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Two-Phase Segregation of Irregular Fluid Al-Zn-Sn Solution

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ABSTRACT. Based on the canonical form of the Swallowtail catastrophe a new form of Gibbs potential is worked out, which is used for thermodynamic analysis of irregular ternary systems. By means of minimization of above mentioned potential and by the use of Lagrange transformation the numerical values of coordinates of critical point are calculated for irregular fluid Al-Sn-Zn solution, as the result of which we have determined the process of two-phase segregation of the given solution with the formation of an immiscibility gap. *© 2010 Bull. Georg. Natl. Acad. Sci.*

Key words: *swallowtail catastrophe, Gibbs potential, Lagrange transformation, phase segregation.*

The study and definition of segregation processes is a matter of highly topical interest, allowing to judge the advisability of application of a given alloy for different purposes. The segregation processes have a negative effect on structural alloys. At the same time these processes contribute to the development of composite materials. For experimental study of such processes the traditional methods of X-ray diffraction (XRD) are used. However, application of this method to measuring the parameters of crystal lattice is rendered difficult in multi-component systems.

The theoretical investigation of a three-component Al-Zn-Sn system is presented in this paper. The experimental studies [1] have shown that the thermal effects are especially increased due to the significant composition change during the process of crystallization.

For thermodynamic analysis of irregular ternary solutions, a new form Gibbs potential (1) is worked out, which is an equivalent to the "swallowtail" catastrophe [2]:

$$\begin{aligned} G = {} & zx\left[A_0 + A_1(z-x) + A_2(z-x)^2 + A_3(z-x)^3 \right] + \\ & + zy\left[B_0 + B_1(z-y) + B_2(z-y)^2 + B_3(z-y)^3 \right] + \\ & + yx\left[C_0 + C_1(y-x) + C_2(y-x)^2 + C_3(y-x)^3 \right] + \\ & + x^2yzD_0 + xy^2zD_1 + xyz^2D_2 + \\ & + RT\left[x\ l_n(x) + y\ l_n(y) + z\ l_n(z) \right] + \\ & + {}^0G_1 x + {}^0G_2 y + {}^0G_3 z \ . \end{aligned} \tag{1}$$

Here A_i, B_i and C_i are four-member coefficients of binary interaction; D_i is the three-member coefficient of ternary interaction. They consist of parts linearly dependent and independent on temperature: $A_i = A_{io} + A_{it}T$, $B_i = B_{io} + B_{it}T$, $C_i = C_{io} + C_{it}T$ and $D_i = D_{io} + D_{it}T$, R - constant of entropy, which is equal to 8.31 Joule; T - temperature, K; ${}^0G_1$, ${}^0G_2$, ${}^0G_3$ - potentials of pure elements; x, y, z - mass fractions of constituent elements, where $z=1-x-y$.

Table

The coefficients of binary and ternary interaction $(K_i=K_{0i}+K_{ti}T)$ for irregular fluid Al-Sn-Zn solution; i=0,1,2,3.

Binary and ternary systems	Members of coefficients independent on the temperature $K_{0i}(A_{0i}, B_{0i}, C_{0i}, D_{0i})$				Members of coefficients linearly dependent on the temperature $K_{ti}(A_{ti}, B_{ti}, C_{ti}, D_{ti})$			
	K_{00}	K_{01}	K_{02}	K_{03}	K_{T0}	K_{T1}	K_{T2}	K_{T3}
Al–Zn	10288	-810.56	-6452	578.12	-3.35	5.28	2.75	-2.43
Al–Sn	7998.78	4403.24	3209.13	344.76	-4.41	-2.37	-4.21	1.79
Zn–Sn	12592	-5064	-2893	255.28	-8.72	3.19	-1.94	2.57
Al-Zn-Sn	9518.53	-6930	7754.65	473.44	-41.83	-2.46	6.88	-3.12

The theoretical basis of the given investigation is an analysis of the critical point of irregular three-component solution by means of minimization of Gibbs potential and by the use of Lagrange transformation.

According to the method of Lagrange transformation, the Cartesian coordinate system is the substitute for the initial coordinate system. The possibility of such transformation follows from an explanation of the critical point, where the degree of freedom F is the feature of the system and does not depend on the group of discrete coordinates. According to Lagrange: $F=n-m$, where n is the number of coordinates, m is the amount of limitation. For our case, n=3 and m=2; i.e. we have two limitations ($z=1-x-y$; $0<x+y<1$) and three coordinates: (x,y,z). Accordingly, the degree of freedom is equal to one, which enables to carry out transformation of one of the axes of coordinates (in our case - x). As a result, the Cartesian coordinate x' replaces the coordinate x and connects with the initial one by means of the coefficient φ_x: $x'=x+\varphi_x y$. The coordinate y is not changed, i.e. $y=y'$. Accordingly, for the second derivatives we have:

$$G_{y'y'}=G_{yy},\ G_{x'x'}=G_{xx}-G_{yy}\varphi_x^2,\ G_{x'y'}=G_{xy}+\varphi_x G_{yy};$$

whence $\varphi_x=-\dfrac{G_{xy}}{G_{yy}}$.

According to the proposed mathematical method of analysis, an irregular three-component solution will be segregated into two isomorphic phases, if we calculate such numerical values for the critical temperature and critical concentrations, which will simultaneously equate to zero the Hessian matrix determinant (2) and the third derivative of Gibbs potential (3):

$$|H|=G_{xx}G_{yy}-(G_{xy})^2=0, \quad (2)$$

$$G_{xxx}+3\varphi_x G_{xxy}+3(\varphi_x)^2 G_{xy}+(\varphi_x)^3 G_{yyy}=0 \quad (3)$$

Based on the above mentioned, it became necessary to differentiate the Gibbs potential to the third order, where the critical temperature T and critical concentrations x, y are unknown members. For calculation of these variables we have used standard computer programs: Goal "Seek" and "Solver". The

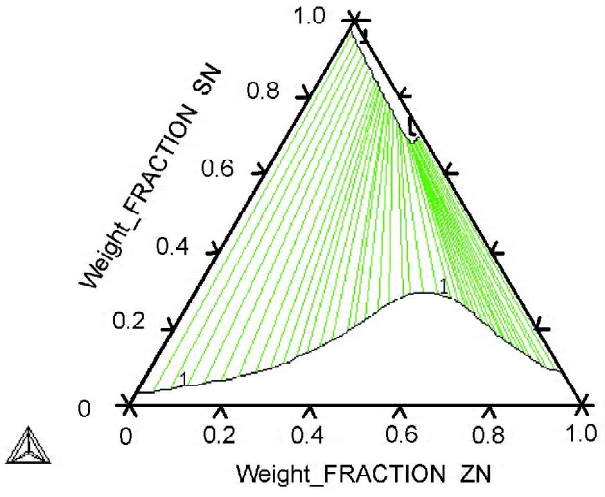

Fig.1. Isothermal section of irregular fluid Al-Sn-Zn solution segregated into two isomorphic phases at 500K temperature

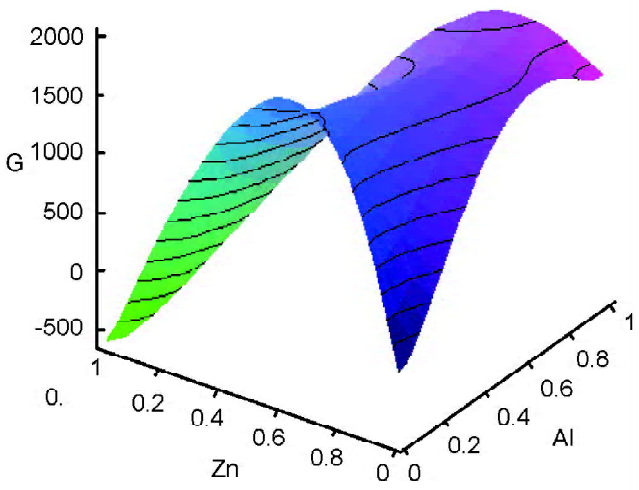

Fig. 2. Diagram of elements concentrations dependency on the Gibbs potential of irregular fluid Al-Zn-Sn solution, segregated into two isomorphic phases at 500K temperature

numerical values of interaction coefficients: A_i, B_i, C_i, D_i are known from the database of alloy systems [3], which are presented in the Table:

As a result, the numerical values of Lagrange transformation coefficient j_x=0.144 and the coordinates of the critical point T_{cr}=517.25 *K;* x_{cr}=0.53(*Al*); y_{cr}=0.44(*Zn*); z_{cr}=1-x_{cr}-y_{cr}=0.03(*Sn*) are calculated for an irregular fluid Al-Sn-Zn solution. On the basis of these values the process of segregation of this solution into two isomorphic phases below the critical temperature is determined.

The isothermal section (Fig.1) of two-phase segregation diagram of irregular fluid Al-Zn-Sn solution and the diagram of elements concentrations dependency on the Gibbs potential (Fig.2) are built by the use of CALPHAD [4] at 500K temperature.

The equilibrium concentrations have been calculated for the segregated phases at 500K temperature:

Al_1=0.51, Zn_1=0.32, Sn_1=0.17; Al_2=0.11,
Zn_2=0.64, Sn_2=0.25

The formation of thermodynamic model of three component system alloys is possible by the use of an equivalent form of catastrophe theory. With the help of this model it is possible to calculate the numerical values of coordinates of critical points for irregular ternary solutions. The phase segregation process with the immiscibility gap formation will be determined on the basis of these values for a given solution.

მასალათმცოდნეობა

არარეგულარული თხევადი Al-Zn-Sn ხსნარის ორ ფაზად განშრევება

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კატასტროფების თეორიის A_4(მაქაონი) კანონიკურ ფორმაზე დაყრდნობით შემუშავდა გიბსის პოტენციალის ახალი ფორმა, რომელიც გამოიყენება არარეგულარული სამკომპონენტიანი სისტემების თერმოდინამიკური ანალიზისათვის. მიღებული პოტენციალის მინიმიზაციით და ლაგრანჟის გარდაქმნის გამოყენებით გაანგარიშდა კრიტიკული წერტილის კოორდინატების რიცხვითი მნიშვნელობები არარეგულარული თხევადი Al-Zn-Sn ხსნარისთვის, რომლის საფუძველზე დადგინდა მოცემული ხსნარის ორ ფაზად განშრევების პროცესის მიმდინარეობა შეურევლობის არეების წარმოქმნით.

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