

# ANALYSIS OF THE EQUILIBRIUM CRYSTALLIZATION OF THE BINARY EUTECTIC IN THE TERNARY SYSTEM

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## Abstract

In the work the mechanism of the equilibrium and non-equilibrium crystallization of the alloys in the ternary system with the monovariant eutectic equilibrium has been investigated. New peculiarities of the equilibrium crystallization of the binary eutectics in the ternary systems have been found out. It is shown that the equilibrium crystallization of the binary eutectics in the ternary systems is going by the diffusion decomposition of the liquid phase ( $M_{DEC}$ ) and the changing of the compositions of the previously precipitated solid phases to the new equilibrium one owing to the diffusion interaction with the liquid phase ( $M_{INT}$ ). A new method of the graphic representation of the element phase equilibrium in the ternary system with the eutectic equilibrium is proposed. Analytical relations have been deduced which make possible to determine the main indices of the equilibrium crystallization of the binary eutectic alloys in the ternary systems  $M_{DEC}$ ,  $M_{INT}$ , i(dm/dt) - crystallization rate at the liquid and solid. Calculations of the equilibrium and non-equilibrium crystallization of the alloys of this system were done using the Thermo-Calc program and experimental investigations of the alloys of this system were carried out.

Keywords: Ternary system, crystallization, binary eutectic, diffusion decomposition, diffusion interaction

#### 1. INTRODUCTION

It is known that the equilibrium crystallization of the solid solution alloys is realized in the crystallization range by the diffusion "decomposition" ( $M_{DEC}$ ) as the result of the temperature decrease and the diffusion interaction ( $M_{INT}$ ), i. e. by changing the composition of the solid phases that precipitated earlier to the new equilibrium composition. The first process is realized by the diffusion of the elements in the liquid phase, the second process - between the liquid and solid phases and in the bulk of the solid phase. These processes are going on simultaneously and when they are completely realized in the crystallization range they provide the balance between the liquid and solid phases [1]. The  $M_{DEC}$  and  $M_{INT}$  factors are the alloy characteristics and by their values one can determine which alloy during the crystallization at the similar heat removal conditions must deviate from the equilibrium faster. The  $M_{DEC}$  and  $M_{INT}$  factors combined with the crystallization rate (*i*) and the values of the equilibrium and particularly non-equilibrium crystallization range make it possible to explain the development of the micro- and macrosegregation, predict the macrograin size and the shrinkage cavity formation in the casting [1, 2]. The practice gives evidence that the crystallization of the binary eutectic in the ternary system follows both the decomposition mechanism, the result is that two solid phases precipitate from the liquid, and the interaction mechanism, since the equilibrium composition of both solid phases changes during the binary eutectic crystallization.

# 2. THEORETICAL INVESTIGATIONS

The present investigations continue our previous work [3, 4].

To analyze the crystallization of the alloys in the ternary system with the monovariant eutectic equilibrium we plotted the phase diagram and set the parameters (**Figure 1**). Two B-C and A-C binary systems represent the phase diagrams of the eutectic type and the third B-A - the diagram with the unrestricted solubility of the



elements in the liquid and solid states. The liquidus and solidus lines and the lines of the changing of the compositions of the solid phases at the three-phase equilibrium are assumed straight (**Figure 1**). The melting temperatures of the elements (A, B, C) and the binary eutectics were the following:  $t_B = 1500 \text{ °C}$ ,  $t_A = 1000 \text{ °C}$ ,  $t_c = 1300 \text{ °C}$ ,  $t_{e1} = 1000 \text{ °C}$ ,  $t_{e2} = 500 \text{ °C}$ . In **Figure 1** the scheme of the changing of the phase composition of the  $C_o$  eutectic alloy (26 % B, 30 % A, 44 % C) at the equilibrium crystallization is shown. At the equilibrium crystallization of the  $C_o$  alloy the liquid phase composition changes along the liquidus line from the  $C_o$  composition to the point 3 composition, the  $\alpha$ -solid solution composition along the a - c line from  $\alpha_1$  to  $\alpha_3$ , the  $\beta$ -solid solution composition along the  $\alpha_3$  and  $\beta_3$  compositions will be revealed in the alloy microstructure. The

mass fractions of these phases will be  $m_{\alpha} = \frac{\beta_3 - C_0}{\beta_3 - \alpha_3}$ ,  $m_{\beta} = \frac{C_0 - \alpha_3}{\beta_3 - \alpha_3}$  (calculations can be made for every

alloy element). The changing of the compositions of all three phases can be perfectly analyzed at the polythermal sections along the a - c,  $e_1 - e_2$ , b - d lines. The analysis of the process shows that the equilibrium crystallization of the alloys with the three-phase monovariant eutectic equilibrium is the crystallization of two solid solutions similar to the continuous solid solutions.



**Figure 1** Projection of the ternary A-B-C system with the eutectic equilibriums in two binary systems (B-C and A-C) and the continuous solubility in the third system (A-B) and the equilibrium crystallization of the  $C_o$  alloy

To analyze in more detail the crystallization process of the alloy compositions located at the  $e_1 - e_2$  line three hypothetic binary phase diagrams were plotted (**Figure 2**) in which the sum of two elements in turn, except one, was assumed the alloy basis and exactly that third element was considered the alloying element [2, 5]. In these hypothetic diagrams the compositions of the coexisting liquid ( $C_L$ ) and solid ( $\alpha$  and  $\beta$ ) phases for every component are indicated and also the average composition of the solid phases for these elements

 $(C_S^{AV})$  is shown. Since the liquid phase composition is always located in the  $e_1 - e_2$  line and the crystallization results in the formation of two phases  $\alpha$  and  $\beta$ , every solid phase will be formed in some peculiar way and will have specific characteristics. Firstly we must determine the equilibrium distribution coefficients for each element for the both solid phases ( $\alpha$  and  $\beta$ ). We need these coefficients to determine the  $M_{DEC}$  and  $M_{INT}$  values.





**Figure 2** Hypothetic binary phase diagrams for ternary alloy compositions located in the  $e_1 - e_2$  line (**Figure 1**)  $C_L$  - equilibrium liquid phase composition;  $\alpha$ ,  $\beta$  - compositions of the equilibrium solid phases;  $C_S^{AV}$  - average equilibrium composition of the two solid phases

In **Figure 2** one can see that the equilibrium distribution coefficient of the A element for the  $\beta$ -solid solution ( $K_{\beta}^{A}$ ) for every alloy composition located at the  $e_1 - e_2$  line is always less than a unity and for the  $\alpha$ -solid solution ( $K_{\alpha}^{A}$ ) differs essentially depending on the initial composition. If the A element content in the initial alloy composition is less than 27 %  $K_{\alpha}^{A}$  <1, when the A content is more than 50 %  $K_{\alpha}^{A}$  >1, and in the alloys with the A content in the range of 27 to 50 % at first  $K_{\alpha}^{A}$  <1, at  $t \approx 620$  °C  $K_{\alpha}^{A}$  =1 and below 620 °C  $K_{\alpha}^{A}$  >1. The equilibrium distribution coefficient of the B element between the  $\alpha$ -solid solution and the liquid is always more than a unity and between the  $\beta$ -solid solution and the liquid is always less than a unity and between the  $\beta$ -solid solution and the liquid is always less than a unity and between the  $\beta$ -solid solution and the liquid is always less than a unity and between the  $\beta$ -solid solution and the liquid is always less than a unity and between the  $\beta$ -solid solution and the liquid is always less than a unity and between the  $\beta$ -solid solution and the liquid is always less than a unity and between the  $\beta$ -solid solution and the liquid is always less than a unity and between the  $\beta$ -solid solution and the liquid is always more than a unity. Since in the hypothetic diagrams the phase composition lines are straight and start from the point of the zero content of the A and B elements and accordingly the distribution coefficients are constant (before the bending) we can determine the crystallization character indices of the alloys located in the binary eutectic line. We have:

$$K = \frac{C_S}{C_L}, \ K_{\alpha} = \frac{C_{\alpha}}{C_L}, \ K_{\beta} = \frac{C_{\beta}}{C_L}, \ m_S = \frac{C_L - C_O}{C_L - C_S} \text{ or } m_S = \frac{C_L - C_O}{C_L (1 - K)},$$
(1)

$$m_{S} = m_{\alpha} + m_{\beta}, \ m_{\alpha} = m_{S} \cdot \frac{C_{\beta} - C_{S}}{C_{\beta} - C_{\alpha}}, \ m_{\beta} = m_{S} \cdot \frac{C_{S} - C_{\alpha}}{C_{\beta} - C_{\alpha}}.$$
(2)

After transformations we obtain: 
$$m_{\alpha} = \frac{C_L - C_O}{C_L (1 - K)} \cdot \frac{K_{\beta} - K}{K_{\beta} - K_{\alpha}}, \quad m_{\beta} = \frac{C_L - C_O}{C_L (1 - K)} \cdot \frac{K - K_{\alpha}}{K_{\beta} - K_{\alpha}}.$$
 (3)

We determine the crystallization rate (i = - dm/dt) for the both solid phases ( $i_{\alpha}$ ,  $i_{\beta}$ ) and the total one ( $i_{tot}$ ):

$$i_{\alpha} = \frac{K_{\beta} - K}{\left(K_{\beta} - K_{\alpha}\right)\left(1 - K\right)} \cdot \frac{t_{L} - t_{e}}{\left(t_{e} - t\right)^{2}}, \ i_{\beta} = \frac{K - K_{\alpha}}{\left(K_{\beta} - K_{\alpha}\right)\left(1 - K\right)} \cdot \frac{t_{L} - t_{e}}{\left(t_{e} - t\right)^{2}}, \ i_{tot} = \frac{t_{L} - t_{e}}{\left(1 - K\right)\left(t_{e} - t\right)^{2}}.$$
(4)

These expressions are true both for K < 1 and K > 1. We obtained the following formulas to determine the alloy fractions crystallizing by the  $M_{DEC}$  and  $M_{INT}$ :

$$M_{DEC}^{\alpha} = \left(\frac{K\ln K}{\left(K-1\right)^2} - \frac{1}{K-1}\right) \cdot \frac{K-K_{\beta}}{K_{\alpha} - K_{\beta}}$$
(5)



$$M_{DEC}^{\beta} = \left(\frac{K \ln K}{(K-1)^{2}} - \frac{1}{K-1}\right) \cdot \frac{K_{\alpha} - K}{K - K_{\alpha}}$$
(6)

$$M_{INT}^{\alpha} = \left(\frac{K}{K-1} - \frac{K\ln K}{\left(K-1\right)^2}\right) \cdot \frac{K-K_{\beta}}{K_{\alpha} - K_{\beta}}$$
(7)

$$M_{INT}^{\beta} = \left(\frac{K}{K-1} - \frac{K\ln K}{\left(K-1\right)^2}\right) \cdot \frac{K_{\alpha} - K}{K_{\alpha} - K_{\beta}}$$
(8)

In the **Table 1** the crystallization character indexes of two alloys located in the  $e_1 - e_2$  line are given, the first alloy is in the region with the radiating liquidus and solidus lines and the second in the region with the converging lines.

 Table 1 Crystallization character indexes of two alloys

Alloy r	10.: (%)	<b>K</b> tot	Κα	Κβ	mα	mβ	М <sup>а</sup> DEC	Μ <sup>α</sup> INT	M <sup>β</sup> DEC	M <sup>β</sup> INT	M <sup>tot</sup> DEC	M <sup>tot</sup> INT
1	15A, 42B, 33C	0.4	0.5	0.2	0.668	0.332	0.432	0.236	0.215	0.117	0.647	0.353
2	60A, 7B, 33C	3	4.5	0.7	0.605	0.395	0.196	0.409	0.128	0.267	0.324	0.676

One can see in the table that the greater fraction of the alloy 1 crystallizes by the diffusion decomposition and the greater fraction of the alloy 2 crystallizes by the diffusion interaction. The crystallization rate at the liquidus and solidus was the following. For the alloy 1:  $i_{\alpha}^{L} = -0.056 \text{ deg}^{-1}$ ,  $i_{\alpha}^{S} = -0.014 \text{ deg}^{-1}$ ,  $i_{\beta}^{L} = -0.028 \text{ deg}^{-1}$ ,  $i_{\beta}^{S} = -0.007 \text{ deg}^{-1}$ . For the alloy 2:  $i_{\alpha}^{L} = -0.007 \text{ deg}^{-1}$ ,  $i_{\alpha}^{S} = -0.03 \text{ deg}^{-1}$ ,  $i_{\beta}^{L} = -0.005 \text{ deg}^{-1}$ ,  $i_{\beta}^{S} = -0.02 \text{ deg}^{-1}$ . This difference will affect the final alloy microstructure and the macrostructure of the cast ingot. In every case the crystallization will go on in the non-equilibrium conditions and both solid phases will have different compositions.



**Figure 3** Relationship of the phase constituents in the Al - 7 % Si - 20 % Ge alloy at the non-equilibrium crystallization (a) and the element distribution in the solid solutions of Al (b) and Si-Ge (c) after the crystallization

Calculations of the equilibrium and non-equilibrium crystallization of two alloy compositions from the Al-Si-Ge system (Al - 9 % Si - 10 % Ge and Al - 7 % Si - 20 % Ge) were made using the Thermo-Calc program. Experimental investigations of the alloy Al - 7 % Si - 20 % Ge were carried out. Both the calculations and experiments showed that two inhomogeneous solid solutions based on Al and Si-Ge form during the crystallization. In **Figure 3** the relationship of the phase constituents in the Al - 7 % Si - 20 % Ge alloy at the completely non-equilibrium process is shown, when the diffusion in the solid phase and between the liquid and solid phases is absent ( $D_S = 0$ ) and the diffusion in the liquid phase is realized in full ( $D_L \rightarrow \infty$ ). In these conditions when the temperature decreases two solid eutectic constituents with different compositions form. The element distribution in the Al solid solution phase is shown in **Figure 3c**.



# 3. EXPERIMENTAL INVESTIGATIONS

Pure commercial elements were used to prepare the Al - 7 % Si - 20 % Ge (wt.%) alloy in the resistance furnace. The total sample mass was 30 g. The aluminum oxide crucible was used. The melting temperature was 800 °C. The melt in the crucible was cooled together with the furnace at the rate ~ 3 K/min. At the temperature 450 °C the sample was rapidly removed from the furnace and cooled in the air. Metallographic sample was prepared and the scanning electron microscope Tescan Vega SBH3 with the Oxford energy dispersive microanalysis attachment was used to analyze its microstructure. In **Figure 4** the map of the element distribution in the alloy microstructure is shown. Three phase constituents result from the analysis: Al crystals, Si-Ge and Ge solid solutions (**Figure 5**). On the basis of the phase composition analysis and calculation results (**Figure 3**) one can suppose that at first the Al based solid solution crystallizes. Then the crystallization of the Al + Si-Ge binary eutectic takes place. The composition of the Si-Ge crystals changes considerably in the course of the crystallization from 55 % Si 45 % Ge to 20 % Si 80 % Ge. In **Figure 5** these are big size grey and white crystals. The further impoverishing of the Si-Ge crystals leads to the fact that at the end of the crystallization there is no Si in them and the formation of the Al + Ge eutectic takes place. These results completely confirm the formation of the phase constituents in the binary eutectic alloys in ternary systems by the non-equilibrium crystallization mechanism.



Figure 4 Electron image (a) and the map of the distribution of the AI (b), Si (c) and Ge (d)in the AI - 7 % Si - 20 % Ge alloy structure





Figure 5 Microstructure of the Al - 7 % Si - 20 % Ge alloy

## 4. CONCLUSION

- 1) It is shown that the equilibrium crystallization of the alloys in the ternary system with the monovariant eutectic equilibrium takes place by the diffusion decomposition  $M_{DEC}$  and the diffusion interaction  $M_{DEC}$ .
- 2) Analytical relationships of the main equilibrium crystallization indexes of the binary eutectic alloys in the ternary system have been deduced.
- 3) It has been found out that at the actual cooling rates the phase constituents of the binary eutectics in the ternary systems have inhomogeneous composition. To balance the compositions it is necessary to apply the homogenizing annealing to the samples.

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