Method for estimation of latent heat released during the solidification of a binary alloy with a controlled solidification rate

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Résumé - Afin de réduire le nombre de tests expérimentaux nécessaires pour caractériser totalement le matériau, nous proposons une méthode dans cette étude tenant compte de la ségrégation et de la surfusion pour estimer la chaleur dégagée pendant la solidification d'un alliage binaire. A partir de la vitesse de solidification, le coefficient de partition peut évoluer entre deux extrema : i) celui obtenu par le diagramme de phase, et ii) un coefficient de partition d'un, obtenu lors d'un changement de phase rapide, ce qui induit des compositions liquide et solide égales. En modifiant le coefficient de partition, on peut obtenir la composition en fonction de la vitesse de solidification, le degré de surfusion du matériau et la chaleur qu'il dégage, information utile pour définir la vitesse de refroidissement dans l'échangeur du chaleur.

Nomenclature

C	Concentration, *mol/mol*		T	Temperature, K
Co	Initial concentration, *mol/mol*		ΔT	Degree of undercooling, K
Cp	Specific heat, J/mol.K		t	Time, s
D	Diffusion coefficient, m^2/s		V	Velocity of solidification, *m/s*
fs	Solid fraction		V_D	Diffusive speed, *m/s*
ΔG	Free energy of change, J		α	Thermal diffusivity, m^2/s^1
ΔH	Heat of solidification, *J/mol. K*		Γ	Capillarity constant, $K\,m$
Iv	Ivantsov function		σ^*	Stability constant
k	Partition coefficient		μ	Interface kinetic coefficient
L	Latent heat, *J/kg*		Subscripts	
m	Liquidus slope		e	Equilibrium
P_C	Solute Péclet number		L	Liquid phase
P_T	Thermal Péclet number		S	Solid phase
R	Dendrite tip radius, m		m	Melting
R_g	Gas constant, *J/mol K*			

1. Introduction

Phase change materials have especially been studied recently due to their larger thermal densities [J/kg] (via latent heat) for a specific range of temperatures. For temperatures over 150ºC, mixtures of materials are commonly used, requiring an optimization of the composition depending on the source of heat. Of the challenges associated with mixture selection, segregation and subcooling have remained two of the most complex. Segregation can change the local composition of the mixture and consequently modify the thermal properties and how the latent heat is released. Undercooling modifies the temperature at which the phase change can occur, on the order of a few tens to hundreds of degrees below the temperature at which the phase change would occur without undercooling. To reduce the number of experimental tests necessary to fully characterize the material, we propose a method taking into account the

segregation and the undercooling to estimate the heat released during solidification for a binary mixture.
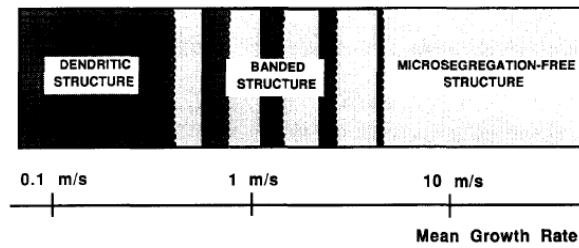

Figure 1: *Schematic representation for common cases of the microstructure transition for growth rates in the range of the limit of absolute stability. [3]*

2. Rapid solidification

While considering global equilibrium, which truly exists only when solidification takes place over geological times [1], the fraction of phases can be calculated with the lever rule, and the phase diagram gives the uniform composition of the liquid and solid phases. But in most cases of casting, the overall kinetics can be described using equilibrium phase transformation with some modification (ex. Scheil-Gulliver)), we can approximately estimate the temperature and compositions at the interface, enabling the thermodynamic description of melting or solidification with sufficient accuracy to evaluate the temperature and compositions of phase boundaries, such as the solid/liquid interface.
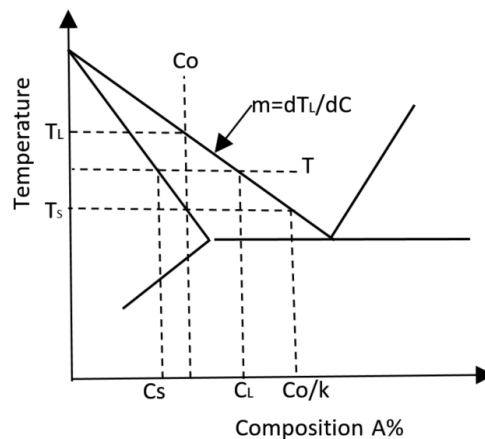

Figure 2: *Schematic region of a phase diagram for an alloy. k is partition coefficient; m is the slope liquidus*

The solidification interface can have four stages in function of the solidification velocity [2]. The first stage of the transformation is full diffusional equilibrium, with uniform phase composition and where the lever rule applicable, represented in *Figure 1* as dendrite structure and with practically null solidification velocities. The second stage considers initial undercooling and liquid diffusional effect. The phase diagram can be used adding corrections such as the Gibbs-Thomson effect or Scheil-Gulliver scheme, due to the interface curvature in the solidification or melting process. The undercooling is very small and only serves to start the nucleation; the solidification forms dendrite or eutectic structure. The banded structure in *Figure 1* is the third stage forming a new metastable phase in equilibrium (ex. banded structure) where the undercooling effect increases due to a greater solidification velocity. Consequently, the cellular/dendritic stable phase cannot nucleate or grow sufficiently fast to reach the phase indicated in the phase diagram. If this happens, one possibility is the formation a new metastable

phase or going directly to another phase described in the phase diagram, missing intermediate stable phases. This metastable transformation can occur at solidification velocities exceeding 0.1 m/s [4] depending mainly on the type of properties and composition of the material. Due to this new metastable phase, composition and undercooling have strong differences in comparison with the first stage. In the fourth stage, microsegregation structures (*Figure 1*) and the undercooling effect increase and the solidification velocity is above 5m/s [4], exceeding the diffusive speed of solute atoms in the liquid phase. Consequently, the phase diagram fails to give temperatures and compositions at the interface, and the chemical potentials are not equal at the interface.

3. Mathematical model

3.1. Interface equilibrium

Lever Rule Solidification (LRS) uses complete diffusion for liquid and solid phases. At temperature T the relations between temperature, composition and phase is based on the expression $fs = \frac{C_L - C_o}{C_L - C_S}$ at each temperature during cooling (Figure 2). The starting composition of the liquid is *Co*, *m* is the liquidus slope and the partition coefficient in equilibrium k_e is defined as:

$$k_e = \frac{C_S}{C_L} \tag{1}$$

The latent heat released during solidification in equilibrium is defined as:

$$L_{AB} = [L_A C_S + L_B(1 - C_S)]fs \tag{2}$$

where L_{AB}, L_A and L_B are the latent heats of mixture, component A and B respectively, and C_S is the composition during the solidification. To estimate the heat released during the solidification using (2) in nonequilibrium, it's necessary to know the variation of the composition and the undercooling during the solidification. k_e

3.2. Interface nonequilibrium

The necessary condition for interface equilibrium is $V << D/a_o$, where a_o is the atomic jump distance. For rapid solidification, when $V>>D/a_o$, the equality between the chemical potentials is lost but the partition coefficient becomes one. This means that the composition becomes uniform across the interface $C_S = C_L$, indicating that the solute trapping occurs. The partition coefficient is one and the interface temperature is significantly undercooled with respect to T_L, defining the so called *To* temperature, for which the molar free energies of the solid and liquid phases are equal for a given composition. The locus of *To* over a range of compositions constitutes a curve where the liquid and solid phase compositions are equal along the curve.

We examine a system with nonequilibrium rapid solidification to evaluate the change of the latent heat and to estimate the temperature at which the nucleation occurs. The cooling rate modifies the solidification velocity, generating sub-cooling effects and a variation in solidification composition, modifying the microstructure and presenting an opportunity to exploit the structural control and property enhancement for storage energy. The composition at the solidification frontier linked to Rapid Solidification Process (RSP) is defined by the partition coefficient [5], which can be defined as:

$$k\,(V) = \frac{k_e \Psi + V/V_D}{\Psi + V/V_D} \,, \qquad\qquad V < V_D$$

$$k\,(V) = 1, \qquad\qquad V \geq V_D \qquad (3)$$

where $\Psi = 1 - V^2/V_D^2$, and VD is the diffusive speed, interpreted as the maximum speed solute-solvent redistribution across the interface. The tangent of the nonequilibrium liquidus line slope mL as function of nonequilibrium solute partitioning and the solidification velocity is defining as in [6]:

$$m_L\,(V) = \frac{m_e}{1 - k_e}[1 - k + ln(k/k_e) + (1 - k)^2(V/V_D)], \qquad V < V_D$$

$$m_L\,(V) = \frac{m_e\,ln(k_e)}{k_e - 1}, \qquad\qquad V \geq V_D \qquad (4)$$

The composition for nonequilibrium, defining the solid concentration C_S^k at the tip of the solute dendrite in function of k is described as [6,7]:

$$C_S^k = \frac{C_o\,k}{1 - (1 - k)Iv(Pc)} \qquad\qquad V < V_D$$

$$C_S^k = C_o, \qquad\qquad V \geq V_D \qquad (5)$$

Where $Pc = VR/2D$. Iv is the Ivantsov function defined as: Iv(P)=Pexp(P)Ei(P), typically, for casting solidification P<1 where P could be the solute or thermal Péclet number, using the following approximation [8]:

$$Iv(P) = Pexp(P)[a_0 + a_1P + a_2P^2 + a_3P^3 + a_4P^4 + a_5P^5 - ln(P)] \qquad (6.1)$$

Where a_o=-0.57721566, a_1=0.99999193, a_2=-0.24991055, a_3=0.05519968, a_4=-0.00976004, a_5=0.00107857. For limiting values of the Péclet number, the Ivantsov function for a paraboloid of revolution can be approximated as [9]:

$$for\ P \ll 1:\ Iv(P) \approx -Pln(P) - 0.5772P \qquad (6.2)$$
$$for\ P \gg 1:\ Iv(P) \approx 1 - 1/P + 2/P^2 \qquad (6.3)$$

The dendrite tip radius R is a fundamental parameter to estimate the undercooling temperature and the solidification velocity [10]. Using the marginal stability criterion [11] in combination with the transport solution of Ivantsov [12] defines the IMS model, linking molecular structural features to RSP, defined as [13]:

$$R = \frac{\Gamma}{\sigma^*}\left(\frac{P_T\Delta H\xi_L}{Cp} - \frac{2m(1 - k)C_oPc}{\Psi[1 - (1 - k)Iv(Pc)]}\xi_C\right)^{-1} \qquad V < V_D$$

$$R = \frac{\Gamma Cp}{\sigma^*P_T\Delta H\xi_L} \qquad\qquad V \geq V_D \qquad (7)$$

with

$$\xi_C = 1 + \frac{2k}{1 - 2k - [1 + \Psi/\sigma^*Pc^2]^{1/2}} \qquad V < V_D$$

$$\xi_C = 0 \qquad\qquad V \geq V_D \qquad (7.1)$$

$$\xi_T = 1 - \left(1 + \frac{1}{\sigma^*P_T^2}\right)^{-1/2} \qquad\qquad (7.2)$$

where $\sigma^* = 1/4\pi^2$ denotes a stability constant and $P_T = VR/2\alpha$. To estimate the velocity of solidification we consider the free-energy responsible for interaction motion, in the equation describing the dependence on composition and temperature of the interface velocity (Eq. 10)

$$V = V_D \left[1 - exp\left(\frac{\Delta G}{R_g T}\right) \right] \tag{10}$$

When ΔG is zero, $V_D = V$ and the transition between local equilibrium and solute tramping occurs (k=1). The value of V_D is a property for each mixture that can be approximated using $V_D = Di/a_o$ where Di is a constant. Usually the assumption of constant solute diffusion coefficient is invalid for rapid solidification, especially for alloys with large undercooling [4]. The dependence of D on dendrite tip temperature directly affects the nonequilibrium partition coefficient if V_D is used as a function of a_o and D. The value of D has been assumed to exhibit Arrhenius behavior and is defined as Equation (11). The inclusion of a solute diffusion coefficient depending on temperature requires an iterative method to calculate the tip temperature and the subsequent equation.

$$D = Di \, exp(\Delta G/R_g T_i) \tag{11}$$

3.3. Undercooling component

The undercooling ΔT consists of five components, curvature ΔT_R, constitutional ΔT_C, kinetic ΔT_K, thermal undercoolings ΔT_T and ΔT_N; The difference between equilibrium and nonequilibrium liquidus temperature is thus defined as:

$$\Delta T = \Delta T_R + \Delta T_C + \Delta T_K + \Delta T_T + \Delta T_N \tag{12}$$

where:

$$\Delta T_R = 2\Gamma/R \tag{12.1}$$

$$\Delta T_C = mC_o \frac{(1-k)Iv(Pc)}{1-(1-k)Iv(Pc)} \qquad V < V_D$$

$$\Delta T_C = 0 \qquad\qquad V \geq V_D \tag{12.2}$$

$$\Delta T_K = V/\mu \tag{12.3}$$

$$\Delta T_T = (\Delta H/Cp) \, Iv(P_T) \tag{12.4}$$

$$\Delta T_N = (m_e - m)C_o \tag{12.5}$$

The previously stated equations, completely define the dendrite solidification model. The values for the dendrite tip radius, the velocity of solidification, the undercooling and the composition can be uniquely solved for a given condition solving with iterative methods. The two objective parameters to find using this method are the value of undercooling as a function of the solidification velocity and the change in the composition as a function of the solidification velocity, allowing estimation of how the heat is released. A general scheme of the steps to predict the solidification velocity is shown in *Figure 3*.

4. Application of the model

We compare the prediction of the results for undercooling and dendrite tip radius model with experiments results [14,15] of the alloy Ni-0.7 at% B, which is selected because it does not present metastable formation at rapid solidification. k_e and m_e are assumed constant using (1). The material properties [15] used are given in Table 1. The diffusion constant was chosen in accordance with [14].

Figure 4 compares experimental data [14,15] and the results of models to predict the solidification velocity. The solidification velocity ranges from 0.5 m/s to 28 m/s. The behavior

and the prediction for the undercooling as a function of the dendrite tip solidification velocity, show good agreement with the experimental results. In the interval between 5 and 18 m/s we found big instabilities when the equations are solved. The relationship between the velocity and the dendritic tip radius substantially affect the value of undercooling resulting in this kind of variation. Figure 5 shows the change in the composition as a function of the undercooling. At diffusive speed, the coefficient of partition is one, and the C_L and C_S are equal. Using (2) and the variation of composition we can estimate the release of latent heat.
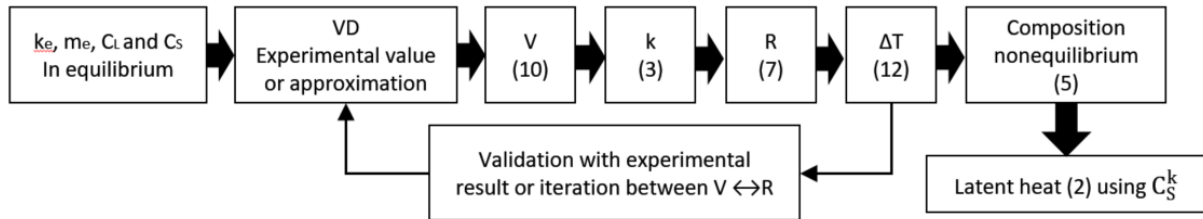

Figure 3: *General scheme to predict the solidification velocity and its effect on the latent heat released during the solidification.*
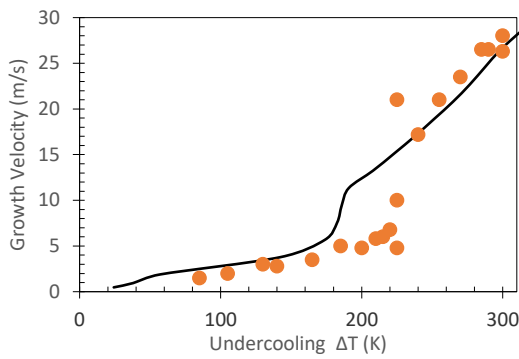

Figure 4: *Dendritic solidification velocity V vs. undercooling ΔT for the Ni 0.7 at%B alloy. Circles: experimental data [14,15]; Continuous line : mathematical model*
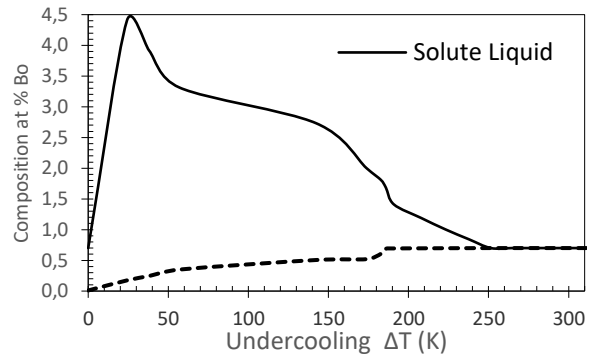

Figure 5: *Result of Eq. 5, evolution of the solute concentration in the liquid and solid taking into account the nonequilibrium coefficient k, as a function of the undercooling for the alloy Ni 0.7 at%B*

Parameter	Units	Value
Boron concentration	at%	0.7
Heat of solidification	J/mol	1.72×10^4
Specific heat	J/molK	36.39
Melting temperature	K	1726
Liquidus slope	K/%at	-14.3
Capillarity constant	K m	3.42×10^{-7}
Partition constant		0.0155
Diffusion coefficient	m^2/s	5.5×10^{-9}
Thermal diffusivity	m^2/s	8.5×10^{-6}
Maximum diffusivity velocity	m/s	18.9
Interfacial kinetic coefficient	m/sK	0.25

Table 1: *Material parameters of Ni-B alloy used in the model calculation*

5. Discussion

In our example (Figure 4 & Figure 5), the effect of the solution trapping generates an undercooling of 240 K, this behavior is inadmissible for using the system in an industrial application. Considering the RSP between equilibrium and nonequilibrium, it's possible to have three different scenarios represented in Figure 6. The first scenario, where $k \approx k_e$, has a poor cooling rate, and the value of the undercooling is only the necessary to start the solidification. In the second scenario, where $k_e < k << 1$, the cooling rate is stronger, the undercooling is more significant and all the material under the melting temperature solidify almost instantly, the liberated heat is sufficient to elevate the temperature significantly. In the third scenario, the cooling rate produces a large undercooling during the solidification, causing the effect of release the heat to be insignificant. In this case, the energy storage system is not useful, the temperature decreases significantly and as any recuperation of the latent heat stored is made. In this situation, it could be better to reduce the cooling rate before trying other solution. Knowing the relationship between solidification velocity and undercooling can be useful to place limits on the cooling by the heat exchanger and if is necessary change the design or selection for the heat exchange to improve the recuperation of the thermal energy stored.
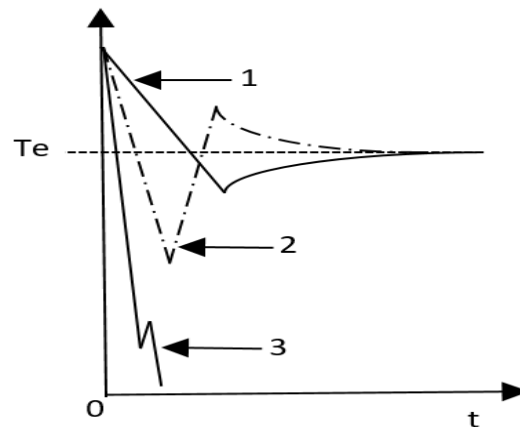

Figure 6 : *Cooling curves where Te is melting temperature, and t is time. 1) Normal solidification; 2) The cooling rate generates a significant undercooling; 3) Fast cooling rate where the heat released is almost insignificant.*

Another concept poorly studied is the generation of metastable phases beyond the phase diagram due to the rapid solidification. This consideration can be useful if we consider the augmentation of the solute that can be integrated in the solvent, for example in the utilization of mixtures with lithium where the quantity of material has an important role in the energy that can be stored and released. Also, the extension of solute solubility can improve the thermal properties and reduce the melting temperature [16,17].

6. Conclusion

A method has been described (Figure *3*) to estimate the latent heat released during the solidification of a binary alloy. We take into account the growth velocity to estimate the segregation and the amount of undercooling. Our results have good agreement with experiment data (Figure 4) and this methodology can be applied to predict the amount of energy released in function of the solidification velocity. The material data used has been for an ideal solution, in practice could be necessary take into account impurities that can reduce the amount of

undercooling, or even the contact surface can affect the point to start the nucleation. But the use of this methodology can be used as first estimation to select the mixture.

Our research continues in development to take into account the internal energy of the mixture by the Gibbs energy to propose an optimal point to store thermal energy between change in mixture (segregation) and the solidification speed. Our main objective is control the amount of undercooling and predict the behavior to favorize the thermal store for industrial applications.

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