Changes in the composition of the condensed and vapor phase when heating the wood alloy

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Abstract. The concentration and temperature dependences of the melt components are calculated and the composition of the steam phase and partial pressures of the steam components over the melt Bi-Pb-Sn-Cd are determined by thermodynamic modeling, using the TERRA software package and the model of the ideal solution of interaction products at a temperature of 300 to 3000 K and a pressure of $10^5$ PA.

1. Introduction
The processes occurring during the evaporation of metals are of interest for vacuum metallurgy (alloys production, metal purification) and nuclear power engineering (distillation purification of liquid metal heat carriers) [1].

The paper [2] presents the vapor pressure and the boundaries of the liquid-vapor phase transitions for lead-bismuth melts at a pressure of 0.1 MPa to 1 PA. The composition of the vapor and partial pressure are not determined. Such studies of metallurgical systems are complicated by high temperatures of experiments, the difficulty of determining the concentrations of components in the vapor phase, the equilibrium with the alloy, the problems of instrument design of experiments.

In this work, the method of thermodynamic modeling was used to study the physical and chemical processes occurring in the wood alloy during heating and evaporation of the wood alloy and to study the physical and chemical processes occurring in the vapors [3,4]. This method was successfully applied to study the thermal properties of Pb-Bi alloy [5-10].

The results of thermodynamic modeling for Pb-Bi alloy are close to experimental data on thermophysical properties [11]. This indicates the adequacy of thermodynamic modeling.

2. The modeling technique
Thermodynamic modeling is a thermodynamic analysis of the equilibrium state of the system as a whole. Calculation methods are developed on the basis of the variational principles of thermodynamics. One of the most effective programs that implement such thermodynamic calculations is the TERRA software package, which is a further development of the ASTRA software package [4]. The melt Bi-Pb-Sn-Cd is represented by a model of ideal solutions of interaction products [5], which includes condensed Bi, Pb, Sn, Cd, as well as double and triple metal compounds. The gas
phase includes Pb, Bi, Cd, Sn, Pb₂, Bi₂, Bi₃, Bi₄, Sn₂, Cd₂, electron gas, ionized lead, bismuth, cadmium and tin vapors. The thermodynamic functions of individual substances are taken from databases of IVTANTERMO, TERRA, ASTRA, HSC Chemistry. The thermodynamic functions of double and triple metal compounds, which are not present in the databases, are taken from [12].

3. Results and discussion

Figure 1 shows the equilibrium composition of the condensed phase of alloy Bi(42.0%)+Pb(30.6%)+Sn(10.0%)+Cd (7.4%) at a pressure of 10⁵ Pa in the temperature range of 300-3000 K.

At a total pressure of 10⁵ PA in the metal melt except Bi, Pb, Sn, Cd there are a number of metal compounds. The temperature dependence of the concentrations of the alloy components is complex and nonlinear. The temperature rise from 500 to 1500 K leads to a slight increase in the concentration of Bi, Pb, Sn, Cd due to thermal dissociation of metal compounds. At 1500 K the concentration of Cd₃Bi₂, Pb₃Bi₂, Sn₂Bi₃, Sn₂Bi₄, Bi₄Pb, SnBi, Bi₃Pb, SnBi compounds is less than 10⁻⁵ molar fractions. Compounds Cd₃Bi₂, Bi₄Pb, PbSn, PbBi, SnBi, PbSn, CdSn, SnBi, PbBi₂Sn₂ are present in the metal melt and their concentration decreases due to thermal dissociation.

![Figure 1. Equilibrium composition of the metal phase for bi-Pb-Sn-Cd alloy at 10⁵ Pa](image)

With a further increase in temperature to 2500 K, the concentration of Sn increases, and the concentration of Pb, Bi, Cd decreases due to their evaporation from the melt. At 2500 K the concentration of Cd₃Bi₂ compounds, Pb₃Bi less than 10⁻⁵ molar fractions. In the temperature range of 1500-2500 K the concentration of PbSn and Sn₂Bi compounds has a complex dependence, and the concentration of PbSn, SnBi, BiPb, CdSn decreases. In the temperature range 800-1900 K to the
formation of ternary compounds Pb₃Bi₄Sn₄, its concentration increases, respectively, from 4.197*10⁻⁵ to 2.824*10⁻⁵ mole fraction.

Compounds found in the metal melt, are involved in the reactions of thermal dissociation (1-22).

\[
\begin{align*}
\text{Bi}, \text{Sn}_4 &= \text{Bi} + \text{Sn} + 2\text{SnBi}, \text{Sn} \\
\text{Bi}, \text{Sn}_3 &= \text{Bi} + \text{Pb} + \text{BiPb} + \text{Pb}_2\text{Bi} + \text{Bi} + \text{Pb} \\
\text{Bi}, \text{Pb}_3 &= 5\text{Bi} + \text{Pb} + \text{BiPB} + \text{Pb} + \text{Bi} + \text{Pb} \\
2\text{Bi}, \text{Pb} &= 13\text{Bi} + \text{Pb} + \text{BiPb} \\
2\text{Pb}, \text{Bi}_i &= 3\text{Bi} + \text{Pb} + 2\text{BiPb} + \text{Pb}_2\text{Bi} \\
2\text{Pb}, \text{Bi} &= \text{Bi} + 5\text{Pb} + \text{BiPb} \\
2\text{Pb}, \text{Sn}_n &= 5\text{Sn} + \text{Pb} + \text{PbSn} \\
3\text{Sn}, \text{Bi}_i &= \text{Sn} + 5\text{Bi} + \text{SnBi} + \text{SnBi} + \text{SnBi} \\
2\text{Sn}, \text{Bi} &= 5\text{Sn} + \text{Bi} + \text{SnBi} \\
\text{Sn}, \text{Bi}_i &= 3\text{Sn} + \text{Bi} + 2\text{SnBi} + \text{SnBi} \\
3\text{Sn}, \text{Bi} &= 11\text{Sn} + \text{Bi} + \text{SnBi} + \text{SnBi} \\
2\text{Sn}, \text{Bi}_i &= 3\text{Sn} + \text{Bi} + \text{SnBi} + 2\text{SnBi} + \text{Bi} + \text{SnBi} \\
2\text{Sn}, \text{Bi} &= \text{Sn} + 9\text{Bi} + \text{SnBi} \\
2\text{Pb}, \text{Bi}_i, \text{Sn}_n &= 6\text{Bi} + \text{Sn} + 2\text{Pb} + \text{BiPb} + \text{SnBi} + \text{PbSn} \\
2\text{Pb}, \text{Bi}_i, \text{Sn}_n &= 6\text{Bi} + \text{Sn} + \text{Pb} + 2\text{BiPb} + 6\text{SnBi} + \text{PbSn} \\
\text{Pb}, \text{Bi}_i, \text{Sn}_n &= 2\text{Bi} + 2\text{Sn} + \text{Pb} + \text{BiPb} + \text{SnBi} + \text{PbSn} \\
\text{Pb}, \text{Bi}_i, \text{Sn}_n &= 2\text{Bi} + \text{Sn} + \text{Pb} + \text{BiPb} + \text{SnBi} + \text{PbSn} + \text{SnBi} \\
3\text{Pb}, \text{Bi}_i, \text{Sn}_n &= \text{Bi} + 10\text{Sn} + 4\text{Pb} + \text{BiPb} + \text{SnBi} + \text{PbSn} \\
\text{Pb}, \text{Bi}_i, \text{Sn}_n &= 2\text{Bi} + 2\text{Sn} + 3\text{Pb} + \text{BiPb} + \text{SnBi} + \text{PbSn} \\
\text{Pb}, \text{Bi}_i, \text{Sn}_n &= \text{Bi} + 2\text{Sn} + 2\text{Pb} + \text{BiPb} + \text{SnBi} + \text{PbSn} + \text{PbBi} \\
3\text{Pb}, \text{Bi}_i, \text{Sn}_n &= 4\text{Bi} + 4\text{Sn} + \text{Pb} + \text{BiPb} + \text{SnBi} + \text{PbSn} \\
3\text{Pb}, \text{Bi}_i, \text{Sn}_n &= 10\text{Bi} + 10\text{Sn} + \text{Pb} + \text{BiPb} + \text{SnBi} + \text{PbSn} \\
\end{align*}
\]

According to the thermal stability of the compounds are arranged in a row in descending order at 10⁵ Pa: Sn₂Bi₂, Sn₂Bi, Bi₂Sn₃, Sn₂Bi₄, Pb₂Bi₄Sn₄, Pb₂Bi₃, Pb₂Bi₂Sn₄, Pb₂Bi₂Sn₃, Pb₂BiSn₄, Pb₂BiSn₃, Pb₂BiSn₂, Sn₂Bi₄, Sn₂Bi₃, Pb₂Bi₄, Pb₂Bi₃, Pb₂Bi₂Sn₄, Pb₂Bi₂Sn₃, Pb₂BiSn₄, Pb₂BiSn₃, Sn₂Bi, Pb₂Bi₄, Pb₂Bi₃, Pb₂Bi₂Sn₄, Pb₂Bi₂Sn₃, Sn₂Bi, Pb₂Bi₄, Pb₂Bi₃, Pb₂Bi₂Sn₄, Pb₂Bi₂Sn₃, Sn₂Bi, Pb₂Bi₄, Pb₂Bi₃, Pb₂Bi₂Sn₄, Pb₂Bi₂Sn₃, Sn₂Bi, Pb₂Bi₄, Pb₂Bi₃, Pb₂Bi₂Sn₄, Pb₂Bi₂Sn₃, Sn₂Bi, Pb₂Bi₄, Pb₂Bi₃, Pb₂Bi₂Sn₄, Pb₂Bi₂Sn₃, Sn₂Bi, Pb₂Bi₄, Pb₂Bi₃, Pb₂Bi₂Sn₄, Pb₂Bi₂Sn₃, Sn₂Bi, Pb₂Bi₄, Pb₂Bi₃, Pb₂Bi₂Sn₄, Pb₂Bi₂Sn₃, Sn₂Bi, Pb₂Bi₄, Pb₂Bi₃, Pb₂Bi₂Sn₄, Pb₂Bi₂Sn₃.

The vapor pressure over the melt Bi(42.0%) + Pb(41.0%) + Sn(10.0%) Cd (7.0%) was studied in the argon atmosphere at a total pressure of 10⁵ Pa in the temperature range of 300-3000 K. The argon content in the systems was 2 mass %. Under these conditions, the steam can be considered saturated. Temperature dependences of the equilibrium partial pressures of the gas phase components at a total pressure of 10⁵ Pa are shown in figure 2.

At a total pressure of 10⁵ Pa the main component of the gas phase is argon. Its partial pressure is 4.197*10⁻⁵ Pa, and at 3000 K is 7.9*10⁻³ Pa. This behavior is associated with an increase in the partial pressure of metal vapor. At 800 K, the partial pressure of Cd vapor is 1.5 Pa, the temperature increase up to 1900 K leads to an increase in the partial pressure up to 1.9*10⁴ Pa and practically does not change to 3000 K. At 1000 K, the partial pressure of Pb vapor is 1 Pa, the temperature increase up to 2200 K leads to an increase in the partial pressure up to 3.1*10⁴ Pa and practically does not change to 3000 K. At 1030 K the partial pressure of Bi vapor is 1 Pa, the temperature increase up to 2200 K leads to an increase in the partial pressure up to 3.1*10⁴ Pa and practically does not change to 3000 K. At 1700 K the partial pressure of Sn vapor is 3.1 Pa, the temperature increase up to 2500 K leads to an increase in the partial pressure up to 1.2*10⁴ Pa and practically does not change to 3000 K.

For Bi₂, Bi₃, Bi₄Pb₂, Sn₂, Cd vapors, the following regularities are observed when the pressure increases: the temperature of the partial pressure maximum shifts towards higher temperatures; the slope of the ascending and descending parts of the partial pressure curve decreases, the region of the curves becomes wider, stretched along the temperature axis; the maximum of the partial pressure increases.
The increase in the external pressure leads to the displacement of the partial pressure curves in the region of higher temperatures.

Thermal dissociation reactions take place in the steam phase

\[
\begin{align*}
\text{Bi}_2 &= 2\text{Bi} \\
\text{Bi}_3 &= 3\text{Bi} \\
\text{Bi}_4 &= 4\text{Bi} \\
\text{Sn}_2 &= 2\text{Sn} \\
\text{Pb}_2 &= 2\text{Pb} \\
\text{Cd}_2 &= 2\text{Cd}
\end{align*}
\]

Figure 2. Temperature dependences of partial pressures of gas phase components at 10^5 Pa

4. Conclusion
In this paper, the composition of the condensed phase and the pressure of the components of the vapor phase above the melt are determined by thermodynamic modeling using the model of the ideal solution of interaction products for the melt Bi(42%)+Pb(30.6%)+Sn(10%)+Cd(7.4%) at a pressure of 10^5 Pa.

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