

Thermodynamic Calculation and 3D Modeling of the Liquidus and Immiscibility Surfaces of the Ge–Cu–Tl System

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Authors' contributions

This work was carried out in collaboration between all authors. Authors ANM and LFM managed the literature searches and wrote the first draft of the manuscript. Author ZES synthesized samples and carried out their DTA. Authors ANM and MBB carried out the calculation and 3D visualization of the crystallization and immiscibility surfaces. All authors read and approved the final manuscript.

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ABSTRACT

This work devoted to the calculation and 3D visualization of the crystallization surface of Ge and immiscibility surface of alloys based on thallium and copper in the Cu-Tl-Ge system. For determining and modeling these properties were used thermodynamic equations which are solved based on thermodynamic information obtained from the phase diagram of the binary boundary systems by using a limited number of experimental data for the ternary system. The calculation and visualization of immiscibility in the concentration range $x_{Ge}=0\div 0.55$ and crystallization surfaces of Ge in the concentration range $x_{Ge}=0.55\div 1.0$ mole fraction for section $y_{Pb}=x_{Pb}/(x_{Pb}+x_{Tl})=0\div 1$ were performed by the program OriginLab2015 and grafikus.ru/plot3d.

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Keywords: Thermodynamic calculation; free energy; 3D visualization; immiscibility and crystallization surfaces; Cu-Tl-Ge system.

1. INTRODUCTION

The solid solutions and intermetallic phases of the ternary Cu–Tl–Ge(Sn,Pb) system are perspective materials due to their high values of electrical and thermal conductivity, corrosion resistance and ductility. 3D modeling of the surface for liquid phases and crystallization surface in the Cu-Pb-Tl ternary system carried out in [1,2]. The phase diagrams of Ge-Cu, Ge-Tl, Cu-Tl boundary subsystems and the Ge-Cu-Tl ternary system have been studied in [3-6]. The germanium crystallization surface in the ternary system Cu-Ge-Tl has been calculated and 3D modeled in [7]. The Cu-Ge-Tl system is characterized by immiscibility region in the liquid phase. At the 1241 K monotectic temperature, the immiscibility region extends from 0.17 to 0.845 mole fraction Cu. The critical temperature of solubility is 1533 K. With the addition of germanium critical temperature decreases and further intersects with the surface of the liquidus of germanium since the composition of $x_{Ge} = 0.55$. However, the thermodynamic analysis and 3D modeling of the Cu-Ge-Tl system is not carried out yet.

The aim of present work is thermodynamic calculation and 3D modeling of the Ge

crystallization surface and immiscibility surface of ternary alloys in the Cu-Tl-Ge system.

2. METHODS

2.1 Thermodynamic Calculations

The partial molar excess free energy of Ge for saturated liquid alloys of the Ge-Cu and Ge-Tl systems are calculated by the equation from [8]:

$$\overline{\Delta G_{Ge}^{exs,l}} = T[\Delta S_{Ge}^m - 8.311 \ln(x_{Ge}^l)] - \Delta H_{Ge}^m \quad (1)$$

x_{Ge}^l - is mole fraction of Ge in liquid solution; T - is liquidus temperature of Ge;

$T_{Ge}^m, \Delta H_{Ge}^m$ - are melting point and molar enthalpy of Ge: $T_{Ge}^m = 1211$ K; $\Delta H_{Ge}^m = 37000$ J·mol⁻¹ [9];

$\Delta S_{Ge}^m = \Delta H_{Ge}^m / T_{Ge}^m$ - is molar entropy of melting of Ge; $\Delta S_{Ge}^m = 30.53$ J·mol⁻¹K⁻¹ [9];

$\overline{\Delta G_{Ge}^{exs,l}}$ - is partial molar excess free energy of Ge (in J·mol⁻¹), associated with the thermodynamic activity and activity coefficient on relation $\overline{\Delta G_{Ge}^{exs,l}} = RT \ln \gamma_{Ge} = RT \ln \left(\frac{a_{Ge}}{x_i} \right)$.

The values of the partial excess free energy of Ge in the Ge-Cu and Ge-Tl systems are presented in Fig. 1.

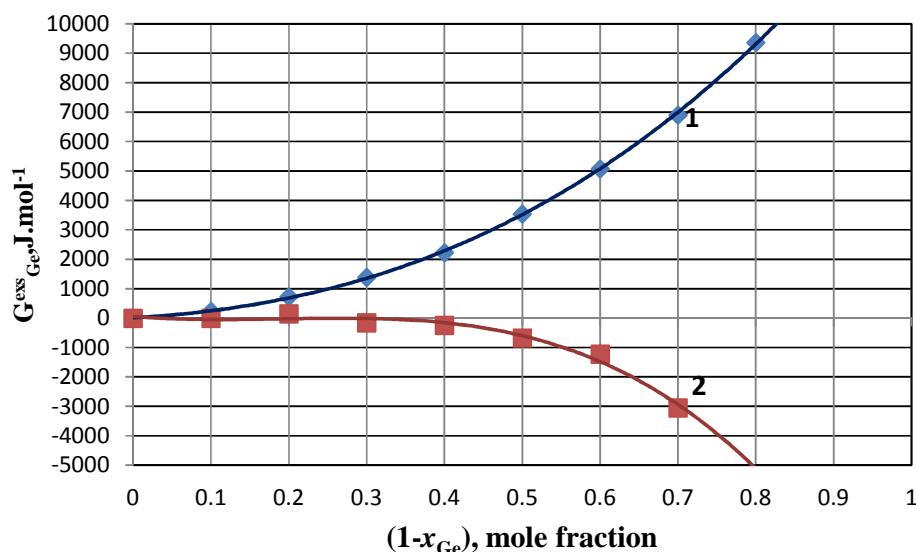


Fig. 1. The relationship between the partial excess free energy of Ge and concentration

1: $\overline{\Delta G_{Ge}^{exs,l}} = 5357x^3 + 8412x^2 + 1466x$; Ge-Tl; $x=(1-x_{Ge})$

2: $\overline{\Delta G_{Ge}^{exs,l}} = -23449x^3 + 13311x^2 - 2100x$; Ge-Cu; $x=(1-x_{Ge})$

On the basis of analytical expressions given below the Fig. 1 the following relationship, which approximates the partial excess Gibbs free energy of Ge on crystallization surface of this compound in the Ge–Cu–Tl system were received:

$$\begin{aligned} \overline{\Delta G}_{Ge}^{exs,l}(Ge - Cu - Tl) = & \\ (5357x^3 + 8412x^2 + 1466x)y + (-23449x^3 & \\ + 13311x^2 - 2100x)(1-y) + 500x(1-x)y(1-y) & \end{aligned} \quad (2)$$

In equation (2):

$$x = x_{Ge} = 0.55 \div 1; \quad y = x_{Tl} / (x_{Cu} + x_{Tl}) = 0 \div 1;$$

$$T = \left[\frac{37000 + (5357x^3 + 8412x^2 + 1466x)y + (-23449x^3 + 13311x^2 - 2100x)(1-y) + 500x(1-x)y(1-y)}{30.53 - 8.311 \ln x} \right] \quad (4)$$

By using this equation the 3D modeling of liquidus surface of germanium in the ternary system Ge–Cu–Tl is carried out (Fig. 3).

Function $500x(1-x)y(1-y)$ is determined on the basis of a limited number of data points on the phase diagram of ternary system [6]. 3D model of the surface of the partial excess Gibbs free energy of Ge in liquid alloys, saturated by this component, is shown in Fig. 2.

Let's write equation (1) in the following form:

$$T = \frac{\Delta H_{Ge}^m + \overline{\Delta G}_{Ge}^{exs}}{\Delta S_{Ge}^m - 8.311 \ln x_{Ge}} \quad (3)$$

By inserting values $\Delta H_{Ge}^m = 37000$, $\Delta S_{Ge}^m = 30.53$ and analytical expression (2) in (3), we get following the equation:

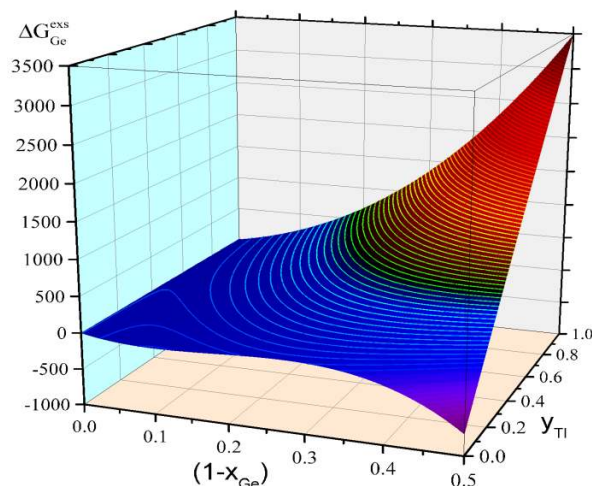


Fig. 2. 3D model of partial excess Gibbs free energy of Ge on crystallization surface of this component in the Ge–Cu–Tl system

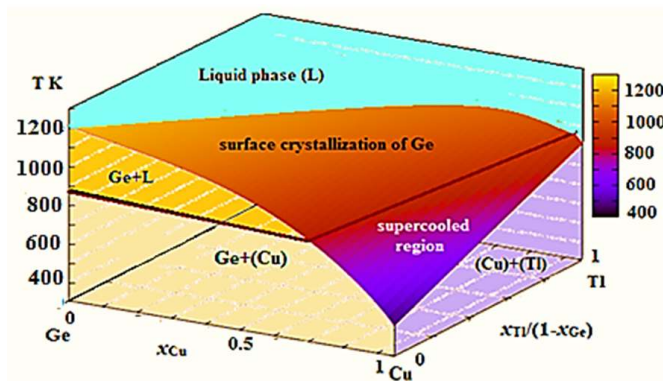


Fig. 3. 3D model of crystallization surface of the Ge in the Ge–Cu–Tl system [7]

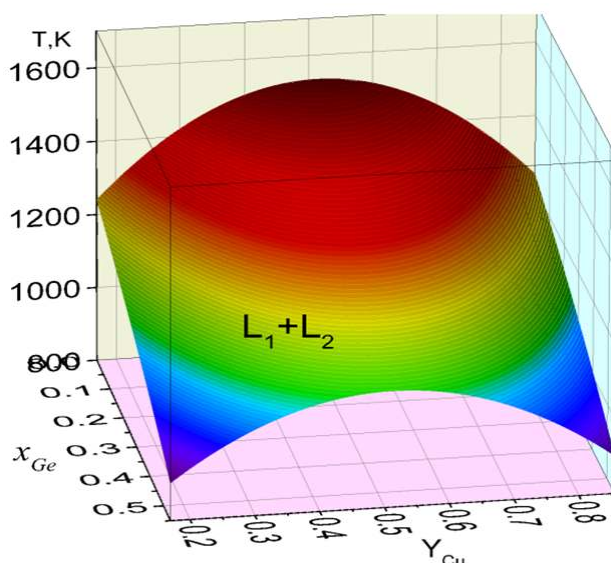


Fig. 4. 3D model of immiscibility surface in the Ge–Cu–Tl system

2.2 Modeling of Immiscibility Surface

The Cu-Tl system has a phase diagram with a monotectic (1241 K) and a eutectic (566 K) equilibrium. At the monotectic temperature, the immiscibility region is located in the concentration range $x_{Cu}=0.17 \div 0.845$. The critical temperature of solubility (1533 K) is decreased with the addition of germanium [6]. Proceeding from the above and using limited number of data points of DTA, the immiscibility surface for the Ge–Cu–Tl system was approximated by a following relationship:

$$T^{\circ}K = \frac{1241(1-x_{Ge})^{0.4} + 2500(0.855-y)(y-0.17)}{(1-x_{Ge})^{0.4}} \quad (5)$$

where: $y=y_{Cu}=0.17 \div 0.855$; $x_{Ge}=0 \div 0.55$. Relationship (5) in the form of 3D to graph in above Fig. 4.

3. RESULTS AND DISCUSSION

The behavior of partial excess Gibbs free energy of Ge on the liquidus in the Ge-Cu and Ge-Tl systems is significantly different (Fig.1). In the Ge-Cu system with increasing of copper content negative deviation from the properties of ideal solutions increases, which is related to the formation of extensive (up to 12 at %Cu) solid solution region and a number of intermediate phases in phase diagram of Ge-Cu [4,5]. Alloys of the Ge-Tl systems and Ge-Cu-Tl at $x_T > x_{Cu}$ exhibit a positive deviation from the properties of

ideal solutions, which increases with increasing of the thallium content. This is due to the immiscibility region for liquid alloys with a high content of thallium [5,6]. The partial excess free energy Ge monotonically depends on the ratio $x_T > x_{Cu}$ (Fig. 2). This is in accordance, that the ternary compound in the Ge-Cu-Tl system is not formed. Thus, the thermodynamic data of alloys in accordance with 3D model of monovariant equilibria surfaces of the Ge-Cu-Tl system.

4. CONCLUSION

3D analytical modeling of the crystallization surface of Ge and immiscibility surface of alloys, based on thallium and copper in the Cu-Tl-Ge system are carried out for the first time. This problem is solved by using the thermodynamic information obtained from the phase diagram of the binary boundary systems and a limited number of experimental data for the ternary Cu-Tl-Ge system. This analytical method can be used for the 3D modeling of more complex ternary system.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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