. INTRODUCTION

In view of the fact that directional solidification technique was firstly used to prepare turbine blades, research works developed in the last decades has provided an understanding of relationship between type of alloys, microstructure, size of samples and geometry and process conditions. The application of this knowledge to metallurgy industry has proven to be challenging in order to improve the processes [1-3]. Directional solidification technology is also an important research to study solidification theories and becomes more important research area in the field of materials science and technology. Because directional solidification can achieve controllable cooling rate with a extensive range and solidification structures from near-equilibrium to far-from equilibrium condition can be obtained. The variation of parameters controlling the processes, such as “interface” evolution, crystal growth instability, solute redistribution, and phase selection during

the course have received significant attention in recent years [4-25]. Some equations have been proposed for determining the solid fraction, f_s , in pure metals and alloys. The assumptions made for the determination of the position of the solid / liquid “interface” generally are due to expressions like [3,4]:

$$x = K\sqrt{t} \quad (1)$$

Where, x is the position of the “interface” at any given time, t , and K is assumed constant. The above equation is estimated accurately if the solid/liquid “interface” is flat, if the temperature of the mold in the heat extraction takes a constant value, T_0 , after the initial transients and if the liquid is not in superheated state. For the case of binary alloys, have been proposed two kinetic equations of solidification, from which it is possible to estimate the fraction of solid in terms of time, that is, adopts that the position of each of the “interfaces” can be expressed by an equation of the square root type [5, 6], from which it is possible to determine a range of values in which could be found the fraction of solid formed versus time. However, the above equations are valid if both interphases $L/(S+L)$ and $(S+L)/S$ do not start from the mold surface at the same moment, i.e., for $t(0) = 0$, $t_s(0) = 0$ and $t_L(0) \neq 0$. As we have clarified in previous studies [21, 25], 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”. From the above, the aim of this work is to obtain the solid fractions from experimental data of temperature versus time data in samples of diluted Zn-Al alloys.

II. EXPERIMENTAL PROCEDURE

Into cylindrical glass molds, Zn-Al alloys of the following concentrations were unidirectionally solidified: commercial pure Zn (99.89 wt.%), Zn-1wt.% Al, Zn-2wt.% Al, Zn-3wt.% Al; Zn-4wt.% Al and Zn-5wt.% Al. The temperatures of the alloys were measured at equally spaced intervals (2 cm) from the base of the cylinder with the K-type thermocouples sheathed in glass tubes were placed approximately on the longitudinal axis of the samples. The temperatures of each of the alloys were recorded by a temperature acquiring CT 7003 eight channels RS232 type, whose outlet was connected to a

computer for obtaining records in intervals of one minute during the solidification of each alloy [17-25]. From the temperature versus time records for each test piece of the alloy, the following variables were calculated, the average cooling rate at one minute intervals using $\Delta T_i / \Delta t$ for each longitudinal position, the derivative of the average cooling rate with respect to time calculated by centered difference or second derivatives of the temperature with respect to time twice, the average gradients $G(x_j-x_i) \cong (T_j-T_i)/(x_j-x_i)$ in each minute for $\Delta x = 2\text{cm}$, the centered derivative of the average gradient with respect to the position or $\nabla^2 T \cong (G_j-G_i)/(x_j-x_i)$, etc. With experimental data obtained were also determined moments of start and end of solidification, t_L and t_S , corresponding liquidus and eutectic temperatures, T_L and T_e , the positions of the L/(S+L) and (S+L)/S interphases in function of time and, thereafter average velocities and accelerations of the interfaces, $v_L(t)$, $v_S(t)$, $a_L(t)$ and $a_S(t)$, were determined in function of time and/or $v_L(x)$, $v_S(x)$, $a_L(x)$ and $a_S(x)$ in function of position. To determine the shape of the evolution of the solid fraction versus time, cylindrical volumes which characteristics were estimated (whose average temperature characteristics were estimated from measurements of temperature experimentally determined) [21-25]. From decreasing exponential functions that simulate the temperature versus time curves experimentally determined for the material in the liquid state, in a state of superheated liquid, in a state of superheated solid, and solid state after the disappearance of thermal transients, it was possible estimate the evolution of the fractions of solid as time and position dependent functions. The cooling curves of the alloy in the liquid state for the experiments conducted can be expressed by functions of the form of equation (2):

$$T_{liquid} = A_L \cdot \exp(-b_L \times t) \quad (2)$$

Where the pre-exponential factor A_L is a constant temperature value that mainly depends on the distance from the base of the sample and the moment that has been selected as the start point for the cooling of the alloy. This factor can be expressed by a function that depends only on the distance from the base of the sample, usually parabolic or quadratic type, of the form $A_L = A_{2L} \cdot x^2 + A_{1L} \cdot x + A_{0L}$ [°C]. Similarly, the exponent b_L can be expressed by a function that depends only on the distance from the base of the cylinder, usually linear, of the form: $b_L = b_{1L} \cdot x + b_{0L}$ [min^{-1}], where the function of temperature versus time for a given alloy in the liquid state can be expressed generally by equation (3):

$$T_{liquid} = (A_{2L} \cdot x^2 + A_{1L} \cdot x + A_{0L}) \cdot \exp(-(b_{1L} \cdot x + b_{0L}) \times t) \quad (3)$$

Where: x = distance from base (cm), t = time (min).

The above equation determines the temperature of any point of the alloy in the liquid state (before the onset of solidification) versus time. If in particular the time $t = 0$ as the

cooling start time is selected, the temperature of the liquid is the initial temperature T_0 which is in the different positions of the sample measured from the base to the initiation of cooling of the alloy. Also, the cooling curves of the alloy in the solid state for the experiments carried out can also be expressed by functions of the type of equation (4):

$$T_{solid} = A_S \cdot \exp(-b_S \times t) \quad (4)$$

where the pre-exponential factor A_S is also a constant temperature value that mainly depends on the distance from the base of the sample and the moment has been selected as the start point for the cooling of the alloy. The pre-exponential factor A_S can be expressed by a function that depends only on the distance from the base of the cylinder, generally parabolic type or quadratic, of the shape

$$A_S = A_{2S} \cdot x^2 + A_{1S} \cdot x + A_{0S} \text{ [°C]}.$$

Also the exponent b_S can be expressed by a function that depends only on the distance from the base of the cylinder, usually linear, of the form: $b_S = b_{1S} \cdot x + b_{0S}$ [min^{-1}], where the function of temperature versus time for a given alloy in the solid state can be expressed generally by equation (5):

$$T_{solid} = (A_{2S} \cdot x^2 + A_{1S} \cdot x + A_{0S}) \cdot \exp(-(b_{1S} \cdot x + b_{0S}) \times t) \quad (5)$$

where: x = distance from base (cm), t = time (min).

The above equation determines the temperature of any point of the alloy in the solid state (after completion of solidification) versus time. If in particular time $t = 0$ as the cooling start time is selected, the temperature of the initial solid is T_{0s} which have different positions on the sample as measured from the base of a solid whose temperature is that of the alloy in the liquid state prior to the onset of solidification. Cooling curves of alloy superheated liquid state to the experiences may also be expressed by functions of the type of equation (6):

$$T_{heated\ liquid} = A_{Lc} \cdot \exp(-b_{Lc} \times t) \quad (6)$$

where the pre-exponential factor A_{Lc} is a constant temperature value that mainly depends on the distance from the base of the sample and the moment has been selected as the start point for the cooling of the alloy. The pre-exponential factor A_{Lc} can be expressed by a function that depends only on the distance from the base of the cylinder, usually of quadratic or parabolic type, of the form:

$A_{Lc} = A_{2Lc} \cdot x^2 + A_{1Lc} \cdot x + A_{0Lc}$ [°C]. Also the exponent b_{Lc} can be expressed by a function that depends only on the distance from the base of the cylinder, usually linear, of the

form: $b_{Lc} = b_{1Lc} \cdot x + b_{0Lc}$ [min^{-1}] where the function of temperature versus time for a given alloy in the liquid state can be expressed generally by equation (7):

$$T_{\text{heated liquid}} = (A_{2Lc} \cdot x^2 + A_{1Lc} \cdot x + A_{0Lc}) \cdot \exp(-(b_{1Lc} \cdot x + b_{0Lc}) \times t) \quad (7)$$

The above equation determines the temperature of any point of the alloy in the state of superheated liquid (after the start of solidification of the sample and before the start of the solidification of the respective zone) in function of time. The cooling curves of the alloy in solid state reheated the experiences can also be expressed by functions of the type of equation (8):

$$T_{\text{heated solid}} = A_{Sc} \cdot \exp(-b_{Sc} \times t) \quad (8)$$

where the pre-exponential factor A_{Sc} is worth constant temperature mainly depends on the distance from the base of the sample and the moment has been selected as the start point for the cooling of the alloy. The pre-exponential factor A_{Sc} can be expressed by a function that depends only on the distance from the base of the cylinder, of the form:

$A_{Sc} = A_{2Sc} \cdot x^2 + A_{1Sc} \cdot x + A_{0Sc}$ [$^{\circ}\text{C}$]. Also the exponent b_{Sc} can be expressed by a function that depends only on the distance from the base of the cylinder, usually linear, of the form: $b_{Sc} = b_{1Sc} \cdot x + b_{0Sc}$ [min^{-1}] where the function of temperature versus time for a given alloy in the solid state can be expressed generally by equation (9):

$$T_{\text{heated solid}} = (A_{2sc} \cdot x^2 + A_{1sc} \cdot x + A_{0sc}) \cdot \exp(-(b_{1sc} \cdot x + b_{0sc}) \times t) \quad (9)$$

where: x = distance from base (cm), t = time (min).

The above equation determines the temperature of any point of the reheated alloy in solid state (after completion of solidification in the lower region and the upper region while the specimen is releasing latent heat) as a function of time. The function of the temperature difference obtained as the difference between the function of the temperature function of the solid and the reheating temperature is solid:

$$T_{\text{solid}} - T_{\text{heatedsolid}} = A_s \cdot \exp(-b_s \times t) - A_{Sc} \cdot \exp(-b_{Sc} \times t) = \Delta T_A^S(x) \times t + \Delta T_b^S(x)$$

Where the slope $\Delta T_A^S(x)$ as the intercept $\Delta T_b^S(x)$ are

functions of the distance from the bottom of the specimen, which may be approximated by polynomials. This is equivalent to express variations of the normal curve of solid and cooling:

$$T_{\text{heated solid}} = (A_{2S} \cdot x^2 + A_{1S} \cdot x + A_{0S}) \cdot \exp(-(b_{1S} \cdot x + b_{0S}) \times t) - (\Delta T_A^S(x) \times t + \Delta T_b^S(x)) \quad (10)$$

where $\Delta T_A^S(x)$ and $\Delta T_b^S(x)$ can be approximated, in general, by linear or quadratic functions and they depend on the distance measured from the bottom of the specimen. From these two functions for cooling the liquid and the solid given by equations (2) and (4) it is possible to determine two functions $\Phi_L(x,t)$ and $\Phi_S(x,t)$ defined as the following equations (11) and (12) [25]:

$$\Phi_L(x,t) = \frac{K}{K_{fL}} = \frac{T_{\text{solid}}(x,t) - T(x,t)}{T_{\text{solid}}(x,t) - T_{\text{liquid}}(x,t)} \quad (11)$$

$$\Phi_S(x,t) = \frac{K}{K_{fS}} = \frac{T(x,t) - T_{\text{liquid}}(x,t)}{T_{\text{solid}}(x,t) - T_{\text{liquid}}(x,t)} \quad (12)$$

It is noteworthy that the function Φ_S thus determined is a function of the modified hyperbolic tangent type but can be approximated by a polynomial function which is generally third grade [21]. A simple way to estimate the evolution of the solid fraction versus time for each volume to be considered a feature position x , is from the functions of superheated liquid and superheated solid, following a procedure analogous to that used for determining functions $\Phi(x,t)$. In this way is adopted here that the formed solid fraction can be estimated by the equation (13):

$$f_s(x,t) = \frac{T(x,t) - T_{\text{heated liquid}}(x,t)}{T_{\text{heated solid}}(x,t) - T_{\text{heated liquid}}(x,t)} \quad (13)$$

where the functions $T_{\text{liquid}}(x,t)$ are replaced by the functions $T_{\text{heated liquid}}(x,t)$ and the functions T_{solid} are replaced by the corresponding $T_{\text{heated solid}}(x,t)$ given by equations (6) and (8), which is always possible to estimate the functions $T_{\text{heated liquid}}(x,t)$ and $T_{\text{heated solid}}(x,t)$ if the functions $T_{\text{liquid}}(x,t)$ and $T_{\text{solid}}(x,t)$ are known and functions of variation in space and time of said functions during thermal transients due to the release of latent heat caused by the mobile mushy zone and whose size is generally variable.

III. RESULTS AND DISCUSSION

Figure 1 shows as an example, the typical result of a cooling curve, T vs. t, for an alloy of Zn-4wt.% Al, determined by a thermocouple (T₃) of type K, located approximately in the center of a cylindrical test piece and at a distance of 4 cm as measured from the base of the cylinder, where the heat extraction is predominant. Note that in Figure 1 there are four functions which represent the bulk of cooling curve. It is convenient to note here that for the case of Zn-Al alloy is still possible to find a further function to the solid at temperatures below 275 °C, which accounts for differences in the thermal conductivities of the solid at high temperatures (275 °C < T < 382°C) and solid at low temperatures (T < 275 °C). Using

equation (12), for each curve, was determined experimentally the cooling in each position located at equally spaced distances of 2 cm and for each selected alloy (commercially pure Zn, Zn-1wt.% Al, Zn-2wt.% Al-Zn-3wt.% Al, Zn-4wt.% Al and Zn-5wt.% Al), the solid fractions were determined for each volume of the sample as a function of time and / or temperature as shown in Figure 2 for Zn-4wt.% Al alloy. From the evolution of the partial fractions of solid determined in each finite volume of area equal to the transversal area of the cylindrical sample and a height of 2 cm, the evolution of the cumulative fraction of solid or solidified fraction of the sample was determined for each sample of alloy considered, as shown in Figure 3 for Zn-4wt.% Al alloy.

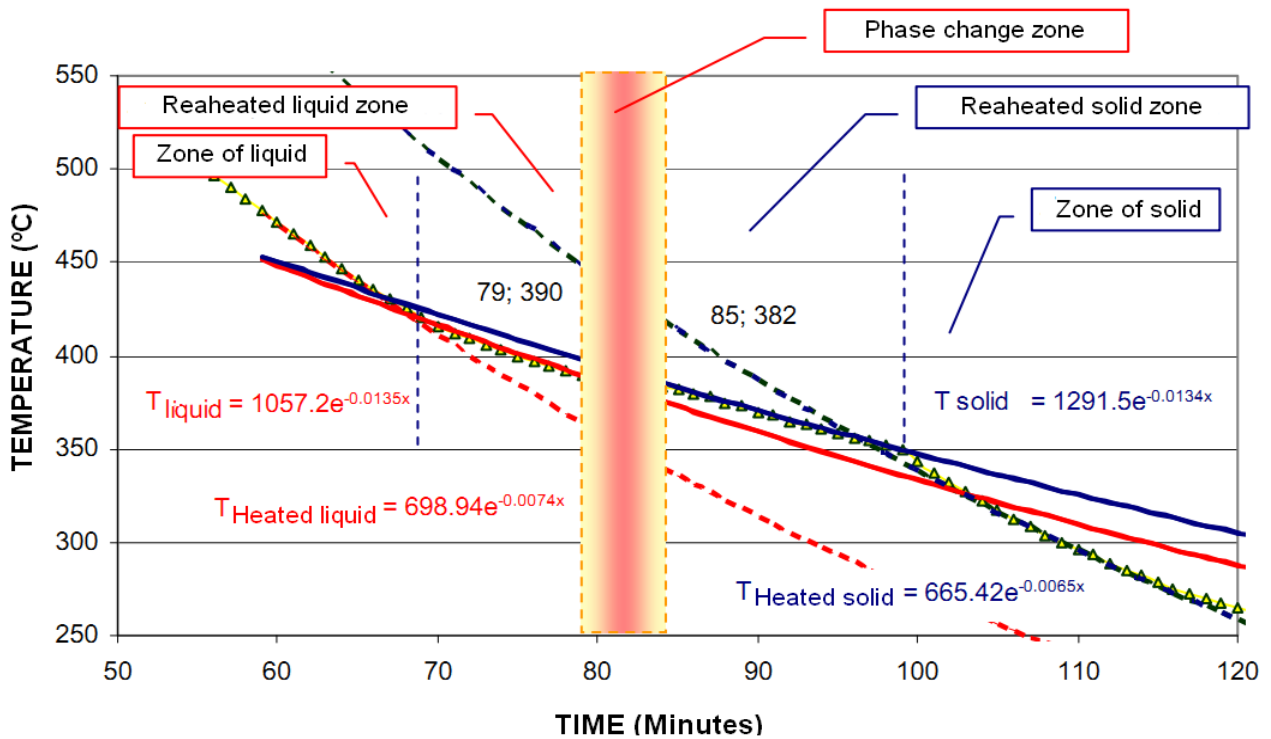


Fig. 1: Functions of fitting the experimental data of temperature versus time for Zn-4wt.% Al alloy on a certain position, x = 4 cm, from the base of a cylindrical sample.

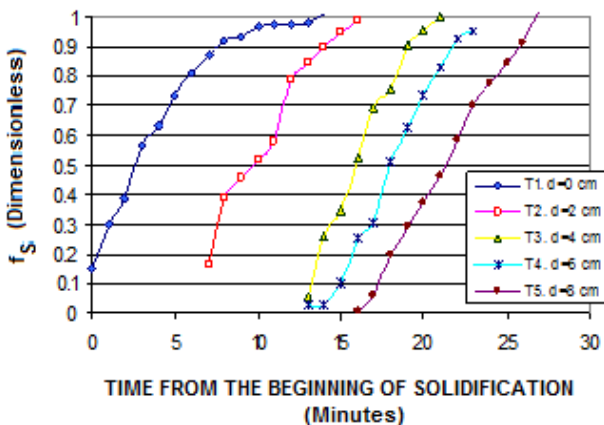


Fig. 2: Evolution of the solid fraction in function of time for Zn-4wt.% Al.

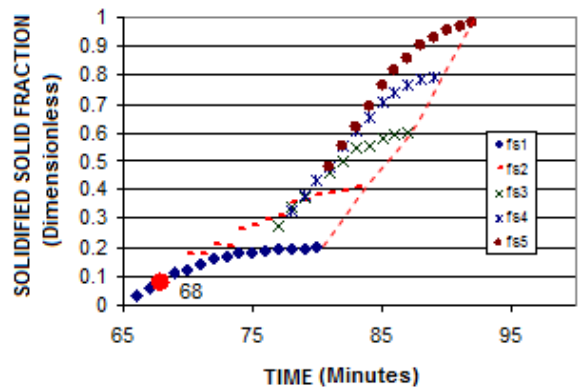


Fig. 3: Evolution of the solidified fraction in function of time for Zn-4wt.% Al alloy.

IV. CONCLUSIONS

1. From experiences in diluted Zn-Al alloys samples with concentrations ranging from commercially pure Zn and Zn-5wt.%Al, solid fractions were obtained from experimental data of temperature versus time, using:

- a) Decreasing exponential functions that describe the evolution of the temperature of the liquid alloy which is cooled down in the absence of transient thermal effects of phase transformations;
- b) Decreasing exponential functions that describe the evolution of the temperature of the superheated liquid alloy as a result of transient thermal effects caused by the release of latent heat during phase transformations in different areas of the samples;
- c) decreasing exponential functions describing the evolution of the temperature of the alloy in solid state once the solidification is concluded and it is overheated as a result of transient thermal effects caused by the release of latent heat during phase transformations in other areas of the samples;
- d) decreasing exponential type function describing the evolution of the temperature of the solid alloy which is cooled in the absence of transient thermal effects of phase transformations, after completion the solidification of the sample.

2. It is concluded that the variation with time of the solid fraction between zero and unity, during the phase change is not linear, nor obeys functions of the square root type over the length of the samples, and can be better estimated by functions of hyperbolic tangent modified type or approximated by third degree polynomials in the finite volumes considered.

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