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A MATHEMATICAL MODEL OF CHANGES IN THE COMPOSITION OF GRAINS DURING COOLING A TWO-COMPONENT MELT

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The growth of individual grains of a solid phase during cooling liquid melt has been studied. During cooling, the compositions of the liquid and solid phases and the equilibrium conditions change. Therefore, each subsequent layer, "freezing" on the grain, will have a slightly different composition. This paper proposes a method for calculating the structure of the grain changes with increasing distance from the center. Corresponding mathematical model has been created. It is based on the following assumptions. Growing grains are considered as spherical. The temperature alignment in the system and the composition alignment in the liquid phase occur instantly. The alignment of the solid phase composition does not occur. Also, it is assumed that local equilibrium of the liquid phase with the solid phase on the grain surface is observed at any temperature. The characteristics of this local equilibrium can be found out from the corresponding equilibrium state diagram. The balance equation of phase masses and masses of their components at infinitesimal temperature decrease was made. It was assumed that the local equilibrium of the liquid phase and the infinitely thin layer of the solid phase, formed during this decrease in temperature, is observed. Taking to the limits, we have obtained a differential equation describing the investigated process. The solution of this equation has been obtained in the form of the solid phase mass as an integral function of the temperature. The grain composition depending on the distance from its center is obtained in the form of parametric functions expressing the radius of the current grain point and its composition at this point depending on the temperature. A computer program for the calculation of the mathematical model equations have been created. To use the model, it is needed to know the composition of the initial melt, the average density of the solid phase and the equations of the liquidus and solidus lines in the form of functions of concentration vs the temperature. An example of the calculation is presented.

Keywords: mathematical model, physical metallurgy, state diagram, liquation.

Introduction

Taking into account the influence of liquation in the crystallization of metal is a long-standing problem of metallurgy [1–7]. One of the approaches to its study is the creation of an adequate mathematical model that takes into account the main factors affecting the process under study [8–10].

Consider the growth of a separate grain during cooling of a multicomponent melt, namely, changing its size and composition. State diagrams show how the equilibrium compositions of the liquid and solid phases change when the melt is cooled. However, such an equilibrium cooling can be achieved only if the phase composition and temperature have time to align with any decrease in temperature. This is only possible in two cases: the temperature decreases infinitely slow or have infinitely large thermal conductivity and diffusion coefficients of each phase.

Therefore, only a local equilibrium observed at short distances from the phase boundary can be performed. During cooling of the melt from the temperature T to $T+\Delta T$ ($\Delta T<0$), a thin layer of the solid phase freezing (from the surrounding liquid phase) on the grain, will be in equilibrium corresponding to the new temperature composition. With the subsequent decrease in the temperature to $T+2\Delta T$, a new layer of a new composition corresponding to this new temperature will appear on the grain. With subsequent temperature decreases, the grain will be overgrown with new layers, which compositions correspond to the new temperatures, as shown in Fig. 1. In fact, we will not even deal with separate layers, but with a continuous change in composition as we go away from the grain center.

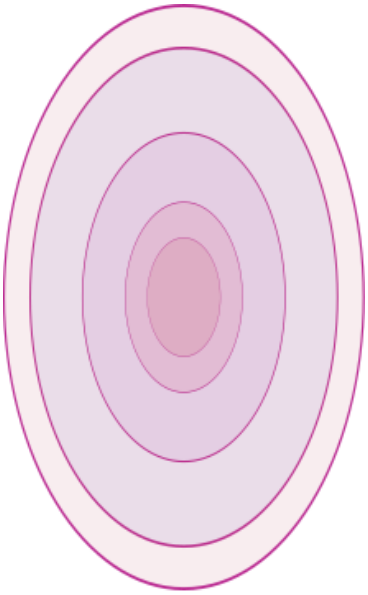

Fig. 1. Changes in grain composition as it grows

The purpose of this work was to create a model that allows calculation of the change in the composition of the grain as it goes away from its center.

1. Basic assumptions

The growth of individual grains, which are considered to be spherical is studied Accepted that:

1) the temperature alignment in all phases (liquid and solid) is instantaneous;

2) the composition alignment in the liquid phase is instantaneous;

3) the alignment of the solid phase composition does not occur.

2. Derivation of basic equations

Consider the model state diagram (Fig. 2).

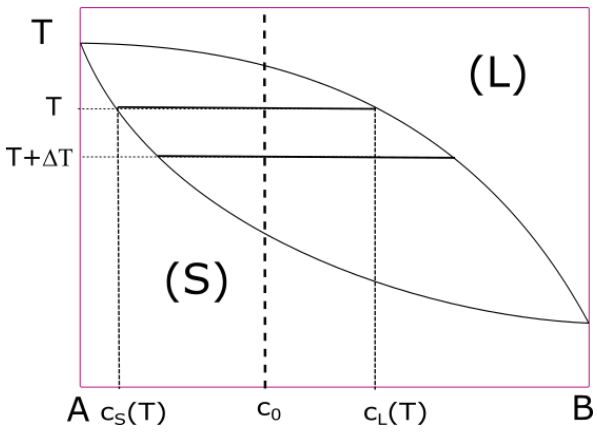

Fig. 2. Model state diagram

Consider a melt A–B with the mass M_0 and the fraction of the component B equaled c_0. Let the system has been cooled to a temperature T. Let the mass of the solid phase be $M_S(T)$ and the number of identical grains in it be N. Let the mass of the liquid phase be $M_L(T)$, and the fraction of the component B in it be $c_L(T)$. Let the system now be further cooled to a temperature $T+\Delta T$ $(\Delta T<0)$. In this case, the new part of the solid phase with a mass ΔM_S and the composition $c_S(\tilde{T})$, where $T+\Delta T\le\tilde{T}\le T$, will be formed. Then the mass of the liquid phase will become $M_L(T+\Delta T)=M_L(T)-\Delta M_S$. Its composition will be $c_L(T+\Delta T)$.

Let's make the balance equation of the component B at the temperature $T+\Delta T$:

$$\Delta M_S c_S(\tilde{T})+(M_L(T)-\Delta M_S)c_L(T+\Delta T)=$$
$$=M_L(T)c_L(T)$$

and obtain

$$\Delta M_S=M_L(T)\frac{c_L(T+\Delta T)-c_L(T)}{c_L(T+\Delta T)-c_S(\tilde{T})}.$$

Divide this equality by ΔT:

$$\frac{\Delta M_S}{\Delta T}=M_L(T)\frac{1}{c_L(T+\Delta T)-c_S(\tilde{T})}\times$$
$$\times\frac{c_L(T+\Delta T)-c_L(T)}{\Delta T}.$$

Let's go to the limits as $\Delta T\to 0$. Taking into account that if $\Delta T\to 0$ then $\tilde{T}\to T$, we get

$$\frac{dM_S}{dT}=M_L(T)\frac{1}{c_L(T)-c_S(T)}\frac{dc_L}{dT}.$$

In this case, $\frac{dc_L}{dT}=c_L'$ and $\frac{1}{c_L(T)-c_S(T)}$ are known values, from equilibrium state diagram.

Because of $M_L(T)=M_0-M_S(T)$ then

$$\frac{dM_S}{dT}=(M_0-M_S(T))\frac{c_L'}{c_L(T)-c_S(T)}.$$

Having solved this differential equation we have obtained

$$M_S=M_0\left(1-\exp\left(-\int_{T_L}^{T}\frac{c_L'}{c_L(T)-c_S(T)}dT\right)\right).$$

We have obtained the dependence of the the crystallized metal mass on the temperature. Assuming that the solid phase has the shape of a sphere of radius R and density ρ, we obtain the ratio $M_S = \frac{4}{3}\pi R^3 \rho N$ from which follows $R(T) = \left(\frac{3M_S(T)}{4\pi\rho N} \right)^{\frac{1}{3}}$ or

$$R(T) = \left(\frac{3M_0}{4\pi\rho N} \left(1 - \exp\left(-\int_{T_L}^{T} \frac{c_L'}{c_S(T) - c_L(T)} dT \right) \right) \right)^{\frac{1}{3}}.$$

Thus, for any T we can calculate the grain radius by this formula, and by the state diagram determine the composition of the corresponding layer. We now have the defined parametrically function $c_S(R)$ using the parameter T:

$$\begin{cases} R(T) = \left(\frac{3M_0}{4\pi\rho N} \left(1 - \exp\left(-\int_{T_L}^{T} \frac{c_L'}{c_S(T) - c_L(T)} dT \right) \right) \right)^{\frac{1}{3}}; \\ c_s(T). \end{cases} \quad (1)$$

3. The calculation algorithm

To calculate, we should know the initial composition of the melt c_0, the initial melt mass M_0, the density of the solid phase ρ, the state diagram of the system (the equations of the diagram lines in the form of $c_L(T), c_S(T)$).

1. Let's find the the liquidus temperature T_L and the solidus temperature T_S.
2. Let's divide the interval $[T_S; T_L]$ into equal parts by points $T_1, T_2, ..., T_{n-1}$, where $T_0 = T_S$, $T_n = T_L$.
3. For the each point, calculate $R(T), c_S(T)$ by the formula (1).
4. Get a table of the values $R(T), c_S(T)$, on which we build a graph of the dependence $c_S(R)$.

According to the above algorithm, a computer program was written in VBA Excel.

4. Calculation example

Consider a cooling of the tin-bismuth alloy (mas. 30% Bi)). Let's use the Sn–Bi state diagram [11] (Fig. 3).

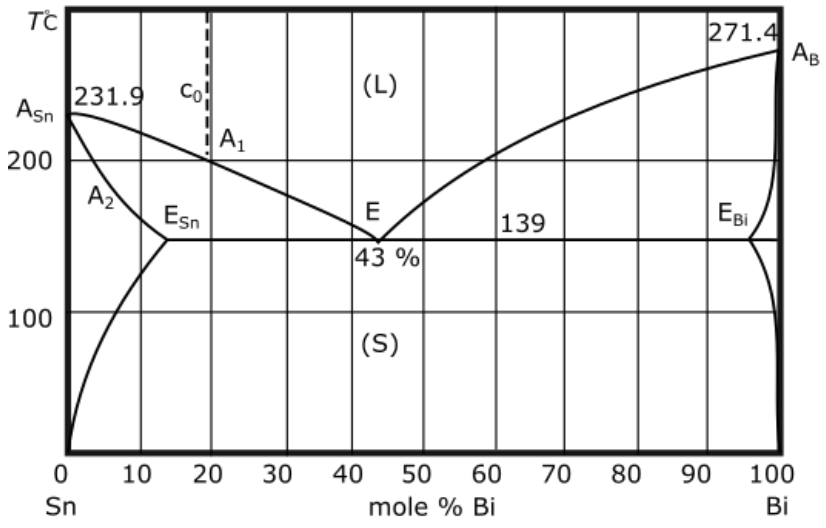

Fig. 3. Sn–Bi phase diagram

The selected composition corresponds to mole 19.576%., that is, between the points E_{Sn} and E. Thus, for the calculation we will need the equations of the liquidus $A_{Sn}A_1E$ and solidus $A_{Sn}A_2E_{Sn}$ lines in the form of $c=\varphi(T)$. To do this, we took these dependencies parabolic, found the coordinates of the points $A_{Sn}, A_1, E, E_{Sn}, A_1, A_2$ on the state diagram, and transferred the concentrations into mass fractions. Further, by the points A_{Sn}, A_1, E the equation of the liquidus line has been determined and by the points A_{Sn}, A_2, E_{Sn} the equation of the solidus line has been determined. We have obtained

$$\begin{aligned} &A_{Sn}A_1E: \quad c=-5,7\cdot10^{-5}T^2+1,4883\cdot10^{-2}T-0,40384; \\ &A_{Sn}A_2E_{Sn}: c=2,25\cdot10^{-6}T^2-3,18\cdot10^{-3}T+0,616724. \end{aligned} \tag{2}$$

The calculation results are shown in Fig. 4–6. To ensure that they do not depend on arbitrarily specified values: the melt mass and the number of grains, some of the results are presented in a normalized form. So the current radius of the grain is presented in the form of its ratio to the maximum radius reached by the time of solidification of the entire melt.

In Fig. 4 the data on the the final composition of the grain are presented. Inconstancy of the grain composition is clearly visible. The alignment of the composition can occur only after a fairly long period of time.

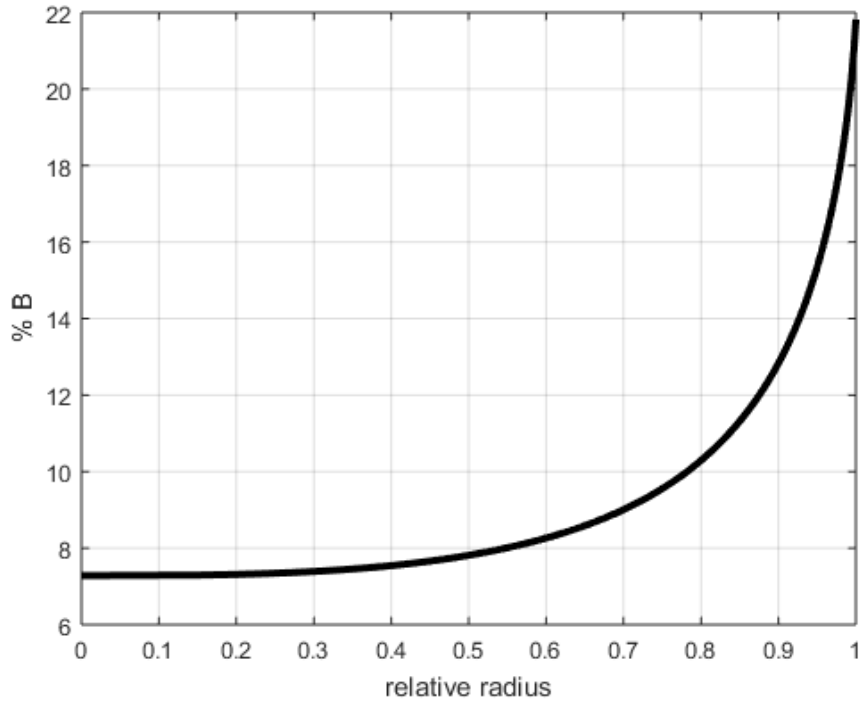

Fig. 4. The composition of the grain phase as a function of the distance to the grain center

Fig. 5, 6 show a comparison of the obtained results with the data that would be obtained directly from the equilibrium state diagrams, which would be realized if the cooling was infinitely slow (or if the diffusion and the thermal conductivity coefficients of both phases were infinitely large).

From Fig. 5 it can be seen that if diffusion in the solid phase is absent, the mass of the crystallized metal is less than it follows from the equilibrium state diagram. When the supercooling is 60.0794 (the temperature drops out to 139 °C), the eutectic precipitates and the "equilibrium" curve rises to 100%. What happens to previously formed growing grains is not considered in this paper.

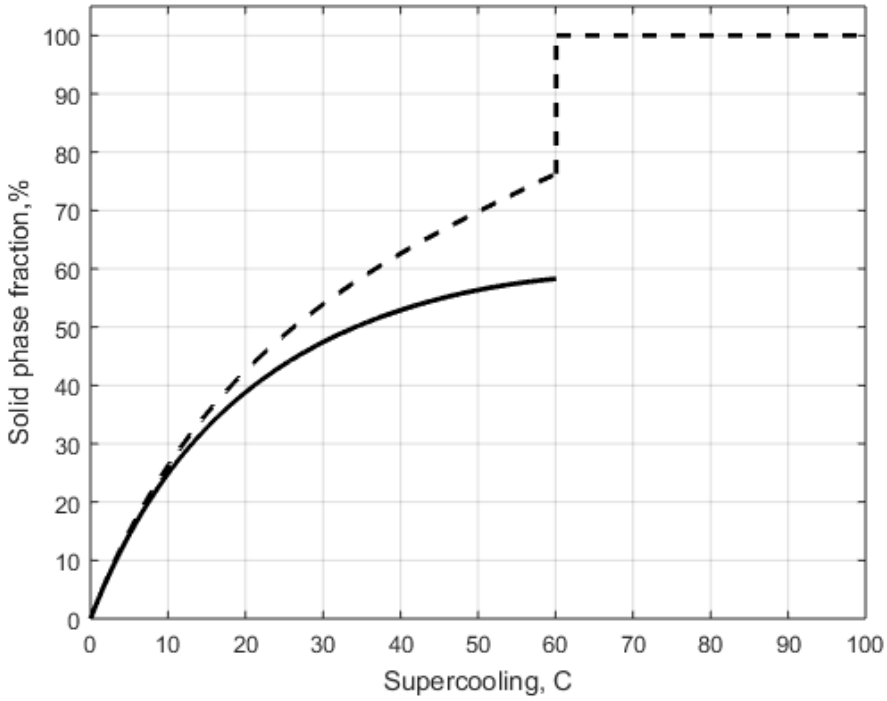

Fig. 5. The fraction of the solid phase as a function of the corresponding supercooling (dotted line – the "equilibrium" case)

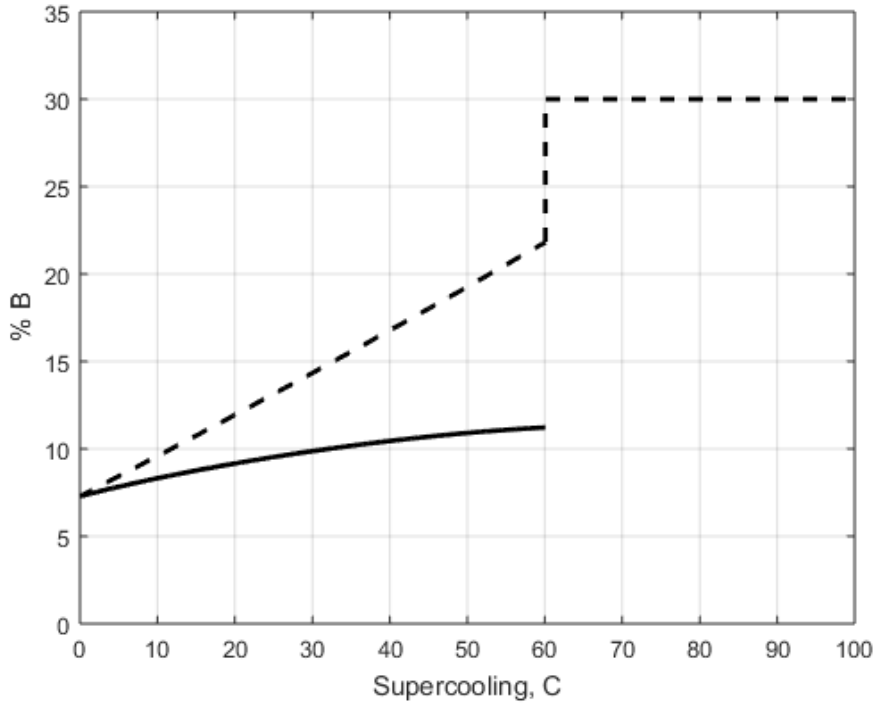

Fig. 6. The average composition of the solid phase in the absence of diffusion in solid phase (solid line) and in accordance with the equilibrium state diagram (dotted line)

Conclusions

The paper considers the limiting (not quite real) case of cooling of a two-component system in the case when the alignment of the solid phase composition does not occur is considered. In this case, there are a number of significant differences from the usual conclusions resulting from the equilibrium state diagram.

- At any supercooling, the mass of the solid phase is less than it follows from the equilibrium state diagram.
- At any supercooling the total fraction of

the dissolved substance in a solid phase is less than it follows from the equilibrium state diagram.

• The solidus temperature of a melt is decreases.

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МАТЕМАТИЧЕСКАЯ МОДЕЛЬ ИЗМЕНЕНИЯ СОСТАВА ЗЕРНА ПРИ ОХЛАЖДЕНИИ ДВУХКОМПОНЕНТНОГО РАСПЛАВА

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Рассматривается рост отдельных зерен твердой фазы при охлаждении жидкого расплава. По мере охлаждения меняются составы жидкой и твердой фаз и условия равновесия. Поэтому каждый последующий слой, «намерзающий» на зерно, будет иметь несколько иной состав. В данной работе предложен метод расчета изменения состава зерна по мере удаления от его центра. Для этого разработана математическая модель, базирующая на следующих допущениях: растущее зерно считается сферическим; выравнивание температуры в системе и выравнивание состава жидкой фазы происходят моментально; выравнивание состава твёрдой фазы не происходит. При этом считали, что при любой температуре соблюдается локальное

равновесие жидкой фазы и поверхностного слоя твердой фазы. Характеристики этого локального равновесия могут быть определены из соответствующей равновесной диаграммы состояния. Было составлено уравнение баланса масс фаз и масс их компонентов при бесконечно малом снижении температуры. Считали, что при этом соблюдается локальное равновесие жидкой фазы и бесконечно тонкого слоя твердой фазы, выделившегося при этом снижении температуры. Переходя к пределам, получили дифференциальное уравнение, описывающее исследуемый процесс. Решение этого уравнения было получено в виде интегральной функции массы затвердевшего сплава от температуры. Так как масса затвердевшего сплава при наших допущениях однозначно связана с его массой, решение всей задачи – определение состава зерна в зависимости от расстояния до его центра – было получено в виде параметрической функции, выражающей радиус текущей точки зерна и его состав в этой точке через температуру. Составлена компьютерная программа расчета по уравнениям математической модели. Для использования модели нужно знать состав исходного расплава, среднюю плотность твердой фазы и уравнения линий ликвидуса и солидуса в виде функций состава от температуры. Представлен пример расчета.

Ключевые слова: математическая модель, металловедение, диаграмма состояния, ликвация.

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