ON THE DISTRIBUTION OF IMPURITIES IN DIRECTIONALLY SOLIDIFIED SAMPLES WITH A PLANAR CRYSTALLIZATION FRONT

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ABSTRACT

Method of directionally controlled solidification with planar crystallization front is used, as a rule, to purify the main component of impurities. It is considered that distribution of each impurity component along the length of directionally solidified sample with planar front is predetermined by the value of the equilibrium distribution coefficient (\(K\)) of each impurity with the main component. The \(K\) value is determined from equilibrium binary phase diagram as the relation \(K = \frac{C_S}{C_L}\), where \(C_S\) and \(C_L\) are contents of the impurity under examination in coexisting solid and liquid phases. On condition that \(D_S = 0\) and \(D_L = \infty\) and \(K < 1\), at crystallization with planar front the impurity content along the length of the directionally solidified sample increases constantly and reaches maximum in the last part of the sample.

In case of the value \(K > 1\) the impurity content on the contrary decreases from the initial part of the sample to the final one. However, when two or more impurity components are present, their redistribution in the directionally solidified sample with planar front obeys conditions of completely non-equilibrium crystallization of multi-component alloys. It is shown that in multi-component continuous solid solutions values of \(K\) of medium melting point components change in the crystallization range from \(K < 1\) (at the starting point of the process) to \(K > 1\) (at the end of the process). Such change of \(K\) predetermines more complex distribution of such components – impurities along the length of the directionally solidified sample with planar crystallization front. At first impurity content gradually increases, reaches the maximum value and then decreases to minimum. Such complex component distribution should be taken into consideration during crystallization purification. In the present work general regularities of component distribution depending on the melting temperatures of the basis component and the impurity components have been established.

1. INTRODUCTION

To predict the evolution of the intracrystalline or dendrite liquation in the course of non-equilibrium crystallization as well as to determine component distribution in directionally solidified ingot with planar crystallization front, it is necessary to know values of equilibrium distribution coefficients (\(K\)), which are estimated from equilibrium phase diagrams as the ratio \(K = \frac{C_S}{C_L}\) at temperatures in the crystallization range \(\Delta t = t_L - t_S\), here \(t_L\) and \(t_S\) are liquidus and solidus temperatures of the alloy respectively, \(C_S, C_L\) – an alloy component content in coexisting solid and liquid phases.
According to binary diagrams it is easy to determine equilibrium distribution coefficients of the alloying component. In these systems, in which extremums on liquidus and solidus lines are absent, the distribution coefficient of the high melting point component of any alloy is always more than a unity \((K > 1)\) and the distribution coefficient of the low melting point component is always less than a unity \((K < 1)\) \([1, 2]\).

2. THEORY

In the ternary system \(A – B – C\) (Fig. 1), where component melting temperatures relate as \(t_B > t_C > t_A\), the equilibrium distribution coefficient of the component \(B\) (the most high melting point one) in all alloys is more than a unity \((K_B > 1)\), the equilibrium distribution coefficient of the component \(A\) (the most low melting point one) in all alloys is less than a unity \((K_A < 1)\). It is much more difficult to speak about the distribution coefficient of the component \(C\) (medium melting point component) in this system.

![Fig. 1 Composition of the liquid (L) and solid (S) phases at the equilibrium crystallization of alloys 1 - 3 and the isothermal sections at the liquidus temperatures of alloys 1, 2 and within the crystallization range of alloy 3](image)

In paper \([3]\), probably for the first time, the authors succeeded in showing that in such systems there exists the area \(Ca_3b_3\) (Fig. 1), in which alloys with changing distribution coefficient of the medium melting point component \(C\) are located: at the beginning of the crystallization process close to the liquidus temperature of these alloys \(K_C < 1\), at temperature equal to \(t_B\), \(K_C = 1\), at the end of the crystallization process close to the solidus temperature \(K_C > 1\). The mentioned area is determined by the isothermal section of the diagram \(A – B – C\) at the melting temperature of the component \(C\). At the equilibrium crystallization of alloys located in the area \(Cb_3B\), adjacent to the high melting point component \(B\), the distribution coefficient of the component \(C\) is less than a unity \((K_C < 1)\), and the alloys located within the area \(Ca_3A\), adjacent to the low melting point component \(A\), have the distribution coefficient of the component \(C\) more than a unity \((K_C > 1)\).

Peculiarities of equilibrium and non-equilibrium crystallization of various alloy compositions in the ternary system as well as the alloy component distribution in the ingot at the directional solidification through the planar front are discussed in papers \([3, 4]\). More precise investigations of equilibrium and non-equilibrium crystallization of alloys in ternary systems with computer modeling have been carried out \([5]\). The obtained data corroborated completely the results of papers \([3, 4]\).

3. RESULTS

A regular tetrahedron was used to estimate the equilibrium distribution coefficients and to study the equilibrium and non-equilibrium crystallization of four-component alloys. In
this figure the tetrahedron vertexes correspond to pure components, six ribs — to binary systems, four sides — to ternary systems and the inner space of the tetrahedron — to the four-component systems [6–8]. Four components which melting temperatures relate as \( t_B > t_C > t_A > t_D \) were analyzed: \( t_B = 1000°C; \ t_C = 800°C; \ t_A = 600°C; \ t_D = 400°C \). The main challengers in plotting the graphs were to construct two-phase regions for different temperatures, to determine directions of tie-lines in these regions and to determine compositions of the liquid and solid phases. Specification of the above mentioned characteristics makes it possible to describe the course of the equilibrium crystallization, estimate mass fractions of the liquid and solid phases, determine equilibrium distribution coefficients of components, predict the development of dendrite liquation and component redistribution in the ingot manufactured at controlled directional solidification with a planar crystallization front.

The structure of the two-phase regions in the four-component system was determined by means of the following graphic constructions [9]. The 3-D tetrahedron figure consisting of components \( A, B, C, D \) was broken down into four ternary systems \( A – B – D, A – B – C, B – C – D \) and \( A – C – D \) in the form of equilateral triangles. Then, on each side of these triangles binary phase diagrams were plotted on the basis of components of the four-component alloy, i.e., \( A, B, C, D \) with specified melting temperatures (Figs. 2 – 6).

Then, the isotherms within the temperature range corresponding to the two-phase state of the four-component system (from \( 400°C \) to \( 1000°C \)) were specified. The selected isotherms made it possible to determine definitely the coexisting equilibrium compositions of the liquid and solid phases in the two-component systems, since the points of intersection of the isotherm with the liquidus and solidus lines correspond to the equilibrium compositions of the liquid and solid phases, and the line itself — the isotherm within the two-phase region — is a tie-line.

The presence of all binary phase diagrams enables to construct 3-D ternary systems as well as all isothermal sections in these ternary systems. Isothermal sections in ternary systems are shown in Figs. 2 – 6. The liquidus and solidus isotherms and the directions of the tie-lines were constructed on the basis of well-known principles [6–8].

Graphical constructions of the isothermal sections and tie-lines enabled to estimate accurately the values of the equilibrium distribution coefficients (more or less than a unity) in binary and ternary systems for the alloy compositions within the two-phase regions at the given temperatures. These values for each component are indicated in Figs. 2 - 6.

To determine the two-phase isothermal spaces in the four-component system, the tetrahedron for the given temperature was “assembled”, i.e. the four ternary systems with specified isothermal sections and tie-lines were joined into a single figure. The liquidus and solidus isotherms as well as the tie-lines in ternary systems turned out to be at the tetrahedron faces and connected at the edges corresponding to the binary systems. Within the internal space of the tetrahedron a two-phase region was formed, bounded by the solidus surface, with its convexity directed at the high melting point component side, and the liquidus surface with the convexity directed at the low melting point component side.

The isothermal sections and tie-line directions in two-, three- and four-component systems for the temperature \( 900°C \) are shown in Fig. 2. The tie-line direction in the two-phase region of the four-component alloy (i.e. in the inner space of the tetrahedron) was specified on the basis of the principle of the gradual change of the tie-line direction from one edge to the opposite one, from one face to another, taking into account that the areas of the sections on the liquidus and solidus surfaces are proportional. By means of the tie-lines we determined the component content in the liquid and solid phases for different four-component compositions and, correspondingly, the equilibrium distribution coefficients within the equilibrium crystallization range. Since it is very difficult to estimate the component content in the liquid and solid phases in four-component alloys, qualitative values of the equilibrium distribution coefficients (more, less than a unity, or equal a unity) were specified on the following principles. First, for each isothermal section, the distribution coefficient values for ternary alloys were determined. Thus, at \( 900°C \) (Fig.2) in the ternary alloy \( A – B – D \) we obtain \( K_B > 1, K_C < 1, K_D < 1 \), in the ternary alloy \( A – C – K_B > 1, K_A < 1, K_C < 1 \), in the ternary alloy \( B – C – D \ K_B > 1, K_C < 1, K_D < 1 \). All alloys in the ternary system \( A – C – D \) at
900°C are in the liquid state. After the assembly of the tetrahedron and derivation of the isothermal space in the four-component system, all tie-lines in this space will be arranged so that equilibrium coefficients of any alloy from this region will be the following: $K_B > 1$, $K_A < 1$, $K_C < 1$, $K_D < 1$. In other words, the equilibrium distribution coefficient of the most high melting point component ($B$) is more than a unity, but all the others ($A$, $C$, $D$) are less than a unity.

Fig. 2
Isothermal sections in two-, three- and four-component systems based on $A$, $B$, $C$, $D$ at 900°C

In Fig. 3 the isothermal sections at the temperature 800°C corresponding to the melting temperature of the component $C(t_C)$ are shown. Correspondingly, we have obtained different isothermal sections and values of the equilibrium distribution coefficients for the alloys in these sections. In the ternary system $A - B - D$ we have $K_B > 1$, $K_A < 1$, $K_D < 1$. In ternary systems $A - B - C$ and $B - C - D$ the tie-line direction is parallel to the opposite side of the component $C$, and its content is the same both in the liquid and solid phases, and the equilibrium distribution coefficient is equal to a unity ($K_C = 1$). For the other components the values of the distribution coefficients are the following: $K_A > 1$, $K_B > 1$, $K_D < 1$. The resulting space isothermal section in the tetrahedron $A - B - C - D$ at 800°C will be characterized by equal contents of the component $C$ in the liquid and solid phases for any alloy composition in the given isothermal space, since any tie-line in this space will be parallel to the face opposite to the component $C$. The equilibrium coefficients of other components will be: $K_B > 1$, $K_A < 1$, $K_D < 1$.

In Fig. 4 the isothermal section at the temperature 700°C, which is less than $t_C$ and more than $t_A$, is shown. At this temperature there are isothermal sections in all four three-component systems and, correspondingly, all four ternary systems were used to construct the isothermal space in the four-component system. The values of the equilibrium distribution coefficients were as follows: for the $A - B - D$ system $K_B > 1$, $K_A < 1$, $K_D < 1$; for the $A - C - B$ system $K_B > 1$, $K_C > 1$, $K_A < 1$; for the $B - C - D$ system $K_B > 1$, $K_C > 1$, $K_D < 1$; for the $A - C - D$ system $K_C > 1$, $K_A < 1$, $K_D < 1$.

For four-component alloys in the two-phase region at 700°C in the $A - B - C - D$ system we have found that $K_B > 1$, $K_C > 1$, $K_A < 1$, $K_D < 1$. Thus, for the alloys in the two-phase region in the four-component system at 700°C, $B$ and $C$ are high melting point components, and their equilibrium distribution coefficients are more than a unity; $A$ and $D$ are low melting point components and their equilibrium distribution coefficients are less than a unity, correspondingly.
Fig. 3 Isothermal sections in two-, three- and four-component alloys based on A, B, C, D at the melting point of the component C equal to 800°C

Fig. 4 Isothermal sections in two-, three- and four-component alloys based on A, B, C, D at 700°C

In Fig. 5 isothermal sections in the systems under investigation at the melting temperature of the component A are shown; correspondingly, the equilibrium distribution coefficient of this component is equal to a unity ($K_A = 1$), for the other components $K_B > 1$, $K_C > 1$, $K_D < 1$.

In Fig. 6 isothermal sections in the systems at 500°C (less than $t_A$ and more than $t_D$) are shown. The values of the equilibrium distribution coefficients are the following: $K_B > 1$, $K_C > 1$, $K_D < 1$. Thus, in the region of the alloy composition close to the most low melting
point component \((D)\) the equilibrium coefficients of all the other components are more than a unity, while that of the component \(D\) is less than a unity.

Fig. 5 Isothermal sections in two-, three- and four-component alloys based on \(A, B, C, D\) at the melting point of the component \(A\) equal to 600°C

Fig. 6 Isothermal sections in two-, three- and four-component alloys based on \(A, B, C, D\) at 500°C
Some general regularities regarding the equilibrium distribution coefficient values in any multi-component solid solution alloy may be derived on the basis of analysis of the isothermal sections in the four-component system with complete solubility of the components in both the liquid and solid states and the previous analysis of ternary systems [3, 4]. With this purpose, the table presents three possible binary alloys on the basis of the components $B - C$, $C - A$, $A - D$ (other combinations on the basis of these four components are possible). Each of these alloys, depending on the compositions, will have its own liquidus and solidus temperatures, which will be between the melting points of the initial components. The equilibrium distribution coefficient values may easily be determined by the phase diagrams. In these systems, the equilibrium distribution coefficient of the most high melting point component is always greater than a unity, while that of the most low melting point component will always be less than a unity.

Analysis of ternary phase diagrams of continuous solid solutions has shown [4] that three regions of alloy compositions with different equilibrium distribution coefficient values are possible here. The table presents these three characteristic compositions of the ternary alloy $A - B - C$. These three regions are specified on the basis of the liquidus and solidus temperatures of the alloy and the melting points of the pure components $t_B$, $t_C$, $t_A$. If the liquidus and solidus temperatures are between the melting points of the most high melting point component and the medium melting point component, the equilibrium distribution coefficient of the most high melting point component will always be more than a unity, while the corresponding coefficients of the medium and low melting point components will be less than a unity. If the liquidus temperature of the alloy is above the melting point of the medium melting point component, and the solidus temperature is below it, the equilibrium coefficient of the high melting point component will be greater than a unity, that of the low melting point component will be less than a unity; the equilibrium coefficient of the intermediate component is first less than a unity (close to the liquidus), then equal to the unity (at the melting point of the intermediate component), and finally greater than a unity. If the liquidus and solidus temperatures of the alloy are less than the melting point of the intermediate component and correspondingly greater than that of the low melting point component, in this alloy the equilibrium distribution coefficients of the high and medium melting point components are always more than a unity, while that of the low melting point component is less than a unity.

In a four-component system with continuous solid solutions five composition ranges with different combinations of distribution coefficients of the components are possible. Like in a ternary system, these compositions are determined by the liquidus and solidus temperatures of the alloy and the melting points of the pure components.

The regularities revealed in the equilibrium distribution coefficient values in multi-component systems are most evident at the completely non-equilibrium crystallization of alloys and the controlled directional solidification of ingots with a planar front, and will predetermine the micro-liquation (dendrite liquation) in the first case and the macro-liquation (zone liquation) in the second.

During the crystallization purification of the alloy of impurities, in the system under investigation, depending on the component – the alloy basis, different patterns of component redistribution along the sample length are possible depending on the crystallized fraction (Fig. 7, a – d). If the alloy basis is the most high melting point component $B$ (the alloy with the composition $85 \% B$, $6 \% C$, $5 \% A$, $4 \% D$, provided $D_S = 0$, $D_L \to \infty$), we will have the component distribution presented in Fig. 7, a. As is evident, the content of the most high melting point component $B$ along the ingot length will gradually decrease from the maximum value (~ $87 \%$) to zero at the end. The content of the most low melting point component ($D$) will gradually increase from about $3.5 \%$ at the beginning of the ingot to $100 \%$ at the end. The content of the medium melting point components ($C$ and $A$) will first increase from the minimum values ($1.5 - 2.5 \%$) at the beginning of the ingot to the maximum ($10 - 20 \%$) after the solidification of $0.7 - 0.8$ of the ingot and then decline to zero at the end. The emergence of maxima in the content of the medium melting point components may be attributed to the change in the equilibrium distribution coefficients of these components from $K < 1$ to $K > 1$. 
Equilibrium distribution coefficients of components in two-, three- and four-component continuous solid solutions estimated by their liquidus and solidus temperatures

**Fig. 7** Distribution of the components in alloys, as a function of the fraction of the directionally solidified ingot with a planar crystallization front at $D_S = 0, D_L \rightarrow \infty$
If other components \((A, C, D)\) are the alloy basis, there will be another component distribution (Fig. 7, b – d). If in the alloy the equilibrium distribution coefficients changes from \(K < 1\) to \(K > 1\), there will always be a maximum in the distribution curve (Fig. 7, b, c). The presence of maxima, as it is shown in [4], must be taken into consideration during the crystallization purification of alloys.

Since it is a common practice to determine the liquation of the components in the alloy by means of the coefficient \(D_c = \frac{C_{BO}}{C_{CT}}\), where \(C_{BO}, C_{CT}\) are the contents of the component at the boundary and in the centre of the dendrite cells, respectively, the analysis here outlined does not permit to estimate quantitatively or even qualitatively the liquation of the medium melting point components \(C\) and \(A\). Hence, for multi-component alloys (three-component or more) it is expedient to have experimental data on the micro- and macro-distribution of the components in tabular or graphical form.

4. CONCLUSION
1. Complex regularities of the redistribution of the medium melting point components in three-, four and multi-component continuous solid solution alloys at the equilibrium and non-equilibrium crystallization have been revealed.
2. It has been found out that the equilibrium distribution coefficients of the components in a multi-component continuous solid solution are more than a unity for components the melting point of which is above the liquidus temperature of the alloy; these coefficients are less than a unity for the components the melting temperature of which is below the solidus temperature of the alloy. For components the melting point of which is within the crystallization range of the multi-component alloy, the equilibrium distribution coefficient is less than a unity at the beginning of the process, then is equal to the unity, and at the end of the process is more than a unity.

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LITERATURE