SOLIDIFICATION AND QUASI-AUTONOMOUS STRUCTURES OF DL TYPE (I)

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Abstract. A solidification model is built, assuming that at the S/L interface quasi-autonomous structures of DL type are developed.

Key words: interface, double layer, solidification front.

1. INTRODUCTION

Decreasing the temperature in the volume of a melt, energy fluctuations are produced and small atoms groups are ordered in space, characteristic positions of a crystalline structure being occupied. These groups define crystallisation centres which are unstable in adjacent melt since the mobility of the atoms is still high. By further cooling, the crystallisation centres become stable, forming crystallisation nuclei, which are capable to grow to the final dimensions of crystalline grains.

The germination can debut from inside the liquid metal, in the case of homogenous germination [1, 2], or on the support-surfaces pre-existent in the melt, in the case of heterogeneous germination [1, 2]. Thus, the primary crystallisation mechanisms in metals and alloys systems will include the germination (homogenous or heterogeneous) of the solid phase nuclei and the growth of the germs by crystalline grain forming.

After stable germ formation, the new phase growth will occur by addition of new atoms or molecules to solid-liquid S/L interface. Thus, it results an atoms flux from the melt to the solid state germ and another one in the opposite direction. Now the growth will be possible only if the flux oriented toward the germ is greater than the one oriented toward the liquid phase. The growing speed is dependent on the probability that the atoms (or molecules) may be fixed on the S/L interface, and in this case the interface must have gaps, at this scale the new...
atoms-interface joints being achieved. A very distorted interface on atomic scale is advantageous for atoms adding, and a plane interface is disadvantageous to this process, therefore the growing mechanism will depend essentially on the interface structure.

In metallic materials with a fast development of the S/L interface, the phenomena which take place at an atomic scale are not generally limited by speed and they represent only a part of the phase transformation process. Another part of the process is the matter ordering on a much greater scale, which is strongly influenced by the diffusion phenomena. These phenomena lead to a varied solidification microstructure, having dimensions $10^{-6}$–$10^{-3}$ mm, mainly represented by dendritic crystals and eutectic grains [1, 2].

In this context, different models which describe the S/L phase transition were developed. The oldest approach is modelling the S/L interface as a surface whose shape is changing in time. It is, thus, assumed that the interface has zero thickness and such models are sometimes referred to as “shape-interface” or “classical” models. Implicit in this idea is the fact that the microscopic structure of the interface, involving a description on the atomic scale, is much smaller than the characteristic length scale of the diffusion field. On the surface representing the interface, boundary conditions are established which permit discontinuities in the temperature or solute fields, or their gradients, across the interface. These boundary conditions express, in part, the microscopic dynamics of the interface as well as the conservation laws for heat and mass [1].

The discovery of the spinodal decomposition led to a theoretical model developed by Cahn and Hilliard [3, 4], which represents the interface between two regions of different composition as diffuse, i.e., of finite thickness. The solution of this theory is the construction of a gradient-weighted free-energy functional, and of a model which ensures that the free energy decreases monotonically in time. This approach does not distinguish the interface from the rest of the system by treating it differently, as is the case in the classical formulation, and so leads to a more coherent description.

Another approach discussed in [1] is the phase field model of a S/L phase transition. This model extends the ideas used by Cahn and Hilliard for spinodal decomposition, by seeking to formulate a S/L phase transition in terms of a gradient-weighted free energy functional. They employ an additional variable, called phase field, to act as an order parameter to identify regions as solid and liquid.

In this paper a solidification model is built assuming that, at interface S/L, quasi-autonomous structures of electric double layer (DL) type are generated, by excitations and ionizations. In this context, a correspondence between the thermal gradient from the S/L interface and the electric field from the electric DL is established, and one verifies such correspondence by numeric simulation.
2. MODEL OF SOLIDIFICATION BY QUASI-AUTONOMOUS STRUCTURE OF ELECTRIC DOUBLE LAYER TYPE

To the thermal gradient from the S/L interface will correspond an electric field $\vec{E}$ (Fig. 1) (for more details see section 3). So, we propose a model similar to that of Sanduloviciu [12, 13] for the spontaneous formation of spatial structure of DL-type in laboratory plasmas. The electrons which are more numerous in melt than in solid [5] will be accelerated by the field $\vec{E}$ up to a certain distance from $S$ as they have kinetic energy for the maximum excitation cross section, $\sigma_e$. After losing energy by neutrals exciting, the electrons are thermalized and localised in the proximity of $S$, forming a negative charge region (a potential barrier) (see Fig. 2). The small energy electrons are trapped by the potential barrier thus constituted.

The electrons having enough energy to break through the negative potential barrier, as well as those which produced no excitations, will gain, being accelerated in the local electric field $\vec{E}'$ (see Fig. 2) localized near $S$, enough kinetic energy to produce ionizations. Both the electrons that have produced the neutrals ionizations, and those resulted from ionizations are quickly collected by $S$, so that, in the region ranging between the negative charge region and $S$, a new solid plasma appears, enriched in positive ions. A separation of charge occurs, resulting in the generation of a double layer (DL) (see Fig. 3).

Between the adjacent layers of spatial electric charge, forces are acting, assimilated to the binding forces (long range correlation forces). These forces cumulated with the dissipative effects (recombinations, emission of radiations) ensure the spatial stability of DL. More exactly, DL holds as long as the excitation and ionization rates ensure in the two adjacent regions a constant excess of negative and positive charges respectively.
The shape and position of DL depends on the potential of $S$. If $V_S = V_i$, the structure bounded by DL and $S$ suffers a transition from a quasi-planar state to an ellipsoidal cap shape [13], the electrostatic forces “over-compensating” for the influence of $S$. A situation of this type is obtained when, by electrons acceleration in DL, the ionization cross area, $\sigma_i$, suddenly increases, and the concentration in positive charge layers reaches a critical value. Since the electrons no longer “feel” the influence of $S$, the positive core of the structure takes over the role of $S$ (it behaves as a virtual anode ($A_V$)) [12], thus the electrostatic force resulting, with which $A_V$ attracts the electrons, is balanced by the resultant force with which the same $A_V$ rejects the positive ions from DL. A quasi-autonomous spatial charge structure (SCA) is generated (see Fig. 4).

The electrons accelerated towards the DL of ellipsoidal cap shape, as well as those recently generated by ionisations, are trapped in the SCA core. At the same time, the electrons accelerated toward $S$ generate in front of it a new planar DL, and the charge of the quasi-autonomous structure decreases due to electron trapping. In this way the part played by the virtual anode of SCA is also diminished.

![Fig. 3. – Charge separation with DL generation.](image1)

![Fig. 4. – Quasi-autonomous structures of DL type.](image2)

![Fig. 5. – Evolution of DL.](image3)

![Fig. 6. – Association of the DL with the primary branch of dendrite.](image4)
The separation between the SCA and $S$ determines, at a certain moment, by narrowing the bounding zone between the planar SCA and quasi-spherical SCA, the appearance of an “umbilical cord” [12]. In this way, the electrons from the quasi-spherical SCA move toward $S$, while the new ions generated in the planar SCA will be injected into the core of the spherical SCA (see Fig. 5).

In such a context, the quasi-autonomous structures of electric double layer will be associated, in our opinion, to the primary branches of the dendrites (see Fig. 6).

3. THE CORRESPONDENCE ELECTRIC FIELD-THermal GRADIENT IN INTERFACE

The temperature gradient in the $S/L$ interface, directed from $L$ to $S$, generates an electric field $\vec{E}$ directed from $S$ to $L$ (reciprocal processes – for details see ref. (6)). The expression of the field will be obtained by annulling the current density $\vec{j}$.

In order to calculate the current density $\vec{j}$ in the interface, we use Boltzmann equation [7]:

$$\vec{v}\partial_{\vec{r}}f + \frac{e\vec{E}}{m}\partial_{\vec{r}}f = -\frac{f_1}{\tau}$$

where $f_1$ is the non-equilibrium function of distribution and $\tau$ is the relaxation time. Since at the $S/L$ transition the quantum mechanical parameters present a classical behaviour, $f_1$ differs only slightly from the equilibrium function of distribution $f_0 = e^{-W/kT}$ [8] i.e.:

$$f = f_0 + f_1 \approx f_0$$

then

$$\partial_{\vec{r}}f \approx \partial_{\vec{r}}f_0 = -\frac{W}{T}\partial_{\vec{r}}T \frac{\partial f_0}{\partial W}$$

$$\partial_{\vec{v}}f \approx \partial_{\vec{v}}f_0 = -m\vec{v}\frac{\partial f_0}{\partial W}.$$  

It follows that:

$$\vec{v} \frac{\partial f_0}{\partial W} \left( -\frac{W}{T}\partial_{\vec{r}}T + e\vec{E} \right) = -\frac{f_1}{\tau}$$

whence:

$$f_1 = -\tau \frac{\partial f_0}{\partial W} \left( -\frac{W}{T}\partial_{\vec{r}}T + e\vec{E} \right) \vec{v}.$$
Under these circumstances, the current density has the expression:

\[ \vec{j} = e \int \nabla \vec{v} \, d^3\vec{v} = -e \int \nabla \left( \frac{f_0}{W} \frac{\partial}{\partial W} \left( \frac{W}{T} \frac{\partial}{\partial T} + e \vec{E} \right) \right) \, d^3\vec{v}. \] (7)

By giving the integrals in (7) for the one-dimensional case explicitly, we obtain successively:

\[ -e \int_0^\infty n \tau \frac{\partial f_0}{\partial W} \left( \frac{W}{T} \frac{\partial}{\partial T} \right) \frac{x^2}{m \sqrt{\pi}} \, dx = \frac{n_0 ke}{m \sqrt{\pi}} \int_0^\infty \tau \frac{\partial T}{\partial x} \alpha^{3/2} \frac{e^{-\alpha}}{\alpha} \, d\alpha = \frac{3n_0 ke}{4m} \left\{ \tau \frac{\partial T}{\partial x} \right\} \] (8)

and

\[ -e^2 \int_0^\infty n \tau \frac{\partial f_0}{\partial W} E_x v_x^2 \, dv_x = \frac{n_0 e^2}{m \sqrt{\pi}} \int_0^\infty \tau E_x \alpha^{1/2} \frac{e^{-\alpha}}{\alpha} \, d\alpha = \frac{n_0 e^2}{2m} \left\{ \tau E_x \right\} \] (9)

with

\[ \alpha = \frac{W}{kT} \] (10)

therefore (7) getting the form:

\[ j_s = \frac{n_0 e^2}{2m} \left\{ \frac{3k}{2e} \frac{\partial T}{\partial x} + \tau E_x \right\} \] (11)

Since at equilibrium \( j_s = 0 \), the last expression gives:

\[ \left\{ E_x \right\} = -\frac{3k}{2e} \left\{ \frac{\partial T}{\partial x} \right\}. \] (12)

This means that to an average temperature gradient in the interface, \( \langle \partial T / \partial x \rangle \), directed from \( L \) to \( S \), will correspond an average electric field \( \langle E_x \rangle \) from the \( S \) to \( L \). The existence of a negative thermal gradient in interface, in agreement with usual theories [1, 2] determines the plane solidification front to transform into a dendritic one, which signifies that our assumption (the assimilation of quasi-autonomous structure of double layer type with primary branches of dendrites) is correct.

4. THERMAL FIELD VARIATION IN S/L INTERFACE

The thermal field variation in S/L interface is obtained by numerical integration of thermal field equations:

\[ \partial_x T_1 = k_1 (\rho_1 c_1)^{-1} \partial_{xx} T_1, \quad 1 = L, S \] (13)

with the frontier condition:
where \( T_1 \) are the temperatures of the solid and liquid phases respectively, \( k_1 \) the thermal conductivity coefficients, \( \rho_1 \) the densities, \( c_1 \) the specific heats, \( \lambda \) the solidification heat and \( \partial_x \) the moving speed of the solidification front.

One admits [9] the following: the initial temperature \( t_f = 20^\circ C \), the thermal properties and size of the moulding box \( k_f = 397 \text{ W/km} \), \( d = 0.01 \text{ m} \), the environment coefficient of thermal transfer \( \alpha = 6 \cdot 10^4 \text{ W/m}^2/\text{K} \), \( t_{solidif.} = 660^\circ C \), \( \rho_S = 2700 \text{ kg/m}^3 \), \( \rho_L = 2385 \text{ kg/m}^3 \), \( k_L = 94 \text{ W/m/K} \), \( k_S = 238 \text{ W/m/K} \), \( c_L = c_S = 1080 \text{ J/kg/K} \), \( \lambda = 387,8 \text{ kJ/kg} \).

If one performs the integration in the one dimensional case, when the size of the moulding box is considered much larger than the other two, we get an additional symmetry-connected condition – the thermal gradient in the symmetry plan is zero. The used scheme is with finite differences, known as the triangle explicite scheme or Schmidt formula [10].

\[
T^{n+1}_j = \beta T^n_{j+1} + (1 - 2\beta) T^n_j + \beta T^n_{j-1}
\]

with

\[
\beta = \frac{\alpha_{L,S} \Delta t}{\Delta x^2}
\]

where \( \alpha_{L,S} \) denotes the fraction in front of the \( \partial_x T \), \( \Delta x, \Delta T \) being the intervals of space and time division.

The resulting space-time configuration of the thermal field is presented in Fig. 7.

Fig. 7. – Space-time variation of the thermal field.
This representation confirms the existence of a maximum value of temperature where the S/L interface is located at a given moment, obviously determined by the latent heat elimination and, at the same time, the temporal dependence of the solidification front coordinates agrees with the known relation [12] \( x(t) = kt^{1/2} \), where \( k \) is a constant, depending on the properties of the studied material.

The spatial variation of the temperature in the S/L interface (see Fig. 8) shows that the premises of dendritic solidification are always created by the occurrence of a negative thermal gradient in the melt. Since this curve has the same shape as the double layer potential [11], it results that the S/L interface can be assimilated to this structure, thus the relation \( V \sim T \) is valid, and indirectly, will verify relation (12).

![interface S/L](image)

Fig. 8. – Space variation of the thermal field.

5. CONCLUSIONS

The main results of the present work are as follows:

i) A model of solidification is built, assuming that at the S/L interface develops, by excitations and ionizations, quasi-autonomous structures of electric double layer type.

ii) A correspondence between the thermal gradient in S/L interface and the electric field from the electric DL is established.
iii) Such correspondence was verified by numerical simulation. In such a context, the dendritic growth mechanism, when there is a negative gradient in the melt, is determined mainly by generation of some protuberances in the S/L interface. Then, the cap of the protuberance will be formed in a melt undercooled more intensely than the rest of the plane surface and will move in the adjacent melt faster then the rest of front, forming the primary branch of the future dendritic structure, i.e. quasi-autonomous DL type structure.

iv) From this model it results that the ionization potential, $V_i$, increases with the increase of the solidification temperature, $T_S$, which is verified for many metals [5]. Then, (12) may be used only as $V_i = \alpha T_S$ where $\alpha$ is a parameter depending on the nature of DL.

v) Such a model may be used to analyse the fire ball in a discharge plasma [13].

REFERENCES