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MULTI-3D MODELING OF THE LIQUIDUS AND IMMISCIBILITY SURFACES IN THE Cu–Pb–Te SYSTEM

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Based on thermodynamic calculations and analysis of experimental literature data the fields of the primary crystallization of the phases, the types and coordinates of non and monovariant equilibria in the Cu–Pb–Te system are determined. It has been revealed that the ternary compound is not formed in the system, and in the solid state it is divided into subsystems with the participation of lead telluride: Cu–PbTe–Pb, Cu–Cu_{2-x}Te–PbTe, Cu_{2-x}Te–Cu₅Te₃–PbTe, Cu₅Te₃–Cu₄Te₃–PbTe, Cu_{3-x}Te₂–CuTe–PbTe, CuTe–Te–PbTe. The projection of the liquidus surface Cu–Pb–Te is determined. On the basis of phase diagrams of the boundary binary systems and the limited number of DTA data of the ternary system by using the OriginLab program, equations are obtained for calculating and 3D modeling of the PbTe, CuTe, Cu_{2-x}Te, Cu_{3-x}Te₂, and Cu₅Te₃ crystallization surfaces and the surface of the liquid immiscibility in the Cu–Pb–Te system. There are regions of immiscibility for the liquid phase from the side Cu–Cu_{2-x}Te and Cu–Pb. With an increase quantity of the third component, the critical temperature immiscibility decreases. Defined in the work 3D model for the system Cu–Pb–Te keeps the corresponding analytical function and table data in the form of matrices.

Keywords: Cu–Pb–Te system, phase diagram, liquidus surface, 3D modeling.

Introduction

Copper chalcogenides with s^2p^2 and s^2p^3 elements have semiconductor, photoelectric, thermoelectric, optical and other functional properties [1–3]. These compounds and phases on the basis of them have mixed ion-electron conductivity and are promising materials for the manufacture of sensors, electrodes and solid electrolytes [4–6]. Cu–Pb–Te alloys also have anticorrosion properties and are used as a coating for electrical cables of underwater installations operating under high voltage conditions [7]. To determine the optimal conditions for the directed synthesis of chalcogenide phases, reliable data on the phase equilibria and thermodynamic functions of the corresponding systems are necessary [8]. Previously, we presented the results of complex studies for ternary systems Ag–Ge–Se [9], Ag–Sn–Se [10], Ag–Pb–Se [11], Ag–Pb–Te [12], Ag–Bi–Se [13], Ag–Bi–Te [14], Cu–Pb–Se [15] and Cu–Bi–Se [16].

To date, the phase diagram of the Cu–Pb–Te system has been insufficiently studied. The phase diagram of the Cu₂Te–PbTe quasibinary section was studied in [4, 17]. The book [3] presents the liquidus surface and the coordinates of invariant equilibria in the Cu–Pb–Te

system. However, in [3], the phases of the composition of Cu₅Te₃ and Cu_{3-x}Te₂ were not taken into account. It should be noted that there is conflicting information about the phase diagram of the Cu–Te boundary system. Thus, according to [18], in this system, Cu_{2-x}Te, Cu_{3-x}Te₂ and CuTe_{1-x} phases are formed. In the state diagram given in [19], instead of the Cu_{3-x}Te₂ phase ($x = 0.2 \div 0.35$), Cu₄Te₃ is indicated. Recalculation of the compositions of the phases showed that the formula Cu₄Te₃ corresponds to the composition Cu_{3-x}Te₂, in which $x = 0.33$. In the phase diagrams given in [18] as well as in [19], the phase regions corresponding to the composition of Cu₅Te₃ are shown. However, this formula is not given by them.

The purpose of this work is thermodynamic analysis and multi-3D modeling of the liquidus surfaces of all phases and immiscibility areas in the Cu–Pb–Te liquid system over the entire concentration range.

Thermodynamic analysis

For triangulation system Cu–Pb–Te is important to determine the direction of reactions involving lead telluride, and copper telluride, in particular reactions:

The temperature dependences of the Gibbs free energies of these reactions were determined using the Ulikh equation [20]:

$$\Delta G_T^0 = \Delta H_{298}^0 - T \Delta S_{298}^0 - \Delta c_{p,298}^0 T \ln \left[\left(\frac{T}{298} \right) + \left(\frac{298}{T} \right) - 1 \right], \quad (3)$$

where ΔH_{298}^0 and ΔS_{298}^0 – integral standard enthalpies and entropies of compounds; $\Delta c_{p,298}^0$ – change in the molar isobaric heat capacity of the substances involved in the reactions. These values are used to determine the temperature dependence of the Gibbs energy of Equation (3), taken from [21, 22]: $\Delta H_{298}^0(\text{CuTe}) = -25100$ J/mol, $S_{298}^0(\text{CuTe}) = 86.67$ Jmol⁻¹K⁻¹, $\Delta c_{p,298}^0(\text{CuTe}) = 54.47$ Jmol⁻¹K⁻¹, $\Delta H_{298}^0(\text{Cu}_2\text{Te}) = -41870$ J/mol, $S_{298}^0(\text{Cu}_2\text{Te}) = 134.8$ Jmol⁻¹K⁻¹, $\Delta c_{p,298}^0(\text{Cu}_2\text{Te}) = 77.67$ Jmol⁻¹K⁻¹, $\Delta H_{298}^0(\text{Cu}_3\text{Te}_2) = -72357$ J/mol, $S_{298}^0(\text{Cu}_3\text{Te}_2) = 195.786$ Jmol⁻¹K⁻¹, $\Delta H_{298}^0(\text{Cu}_5\text{Te}_3) = -115771$ J/mol, $S_{298}^0(\text{Cu}_5\text{Te}_3) = 313.3$ Jmol⁻¹K⁻¹, $\Delta H_{298}^0(\text{PbTe}) = -68575$ J/mol, $S_{298}^0(\text{PbTe}) = 110.039$ Jmol⁻¹K⁻¹, $\Delta c_{p,298}^0(\text{PbTe}) = 50.542$ Jmol⁻¹K⁻¹, $S_{298}^0(\text{Pb}) = 64.810$ Jmol⁻¹K⁻¹, $\Delta c_{p,298}^0(\text{Pb}) = 26.442$ Jmol⁻¹K⁻¹, $S_{298}^0(\text{Cu}) = 33.149$ Jmol⁻¹K⁻¹, $\Delta c_{p,298}^0(\text{Cu}) = 24.434$ Jmol⁻¹K⁻¹.

The temperature dependences of the free energy of reactions (1) and (2), respectively, have the form

$$\Delta G_T^0 = -26705 + 23.273T + 4.702T \left[\ln \left(\frac{T}{298} \right) + \left(\frac{298}{T} \right) - 1 \right], \quad (4)$$

$$\Delta G_T^0 = -43475 + 8.292T + 5.936T \left[\ln \left(\frac{T}{298} \right) + \left(\frac{298}{T} \right) - 1 \right]. \quad (5)$$

From Figure 1 follows that in the considered temperature range the reactions (1) and (2) are directed towards the formation of PbTe. Other reaction options were considered, in particular

The temperature dependences of the free energies of these reactions, as in the case of reactions (1) and (2), showed that reactions (6) and (7) are also directed toward the formation of PbTe. Consequently, in the solidus part, sections with lead telluride are stable. Processing the totality of the experimental data using literature data on the boundary binary systems Cu–Te, Pb–Te and Cu–Pb and the results of thermodynamic analysis allowed us to triangulate the system Cu–Pb–Te in the form shown in Figure 2.

3D modeling surfaces of liquidus and immiscibility

For 3D modeling of the surfaces of monovariant equilibria in the ternary system 1–2–3, the temperature dependences on the composition are determined as an explicit function $T = f(x, y)$, where x is the atomic fraction of the basis component, of let us assume component 1; y is the fraction of component 2. We take such that $x = x_1$, then $y = x_2/(x_2 + x_3)$. In the system Cu–Pb–Te, the basic component 1 is Te, which strongly interacts with Pb (2) and Cu (3), forming a series of compounds. Consequently $x = x_1 = x_{\text{Te}}$, $y = x_2/(x_2 + x_3) = x_{\text{Pb}}/(x_{\text{Pb}} + x_{\text{Cu}})$.

For analytical 3D-modeling of the surfaces of monovariant equilibria of the Cu–Pb–Te system, the method previously successfully tested in [9–12] was used. The following analytical expressions were obtained for the crystallization surfaces of PbTe, Cu_{2-x}Te, CuTe, Cu₅Te₃ and Cu_{3-x}Te₂ compounds (these dependencies are presented in the form used by the computer program OriginLab):

$$T, \text{ K (PbTe, Cu–Pb–Te)} = (600 + 6748x - 38140x^2 + 84742x^3 + 11426x^4 - 308980x^5 + 408942x^6 - 165767x^7)y^{0.249}; \quad (8)$$

where: $x = 0 \div 0.89$, $y = 0.333 \div 1$

Fig. 1. The temperature dependences of the Gibbs free energy: equation (4) – for reaction (1), equation (5) – for reaction (2).

Fig. 2. Triangulation of the ternary system Cu–Pb–Te.

Fig. 3. The projection of the liquidus surface and immiscibility in the system Cu–Pb–Te [3]. Primary crystallization fields: 1 – Cu, 2 – α (Cu_{2-x}Te), 3 – Cu_5Te_3 , 4 – $\text{Cu}_{3-x}\text{Te}_2$, 5 – CuTe, 6 – Te, 7 – $\beta(\text{PbTe})$, 8 – Pb.

Fig. 4. 3D model of the phase diagram of the Cu-Pb-Te system.

$$T, \text{ K } (\text{Cu}_{2-x}\text{Te}, \text{ Cu-Pb-Te}) = (-11509.30 + 101598.92x - 258449.77x^2 + 209448.42x^3) \times (1-y)^{1.06};$$

$$x = 0.29 \div 0.444, y = 0 \div 0.333 \quad (9)$$

$$T, \text{ K } (\text{Cu}_5\text{Te}_3, \text{ Cu-Pb-Te}) = (-1365 + 12525x - 16250x^2)(1-y)^{1.06};$$

$$x = 0.44 \div 0.48, y = 0 \div 0.5 \quad (10)$$

$$T, \text{ K } (\text{Cu}_{3-x}\text{Te}_2, \text{ Cu-Pb-Te}) = (1013.12 + 573.819x - 1673.4143x^2)(1-y);$$

$$x = 0.48 \div 0.675, y = 0 \div 0.5 \quad (11)$$

$$T, \text{ K } (\text{CuTe}, \text{ Cu-Pb-Te}) = (-669.7731 + 4458.45x - 3734.8273x^2)(1-y);$$

$$x = 0.675 \div 0.71, y = 0 \div 0.4 \quad (12)$$

$$T, \text{ K } (\text{immiscibility region}, \text{ Cu-Pb-Te}) = (918 + 11300x - 85822x^2 + 290213x^3 - 377100x^4) \times (1-y)^{0.48}$$

$$(13)$$

where $x = 0.056 \div 0.30$; $y = 0 \div 0.7$. The equations (8–13) are visualized in Figure 4.

Results and discussion

In the Cu-Pb-Te system, ternary compounds are not formed. The PbTe compound forms conodes with all copper tellurides (Figure 2), which is associated with a higher thermodynamic

stability of copper telluride compared to copper tellurides (Figure 1). Solid-phase equilibria diagram consists of six domains of three-phase Cu-PbTe-Pb, Cu-Cu_{2-x}Te-PbTe, Cu_{2-x}Te-Cu₅Te₃-PbTe, Cu₅Te₃-Cu_{3-x}Te₂-PbTe, Cu_{3-x}Te₂-CuTe-PbTe, CuTe-Te-PbTe. The liquidus surface of the Cu-Pb-Te system consists of 8 fields corresponding to the primary crystallization of Cu, α -phase on the basis of Cu_{2-x}Te, Cu_{3-x}Te₂, CuTe, β -phase on the basis of PbTe, Pb and Te (Figure 3, 4). The last 2 fields are degenerate at Te and Pb of the angles of the concentration triangle. There are areas of immiscibility from the side of Cu-Cu₂Te and Cu-Pb (Figures 3 and 4). With the increase of the third component, the critical temperature of the stratification decreases. Figure 4 presents the 3D model of the main crystallization fields and the immiscibility areas at the Cu-Cu-Te section. It should be noted that in this part the α -phase based on Cu_{2-x}Te crystallizes under delamination. In the 3D model, the system is viewed from the PbTe side. From this angle, the presented 3D model of the Cu-Pb-Te phase diagram is more informative. 3D modeling was

performed using the OriginLab computer program. Each part of the diagram in Figure 4 stores the corresponding analytical dependence. For each part of the diagram, using the command of the computer program of OriginLab, it is possible to obtain projections and a two-dimensional graphical dependence for any isothermal section, which is important for choosing the temperature regime for obtaining a given composition of the phase in the Cu–Pb–Te system.

Conclusion

Using a complex of experimental methods of physico-chemical analysis and thermodynamic calculation, the phase diagram of the Cu–Pb–Te system was determined over the entire concentration range. The formation of the ternary compound is not detected. Solid-phase equilibria diagram consists of six domains of three-phase Cu–PbTe–Pb, Cu–Cu_{2-x}Te–PbTe, Cu_{2-x}Te–Cu₅Te₃–PbTe, Cu₅Te₃–Cu_{3-x}Te₂–PbTe, Cu_{3-x}Te₂–CuTe–PbTe, CuTe–Te–PbTe. All conodes are directed to the PbTe side, which has the smallest free Gibbs formation energy. The surfaces of the monovariant equilibria of the Cu–Pb–Te system consist of primary crystallization fields of Cu, α -phase on the basis of Cu_{2-x}Te, Cu₅Te₃, Cu_{3-x}Te₂, CuTe, β -phase on the basis of PbTe, Pb and Te and delamination surfaces from the side of Cu–Cu₂Te and Cu–Pb. Based on the phase diagrams of the boundary binary systems using a limited number of DTA data, analytical 3D modeling and visualization of the liquidus and immiscibility surfaces in the ternary Cu–Pb–Te system was carried out. The presented 3D model stores the corresponding analytical dependence and tabular data in the form of matrices necessary for choosing the temperature regime for obtaining a given composition of the phase in the Cu–Pb–Te system.

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Cu–Pb–Te SİSTEMİNDƏ LİKVIDUS VƏ MAYE FAZADA TƏBƏQƏLƏŞMƏ SƏTHLƏRİNİN MULTİ 3D MODELƏŞDİRİLMƏSİ

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Termodinamiki hesablamalarla və təcrübi ədəbiyyat materialının analizi ilə Cu–Pb–Te sistemində fazaların ilkin kristallaşma səthləri, non- və monovariant tarazlıqların tipləri və koordinatları təyin edilmiş, sistemin trianqulyasiyası və likvidus səthinin proyeksiyası qurulmuşdur. Müəyyən edilmişdir ki, Cu–Pb–Te sistemində üçlü birləşmə əmələ gəlmir, bərk halda aşağıdakı alt sistemlərə bölünür: Cu–PbTe–Pb, Cu–Cu_{2-x}Te–PbTe, Cu_{2-x}Te–Cu₅Te₃–PbTe, Cu₅Te₃–Cu_{3-x}Te₂–PbTe, Cu_{3-x}Te₂–CuTe–PbTe, CuTe–Te–PbTe. Üçlü sistemin binar sərhəd sistemlərinin faza diaqramları və az sayda DTA ölçmələrindən istifadə etməklə OriginLab kompüter proqramı vasitəsi ilə PbTe, CuTe, Cu_{2-x}Te, Cu_{3-x}Te₂, Cu₅Te₃ birləşmələrinin kristallaşma səthi və maye fazada təbəqələşmə həddləri 3D modelləşdirilmişdir.

Açar sözlər: Cu–Pb–Te sistemi, faza diaqramı, likvidus və təbəqələşmə sərhədləri, 3D modelləşmə.

МУЛЬТИ- 3D МОДЕЛИРОВАНИЕ ПОВЕРХНОСТЕЙ ЛИКВИДУСА И РАССЛОЕНИЯ В СИСТЕМЕ Cu–Pb–Te

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На основе термодинамических расчетов и анализа литературных экспериментальных данных определены поля первичной кристаллизации фаз, типы и координаты non- и моновариантных равновесий в системе Cu–Pb–Te. Проведена триангуляция системы Cu–Pb–Te. Выявлено, что в системе тройное соединение не образуется, и что она в твердофазном состоянии разделяется на подсистемы с участием теллурида свинца: Cu–PbTe–Pb, Cu–Cu_{2-x}Te–PbTe, Cu_{2-x}Te–Cu₅Te₃–PbTe, Cu₅Te₃–Cu_{3-x}Te₂–PbTe, Cu_{3-x}Te₂–CuTe–PbTe, CuTe–Te–PbTe. Определена проекция поверхности ликвидуса Cu–Pb–Te. На основании фазовых диаграмм граничных бинарных систем и ограниченного числа данных ДТА образцов тройной системы с использованием программы OriginLab получены уравнения для расчета и 3D-моделирования поверхностей кристаллизации PbTe, CuTe, Cu_{2-x}Te, Cu_{3-x}Te₂, Cu₅Te₃ и поверхности расслаивания в системе Cu–Pb–Te. С ростом количества третьего компонента критическая температура расслаивания уменьшается. Определенная в работе 3D-модель для системы Cu–Pb–Te сохраняет соответствующие аналитические функции и табличные данные в форме матриц.

Ключевые слова: Cu–Pb–Te-система, фазовая диаграмма, поверхность ликвидуса, 3D моделирование.