Calculation of the state diagrams of binary Sn-Pb and Pb-Sb solutions in the framework of the generalized lattice model

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Abstract. This paper is devoted to a theoretical study of mono- and non-invariant equilibria in binary Sn-Pb and Pb-Sb solutions. Modeling of Sn-Pb and Pb-Sb solutions was carried out within the framework of the generalized lattice model, corresponding eutectic phase diagrams were obtained.

1. Introduction

Binary lead-based alloys, such as Sn-Pb and Pb-Sb, are widely used in a wide variety of industries. In particular, solid solutions of Sn-Pb and Pb-Sb are traditionally used as solders in microelectronics, including for particularly strong soldering. In this connection, the study of phase equilibria in Sn-Pb and Pb-Sb systems over a wide range of temperatures and concentrations is an important task in materials science. It should be noted that most of the data on phase equilibria in these binary systems is experimental (see, for example, [1]), which makes it difficult to predict the thermal and mechanical properties of Sn-Pb and Pb-Sb alloys as their compositions and / or temperature change. This paper is devoted to the theoretical construction of phase diagrams of Sn-Pb and Pb-Sb solutions within the framework of the generalized lattice model (GLM) (see, for example, [2-4]).

2. The model

It has been experimentally noted [1] that the phase diagrams of Sn-Pb and Pb-Sb solutions refer to the same type of eutectic phase diagrams and are characterized by the limited solubility of both components in the solid state (see Figure 1).

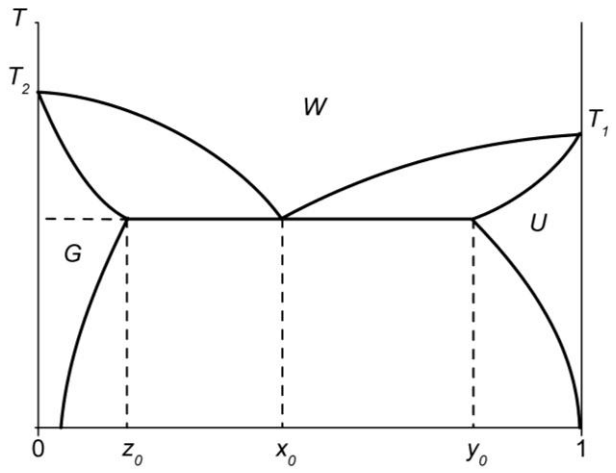

Figure 1. Phase diagram of a binary system of eutectic type in the presence of mutual solubility of components in the solid state.

According to the main provisions of the GLM, the chemical potentials of a binary homogeneous solution (per 1 mole of substance) have the following form [4]

$$\mu_1 = \mu_{10} + RT\ln x + W\lambda\left(\frac{1-x}{x+\lambda(1-x)}\right)^2, \quad \mu_2 = \mu_{20} + RT\ln(1-x) + W\left(\frac{x}{x+\lambda(1-x)}\right)^2, \qquad (1)$$

where μ_{i0} is the standard value of the chemical potential of the *i* component, *x* is the mole fraction of the first component; *T* - temperature of the system, reduced to the absolute scale; R is the universal gas constant, *W* is an analog of the mixing energy in the GLM; $\lambda = \omega_2 / \omega_1$ is the ratio of "owned" atomic volumes of components, here ω_i – the "owned" volume of atoms of the *i* component.

Let *x*, *y* and *z* be the molar fractions of the first component in the liquid phase, in the solid α-solution and in the solid β-solution, respectively. We also agree to denote the mixing energies of the melt and solid-and-solutions by the letters *W*, *U* and *G*. Then the relations (1) determine the concentration dependences of the chemical potentials of the components in the liquid phase (melt), and analogous relationships corresponding to the solid α-solution and the β-solution look like

$$\mu_1^{\alpha} = \mu_{10}^{S} + RT\ln y + U\lambda\left(\frac{1-y}{y+\lambda(1-y)}\right)^2, \quad \mu_2^{\alpha} = \mu_{20}^{S} + RT\ln(1-y) + U\left(\frac{y}{y+\lambda(1-y)}\right)^2, \quad (2)$$

and

$$\mu_1^{\beta} = \mu_{10}^{S} + RT\ln z + G\lambda\left(\frac{1-z}{z+\lambda(1-z)}\right)^2, \quad \mu_2^{\beta} = \mu_{20}^{S} + RT\ln(1-z) + G\left(\frac{z}{z+\lambda(1-z)}\right)^2. \quad (3)$$

For the further calculation of the state diagram, it is necessary to calculate four OPM parameters: W, U, G and λ. To this end, we consider a non-invariant three-phase equilibrium, characterized by the compositions of coexisting phases x_0, y_0 and z_0 at an eutectic temperature T_0. In addition, the conditions of chemical equilibrium in the three-phase system must be met, i.e.

$$\mu_1^L(x_0,T_0) = \mu_1^{\alpha}(y_0,T_0) = \mu_1^{\beta}(z_0,T_0), \quad \mu_2^L(x_0,T_0) = \mu_2^{\alpha}(y_0,T_0) = \mu_2^{\beta}(z_0,T_0). \qquad (4)$$

Using the expressions for the chemical potentials (1) - (3) and the chemical equilibrium conditions (4), it is not difficult to express the parameters W, U, G and λ through the coordinates of the ends of the eutectic conode, the calculation method of which is described in detail in [5].

A further calculation of the phase diagram reduces to modeling the corresponding two-phase equilibria above (or below) the temperature of the eutectic. Thus, in particular, the problem of calculating the liquidus and solidus curves splits into two:

i. Liquid—solid α-solution equilibrium $\left(x > x_0, y > y_0, T > T_0\right)$:

$$T(x,y) = \frac{q_1 T_1 + W\lambda\left(\frac{1-x}{x+\lambda(1-x)}\right)^2 - U\lambda\left(\frac{1-y}{y+\lambda(1-y)}\right)^2}{q_1 - \ln\left(\frac{x}{y}\right)} = \frac{q_2 T_2 + W\left(\frac{x}{x+\lambda(1-x)}\right)^2 - U\left(\frac{y}{y+\lambda(1-y)}\right)^2}{q_2 - \ln\left(\frac{1-x}{1-y}\right)}. \quad (5)$$

ii. Liquid—solid β-solution equilibrium $\left(x < x_0, z < z_0, T > T_0\right)$:

$$T(x,z) = \frac{q_1 T_1 + W\lambda\left(\frac{1-x}{x+\lambda(1-x)}\right)^2 - G\lambda\left(\frac{1-z}{z+\lambda(1-z)}\right)^2}{q_1 - \ln\left(\frac{x}{z}\right)} = \frac{q_2 T_2 + W\left(\frac{x}{x+\lambda(1-x)}\right)^2 - G\left(\frac{z}{z+\lambda(1-z)}\right)^2}{q_2 - \ln\left(\frac{1-x}{1-z}\right)}. \quad (6)$$

Here $q_i = \Delta H_i / RT_i$, where ΔH_i is the latent heat of the liquid-solid transition in pure components; T_i - melting points of pure components, reduced to an absolute scale.

Finally, for a two-phase equilibrium of a solid α-solution — solid β-solution $\left(y > y_0, z < z_0, T < T_0\right)$, we have

$$T(y,z) = \frac{G\lambda\left(\frac{1-z}{z+\lambda(1-z)}\right)^2 - U\lambda\left(\frac{1-y}{y+\lambda(1-y)}\right)^2}{\ln\left(\frac{y}{z}\right)} = \frac{G\left(\frac{z}{z+\lambda(1-z)}\right)^2 - U\left(\frac{y}{y+\lambda(1-y)}\right)^2}{\ln\left(\frac{1-y}{1-z}\right)}. \quad (7)$$

Thus, using the closed system of equations (5) - (7), it is possible to construct a phase diagram of the eutectic type in the entire range of concentrations and temperatures.

3. Diagram calculations and discussion of the results

Using the method of Ref. 6, the GLM parameters for the Sn-Pb and Pb-Sb systems were obtained, which are given in Table 1.

Table 1. GLM parameters

A-B	q_1	q_2	λ	W/R, K	U/R, K	G/R, K
Sn–Pb	0.955	1.684	0.874	688.4	1036.4	1820.3
Pb–Sb	2.717	0.955	4.395	-572.3	2403.8	6726.5

Figure 2 shows the results of modeling the Sn-Pb and Pb-Sb state diagrams, taking into account the GLM parameters given above.

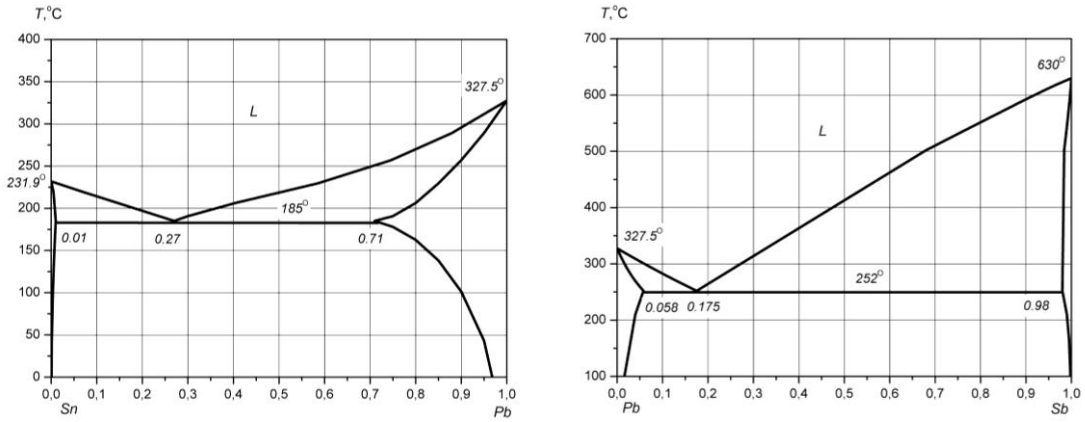

Figure 2. Sn–Pb and Pb–Sb state diagrams

The obtained state diagrams correspond the generalized diagrams of the Sn-Pb and Pb-Sb binary systems presented in [1], which indicates the adequacy of the proposed model.

In conclusion, we note that the GLM can be used to construct phase diagrams of practically any real binary solutions of the eutectic type both in the absence of solubility of the components in the solid state and in the presence of mutual solubility of the components.

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