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DETERMINATION AND MODELING OF THE LIQUIDUS SURFACE, VAPOR PRESSURE AND IMMISCIBILITY BOUNDARIES IN THE Cu–Pb–S SYSTEM

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For the first time using a membrane zero-manometer, the vapor pressure $S_x$ over the surface of the PbS liquidus in the ternary system Cu–Pb–S were determined in the range 1100–1400 K and 0–760 mm Hg. Based on the thermodynamic calculation, the boundaries of the immiscibility of liquid alloys of the Cu–S, Pb–S, and Cu–Pb–S systems were determined and analytically described. Critical temperatures and pressures for immiscibility regions of sulfur-rich liquid alloys are characterized by high values: $T_c=1520\pm1880$ K; $P_c=170\pm510$ atm. The crystallization surfaces of lead sulfide with electronic conductivity ($\rho$-type PbS) and with hole conductivity ($n$-type PbS) are calculated and analytically described, as well as the corresponding values of sulfur vapor pressure over the crystallization surface of lead sulfide. All analytical dependencies for 3D modeling were obtained and visualized using the OriginLab computer program.

Keywords: Cu–Pb–S system, sulfur vapor pressure, immiscibility boundaries, 3D analytical modeling.

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Introduction

The phase diagram of the Cu–Pb–S system is of interest for pyrometallurgy and semiconductor materials science. In pyrometallurgy, data on phase equilibria at various temperatures are needed to determine the conditions for obtaining pure copper from sulfide concentrates suitable for use in electrical engineering. Under copper production conditions phase diagrams can be used to evaluate the properties and sensitivity of different changes in the process to the liquid immiscibility gaps used to separate matte, white metal and blister copper, in the converting process step, where lead as an impurity affects the equilibrium between blister copper and white metal [1, 2]. If in pyrometallurgy the task is to clean copper concentrates from harmful impurities of lead, then in the semiconductor technique the problem of producing lead and copper sulfides by crystallization from liquid alloys and the gas phase Cu–Pb–S is solved [3–5]. More than ten papers have been devoted to the determination of phase equilibrium in the Cu–Pb–S system, as well as in its quasibinary section Cu$_2$S–PbS, in particular [6–8]. A review of these studies was carried out in later works [9, 10]. One ternary phase Cu$_{14}$Pb$_2$S$_9$$_x$ (0 < x < 0.15) was found in the system, which is located very close to the PbS–Cu$_2$S section and is stable only between 801±2 K and 759 ± 4 K. The main part of the phase diagram of Cu–Pb–S at high temperatures region occupies immiscible liquid alloys. Connods of the immiscibility of liquid alloys in the temperature range 1273–1473 K were determined in [11] based on thermodynamic calculations. At high temperatures three separate liquid domains have been determined in the Cu–Pb–S ternary system: the first contains over 98 wt.% sulfur, the second is a sulfide-rich matte containing 20–26 wt.% sulfur in the Cu–S join and 9–27 wt.% sulfur in the Pb–S join, and the third is a metal-rich solution containing less than 2 wt.% sulfur. Miscibility gaps exist between the sulfur-rich and sulfide-rich liquids, and between sulfide-rich and metal-rich liquids [10]. However, to date, the critical temperatures of the immiscibility regions of liquid alloys have not been determined both for the ternary Cu–Pb–S system and for the limiting binary Cu–S and Pb–S systems. There is also no information for the PTX phase diagram of Cu–Pb–S in the region of primary crystallization of n-type and $\rho$-type lead sulfide. In [12–14], using the example of the ternary systems Cu–Pb–Se, Ag–Ge–Se, and Ag–Sn–Se, it was shown...
that these problems can be solved using computer analytical 3D modeling.

This work aims to determine and analytical 3D modeling of the boundaries of the immiscibility of liquid alloys, liquidus surface and PTX equilibrium in the ternary system Cu–Pb–S.

Methods

Immiscibility boundaries for liquid alloys in Cu–S and Pb–S systems

The phase diagram of the ternary Cu–Pb–S system is mainly based on phase diagrams of the boundary binary systems Cu–S and Pb–S. Therefore, at the beginning, the immiscibility boundaries of liquid alloys and the liquidus of the PbS, Cu2S compounds in the binary Cu–S systems (Figure 1) and Pb–S (Figure 2) were modeled.

The calculation of the free energy of mixing liquid alloys is carried out according to the Gibbs-Helmholtz equation in the form [18]:

\[
\Delta G^0 = \Delta H - T\Delta S = [a + b(T - T_{mon}) + c(P - P_{mon})(1 - x) + RT\ln x + (1 - x)\ln(1 - x)]
\]  

(1)

Fig. 1. Phase diagram of the Cu–S system calculated using the model parameters of Shishin et al. [12, 16].

Fig. 2. Phase diagram of the Pb–S system [12]. Formation of gas phase is suppressed. Symbols are experimental data [17]. Dashed lines are S2 isobars [12].
In (14) the first term represents the enthalpy of mixing \( \Delta H \) of liquid solutions in an asymmetric version of the model of regular solutions [19]; the second term represents the configurational entropy of mixing \( \Delta S \) liquid solutions; \( x, T \) — mole fraction of the component, temperature for the immiscibility curve; \( T_{mon}, P_{mon} \) — temperature and pressure for monotectic reaction line; \( R=8.314 \text{ J mol}^{-1} \text{ K}^{-1} \). For liquid solutions decomposing into two phases, the mixing parameter is \( a>0 \); with increasing temperature and pressure, the immiscibility region narrows, therefore mixing parameter \( b<0 \) and \( c<0 \); \( R=8.314 \text{ J mol}^{-1} \text{ K}^{-1} \). To determine the liquid immiscibility boundaries the thermodynamic condition of solutions of internal stability \( (\partial^2 G/\partial x^2)_{P,T}>0 \) was used [20, 21].

In the composition region adjacent to sulfur (Figures 1 and 2), the vapor phase consists only of sulfur molecules, and we assume that the vapor pressure of sulfur is saturated, therefore, the vapor phase is in equilibrium with liquid sulfur. The dependence of the saturated vapor pressure of sulfur over liquid sulfur is described by the equation [22]:

\[
\log P_S(\text{atm}) = 4.499 - 3440/T
\]

(2)

To solve the equation (1) containing three functional parameters (composition, temperature, pressure) and Gibbs excess free energy, the Multipurpose Genetic Algorithm was used [23]. The following conditions were used to carry out the iteration process:

\[ x=0.4; a>0; \quad b<0; \quad c<0; \quad T>T_{mon}; \quad P>P_{mon} \]

In particular, equation (1) for the immiscibility region of liquid alloys in the Cu–S system at \( x_S = 0.4 \pm 1 \) was obtained in the form:

\[
\Delta G^0_T \left( \frac{1}{\text{mol}} \right) = \left[ \frac{30000}{T} - 0.62(T - 1086) - 0.78P \right] x(1 - x) + 8.3147T[x\ln x + (1x) \ln(1 - x)]
\]

(3)

Figure 3 shows dependences of the free energy of mixing liquid Cu–S alloys on the composition at various temperatures and pressures. For critical parameters of the considered immiscibility region of liquid alloys of the Cu–S system, the following data were obtained: \( T^k=1920 \text{ K}; \quad P^k=510 \text{ atm} \). From Figure 3 it follows that for \( T^k=1920 \text{ K}; \quad P^k=510 \text{ atm} \) over the entire concentration range \( x_S=0.4\pm1 \) takes place \( (\partial^2 G/\partial x^2)_{P,T}>0 \).

The same method was used to determine critical parameters for other immiscibility regions of liquid alloys of the Cu–S and Pb–S systems. In the field of compositions with a low sulfur content, the pressure influence factor was not taken into account.

To determine the analytical dependences of the immiscibility boundaries on the composition, we used the calculated data for critical parameters and experimental data for the immiscibility coordinates shown in Figures 1 and 2. In particular, the parameters of the analytical temperature dependence on the composition for the immiscibility curve in the Cu–S system at \( x_S=0.4\pm1 \) were obtained in the form

\[
T, \text{ K} \quad \text{Value}
\]

\[
T, \text{ K} \quad \text{Intercept} -2572.4,
\]

\[
T, \text{ K} \quad \text{B1} 13034.6
\]

\[
T, \text{ K} \quad \text{B2} -9926.8
\]

\[
T, \text{ K} \quad \text{B3} 555.6
\]

\[
\text{Number of Points} \quad 7
\]

\[
\text{Degrees of Freedom} \quad 3
\]

\[
\text{Residual Sum of Squares} \quad 755.47619
\]

\[
\text{R-Square (COD)} \quad 0.99892
\]

\[
\text{Adj. R-Square} \quad 0.99783
\]

Consequently:

\[
T, K= -2572.4+13034*x-9926.2*x^2+555.6*x^3,
\]

Here \( x=x_S \) (4)
From (4) it follows that $T_{kr} = 1880$ K corresponds to the composition $x_S = 0.7$. These parameters are in accordance with the data in Figure 1, according to which $T_{kr} = 1920$ K at $x_S = 0.75$. Using this technique, analytical dependences were determined for the immiscibility boundaries in the Pb–S system and for the crystallization temperatures of Cu$_2$S and PbS compounds.

**Cu–Pb–S system. Determination of sulfur vapor pressure**

The data on phase equilibria of the ternary Cu–Pb–S system were taken from [9–11]. There is no information available for the $P$(sulfur)–$T$–$x$ phase diagram of Cu–Pb–S in the region of primary crystallization of $n$-type and $p$-type lead sulfide. Sulfur vapor pressures over liquid alloys that are saturated with PbS were determined using a quartz membrane zero manometer [22, 24]. The quartz membrane zero-manometer with a flat membrane and a mechanical system for increasing shear is shown in Figure 4.

![Fig. 4. Membrane zero-manometer with the flat membrane and the mechanical shear reinforcement system.](image)

The membrane (1) separates the membrane chamber (2) from the compensation volume (3). To monitor the position of the membrane, a system of two rods–movable (4), which was soldered to the surface of the membrane, and fixed (5) is used. The ends of both rods are soldered together and stretched into a thin needle (6). When the membrane moves relative to the equilibrium position, the rod (4) moves along its axis and leads to the displacement of the needle (6). The equilibrium position of the needle (6), and therefore the membrane, is fixed by a fixed pointer (7). The tube (8) serves to connect the device to a compensation-measuring system, a 9-ram for evacuating the membrane chamber, 10-breaking valves with a thin-walled housing for inputsubstances, 11-glass striker).

Temperature and pressure were measured with an accuracy of $\pm 0.5^\circ$C; $\pm (1\div3)$ mmHg in the range of 0÷760 mm Hg. Alloy samples were synthesized from highly pure Cu (99.9 wt.%), Pb (99.95 wt.%) and S (99.99 wt.%), according to the method of synthesis of substances with a volatile component [15]. High purity lead PbS (99.5 wt.%) and Cu$_2$S (99.95 wt.% ) powders was also used in the synthesis of ternary alloys. Using the membrane method, the total pressure of sulfur vapor over the alloys was measured. Sulfur can form various molecules, from one atomic sulfur to six atomic sulfur, depending on temperature. The data [22] show that the vapor phase of sulfur in the temperature range 800÷1400$^\circ$C (1073÷1673 K) K practically consists of diatomic sulfur molecules. The saturated sulfur pressure was measured by us for the temperature range of 827÷1127$^\circ$C (1100÷1400 K).

The results of measuring the sulfur vapor pressure are shown in Table 1.

<table>
<thead>
<tr>
<th>T, K</th>
<th>$x_{Cu}$</th>
<th>$x_{pb}$</th>
<th>$x_S$</th>
<th>$P(S_2)$, mmHg</th>
<th>$x_{Cu}$</th>
<th>$x_{pb}$</th>
<th>$x_S$</th>
<th>$P(S_2)$, mmHg</th>
<th>$x_{Cu}$</th>
<th>$x_{pb}$</th>
<th>$x_S$</th>
<th>$P(S_2)$, mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1368</td>
<td>0</td>
<td>0.56</td>
<td>0.44</td>
<td>8.6[4]</td>
<td>0.05</td>
<td>0.532</td>
<td>0.418</td>
<td>4</td>
<td>0.1</td>
<td>0.495</td>
<td>0.405</td>
<td>3</td>
</tr>
<tr>
<td>1373</td>
<td>0</td>
<td>0.55</td>
<td>0.45</td>
<td>13; 11[4]</td>
<td>0.05</td>
<td>0.525</td>
<td>0.4275</td>
<td>7</td>
<td>0.1</td>
<td>0.495</td>
<td>0.405</td>
<td>3</td>
</tr>
<tr>
<td>1391</td>
<td>0</td>
<td>0.50</td>
<td>0.50</td>
<td>135; 128[4]</td>
<td>0.05</td>
<td>0.475</td>
<td>0.475</td>
<td>80</td>
<td>0.1</td>
<td>0.45</td>
<td>0.45</td>
<td>48</td>
</tr>
<tr>
<td>1349</td>
<td>0</td>
<td>0.47</td>
<td>0.53</td>
<td>596; 585[4]</td>
<td>0.05</td>
<td>0.4465</td>
<td>0.5035</td>
<td>380</td>
<td>0.1</td>
<td>0.423</td>
<td>0.477</td>
<td>245</td>
</tr>
<tr>
<td>1335</td>
<td>0.05</td>
<td>0.437</td>
<td>0.513</td>
<td>550</td>
<td>0.1</td>
<td>0.414</td>
<td>0.486</td>
<td>339</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1307</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td>0.396</td>
<td>0.504</td>
<td>692</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Vapor pressure of diatomic sulfur molecules over liquid alloys Pb–S and Cu–Pb–S saturated with lead sulfide (accuracy in determining the vapor pressure ± (1÷3) mmHg).
Modeling

Analytical dependences for 3D modeling of the T–x and P–T x phase diagrams of the ternary system are defined as functions:

\[ T, K = f(x_S, y_{Cu}) \]  
\[ P(\text{atm}) = f(T, y_{Cu}) \]  \[ (5) \]
here \( x_S \)-mole fraction sulfur: \( y_{Cu} = x_{Cu}/(x_{Cu} + x_{Pb}) \)

Analytical dependencies for modeling of the phase diagrams of the ternary \( \text{Cu–Pb–S} \) system, as well as boundary binary systems \( \text{Cu–S, Pb–S and Cu–Pb} \) are given in Table 2, 3.

In equations (15–20), the degrees of the mole fraction of copper \( (y_{Cu}) \) are determined on the basis of the liquidus data of the quasi-section \( \text{Cu}_2\text{S–PbS} \) of the ternary system \( \text{Cu–Pb–S} \) [12, Figure 19]. Equations (15–20) in Table 3 are visualized in Figure 5.

**Table 2.** Analytical dependencies for phase diagrams of the \( \text{Cu–S, Pb–S and Cu–Pb} \) systems (equations are presented in computer variation)

<table>
<thead>
<tr>
<th>System, region</th>
<th>Equations: T, K=f(x)</th>
<th>Eq.N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–S, immiscibility, ( x=x_S=0.02+0.33 )</td>
<td>1108+15126<em>x-83023</em>x^2+212487<em>x^3-279753</em>x^4</td>
<td>6</td>
</tr>
<tr>
<td>Cu–S, immiscibility, ( x=x_S=0.4+1 )</td>
<td>-2572.4+13034<em>x-9926.2</em>x^2+555.6*x^3</td>
<td>7</td>
</tr>
<tr>
<td>Pb–S, immiscibility, ( x=x_S=0.7+1 )</td>
<td>-332184+156084E6<em>x-2.74322E6</em>x^2+2.1471E6<em>x^3-631515</em>x^4</td>
<td>8</td>
</tr>
<tr>
<td>Cu–S, ( \text{Cu}_2\text{S} ) liquidus, ( x=x_S=0.32-0.374 )</td>
<td>-306660+2.56618E6<em>x-7.08598E6</em>x^2+6.48E6*x^3</td>
<td>9</td>
</tr>
<tr>
<td>Pb–S, n-type PbS liquidus, ( x=x_S=0.02+0.5 )</td>
<td>923+5569<em>x-30174</em>x^2+68655<em>x^3-53685</em>x^4</td>
<td>10</td>
</tr>
<tr>
<td>Pb–S, p-type PbS liquidus, ( x=x_S=0.5+0.707; y=y_{Cu}=0+47 )</td>
<td>(1808-338<em>x-993</em>x^2)</td>
<td>11</td>
</tr>
<tr>
<td>PbS–CuS [12], liquidus PbS, ( x=x(Cu_S)=0-0.67 ); ( x=0.67-1.0; )</td>
<td>1391-897<em>x^2</em>(0.67-x)<em>(90-141.67</em>x+1176.7<em>x^2-455+1858</em>x+2077*(x-0.67)*(1-x)</td>
<td>12</td>
</tr>
<tr>
<td>PbS–CuS [12], immiscibility, ( x_Cu=x_S=0.37-0.78 )</td>
<td>1229+1268*(x-0.37)*(0.78-x)</td>
<td>14</td>
</tr>
</tbody>
</table>

**Fig. 5.** Multi-3D model of crystallization surfaces of PbS, \( \text{Cu}_2\text{S} \) and immiscibility surfaces in the \( \text{Cu–Pb–S} \) system, visualized by the equations in table 3: 1 – eq.15, 2 – eq.16, 3 – eq.17, 4 – eq.18, 5 – eq.19, 6 – eq.20.
Table 3. Analytical dependencies for phase diagram of the Cu–Pb–S system

<table>
<thead>
<tr>
<th>System, region</th>
<th>Equations: ( T, K = f(x, y); x = x_S; y_{Cu} = x_{Cu}/(x_{Cu} + x_{Pb}) )</th>
<th>Eq.N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–Pb–S immiscibility, ( x = 0.4 \pm 1; y = 0-1 )</td>
<td>((-332184+1.56084E6<em>x-2.74322E6</em>x^2+2.14715E6<em>x^3-631515</em>x^4)<em>(1-y)+(2572.4+13034</em>x-9926.2<em>x^2+555.6</em>x^3)*y)</td>
<td>15</td>
</tr>
<tr>
<td>Cu–Pb–S, immiscibility, ( x = 0.02 \pm 0.33; y = 0.05 \pm 0.32 )</td>
<td>((1258+6852<em>x-22894</em>x^2+9943<em>x^3)</em>(1-y)+(-2572.4+13034<em>x-9926.2</em>x^2+555.6*x^3)*y)</td>
<td>16</td>
</tr>
<tr>
<td>Cu–Pb–S, immiscibility, ( x = 0.02 \pm 0.345; y = 0.3 \pm 1 )</td>
<td>((1108+15126<em>x-83023</em>x^2+212487<em>x^3-279753</em>x^4)*y^0.2)</td>
<td>17</td>
</tr>
<tr>
<td>Cu–Pb–S, p-type PbS liquidus, ( x = 0.5 \pm 0.707; y = 0 \pm 0.47 )</td>
<td>((1808-338<em>x-993</em>x^2)*(1-y)^0.829)</td>
<td>18</td>
</tr>
<tr>
<td>Cu–Pb–S, n-type PbS liquidus, ( x = 0.02 \pm 0.5; y = 0 \pm 0.52 )</td>
<td>((923+5569<em>x-30174</em>x^2+68655<em>x^3-53685</em>x^4)*(1-y)^0.829)</td>
<td>19</td>
</tr>
<tr>
<td>Cu–Pb–S, Cu_2S liquidus, ( x = 0.32 \pm 0.374; y = 0.4 \pm 1 )</td>
<td>((-306660+2.56618E6<em>x-7.08598E6</em>x^2+6.48E6*x^3)*y^0.707)</td>
<td>20</td>
</tr>
</tbody>
</table>

Fig. 6. 3D model of the P–T–X diagram for isolines of the saturated vapor pressure \( S_2 \) over the surface of the PbS liquidus in the ternary system Cu–Pb–S, visualized by eq.21, 22: 1 – region PbS–S (p-type conductivity), 2 – region PbS–Pb (n-type conductivity).

Results and discussion

For temperature-concentration dependence of the vapor pressure \( S_2 \) over the surface of the PbS liquidus in the ternary system Cu–Pb–S the equations are obtained:

\[
\log p_{S_2} \text{ (atm, Cu–Pb–S, p-type PbS)} = 64-320*y + 487*y^2-232*y^3-3.84*x \quad (21)
\]

\[
\log p_{S_2} \text{ (atm, Cu–Pb–S, n-type PbS)} = 1836-6844*y+8499*y^2-3524*y^3-5.77*x \quad (22)
\]

In equations (21, 22): \( y = 1000/(T,K) = 0.712 \pm 0.85 \); \( x = y_{Cu} = 0 \pm 0.26 \) and \( y = 1000/(T,K) = 0.714 \pm 0.83 \); \( x = y_{Cu} = 0 \pm 0.26 \).

Equations (21, 22) are visualized in Figure 6, 7.

Figure 5 shows 3D model of crystallization surfaces of PbS, Cu_2S and immiscibility surfaces in the Cu–Pb–S system. From Figure 5 it follows that the critical temperatures of immiscibility (regions 1, 2, 3) are high. In the field of compositions with a high sulfur content, critical immiscibility temperatures vary in the range from 1520 to 1880 K. Moreover, to achieve saturation of sulfur vapor over liquid alloys, high pressures are required. The critical pressure values of the saturated vapor of sulfur molecules vary in the range from 170 to 510
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In the region of compositions adjacent to lead (Tc=1800 K) and copper (Tc=2080 K), due to the low volatility of metals, high pressure cannot form above the alloys. The crystallization surface of lead sulfide consists of two regions: the crystallization surface of lead sulfide (p-type PbS) with electronic conductivity (field 4) and the crystallization surface of lead sulfide (n-type PbS) with hole conductivity (field 5).

Copper and lead sulfides crystallize not only from the liquidus of these compounds (regions 4, 5, 6), they also form upon cooling of liquid alloys from the immiscibility region (region 1, 2, 3).

Figure 6 presents 3D visualization of the P–T–X diagram for the pressure isolines of the saturated vapor of two atomic sulfur molecules, and projections of this diagram are shown in Figure 7 a, b. The calculated data are in accordance with our experimental data, which are obtained by measuring a zero-gauge membrane in the range \( \lg P(S_2) \) atm from the liquidus of these compounds (region 4, 5, 6).

Conclusions

The analytical 3D model of the phase diagram is very flexible, because it allows you to get a 2D projection on a computer in any coordinate set for use in solving technological problems of metallurgy and semiconductor material science. Analytical dependencies in the form of 2D and 3D models contain, respectively, 100*100=10,000 and 50*50=2500 tabular data in the form of matrices for each area of the phase diagram, which can be used to select the optimal composition, temperature and pressure of saturated steam in the synthesis of copper sulfides, lead and ternary phases from the liquid and gas phases.

Acknowledgment

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References

Из термодинамического расчета определены и аналитически описаны границы несмешиваемости жидких сплавов Pb–S и Cu–Pb–S System с энергетической точки зрения. Фазовые диаграммы были получены и визуализированы с помощью компьютерной программы OriginLab.

**Ключевые слова**: система Cu–Pb–S, структура сплавов, границы несмешиваемости, 3D аналитическое моделирование.