Thermodynamic modeling of melt of the Bi-Pb-Sn-Cd system

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Abstract. Thermodynamic modeling of heating of the Bi-Pb-Sn-Cd system in a wide temperature range is performed in the TERRA software package. The equilibrium constants of thermal dissociation reactions are determined. The equilibrium constants of thermal dissociation reactions for metal compounds formed in the Bi-Pb-Sn-Cd melt as a result of heating are determined: BiPb, PbSn, SnBi, Pb3Bi4Sn4, Pb3Bi6Sn13, Bi2Sn3, Bi2Pb, CdBi2, Bi2Sn3, PbBi, PbSn, Sn3Bi, SnBi, SnBi2, SnSnBi, SnBi2, SnSnBi3, Pb2BiSn4, Pb3BiSn5, Pb3BiSn8, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4.

1. Introduction

Lead-based alloys are promising heat carriers for use in nuclear power plants [1]. The Bi-Pb-Sn-Cd alloy is widely used in laboratory practice and in various fields of engineering. In this paper, to study the heating of the alloy, we apply the method of thermodynamic modeling using the TERRA software package [2–3]. The processes that occur during the evaporation of metals are of interest for vacuum metallurgy (production of alloys, metal purification) and nuclear power (distillation purification of liquid metal coolants) [4].

This paper simulates heating of the system in Ar-42wt%Bi-40.6wt%Pb-10wt%Sn-7.4wt%Cd at a total pressure of 10^5 Pa in the temperature range 300-3000T given the opportunity of education twenty-nine compounds, present in the melt in the form of clusters: PbSn, CdSn, SnBi, BiPb, CdBi2, Bi2Sn3, Bi3Pb3, Bi4Pb, Bi5Pb, PbBi, PbSn3, Sn3Bi4, SnBi, SnBi2, Sn3Bi, Sn12Bi3, SnBi4, Pb3BiSn4, Pb3BiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4, PbBiSn4.

The software package used was tested on a well-studied alloy of the Pb-Bi system [6]. Previously, it was used to obtain data on the enthalpy values of the Cd-Sn system [7] and the vapor pressures of the Bi-Pb-Sn-Cd system [8].

2. Materials and Methods

Thermodynamic modeling consists in the thermodynamic analysis of the equilibrium state of the system as a whole. Calculation methods are developed on the basis of variational principles of thermodynamics.

In thermodynamic modeling, compounds with a multiple of the number of atoms forming them are assumed to be condensed individual substances. Substances with fractional stoichiometric coefficients are considered solutions. Condensed phases consist of compounds in solid (crystalline or amorphous) and liquid states. Individual substances that have the same chemical formula but are included in different phases are considered to be different compound substances. The components of the gas phase are
molecules, radicals, atoms, ions, and electron gas. In order, to explicitly represent any thermodynamic system, you should specify two independent parameters from \( V, S, U, I, P, T, F, G \) and the complete initial chemical composition of the system. In this case, each pair of independent parameters will define a characteristic function [3] – a function of the state of the thermodynamic system of the corresponding thermodynamic parameters, characterized by the fact that all the thermodynamic properties of the system can be expressed explicitly using this function and its derivatives with respect to these parameters. Calculation methods are developed on the basis of 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 [3].

3. Results and Discussion

Melt Bi-Pb-Sn-Cd presented a model of the ideal solutions of the reaction products [2], part of which comprises the condensed Bi, Pb, Sn, Cd, and double and triple intermetallics (PbSn, CdSn, SnBi, BiPb, Cd\(_2\)Bi\(_2\), Bi\(_2\)Sn, Bi\(_3\)Pb\(_3\), Bi\(_3\)Pb, Pb\(_3\)Bi, Pb\(_3\)Bi\(_2\), Sn\(_3\)Bi\(_4\), Sn\(_3\)Bi, Sn\(_3\)Bi\(_2\), Sn\(_2\)Bi, Sn\(_2\)Bi\(_2\), Sn\(_2\)Bi\(_3\), Sn\(_2\)Bi\(_4\), Pb\(_2\)Bi\(_3\)Sn\(_4\), Pb\(_2\)Bi\(_3\)Sn, Pb\(_2\)Bi\(_3\)Sn\(_2\), Pb\(_2\)Bi\(_3\)Sn\(_3\), Pb\(_2\)Bi\(_3\)Sn\(_4\), Pb\(_2\)Bi\(_3\)Sn\(_5\), Pb\(_2\)Bi\(_3\)Sn\(_6\), Pb\(_2\)Bi\(_3\)Sn\(_7\), Pb\(_2\)Bi\(_3\)Sn\(_8\), Pb\(_2\)Bi\(_3\)Sn\(_9\), Pb\(_2\)Bi\(_3\)Sn\(_10\), Pb\(_2\)BiSn\(_4\), Pb\(_2\)BiSn\(_5\), Pb\(_2\)BiSn\(_6\), Pb\(_2\)BiSn\(_7\), Pb\(_2\)BiSn\(_8\), Pb\(_2\)BiSn\(_9\), Pb\(_2\)BiSn\(_10\), Pb\(_2\)BiSn\(_11\), Pb\(_2\)BiSn\(_12\), Pb\(_2\)BiSn\(_13\)). The gas phase includes Pb, Bi, Cd, Sn, Pb\(_2\), Bi\(_2\), Bi\(_3\), Bi\(_4\), Sn\(_2\), Cd\(_2\) vapors, electron gas, and ionized lead, bismuth, cadmium, and tin vapors. Thermodynamic functions of individual substances are extracted from the IVTANTERMO and HSC Chemistry databases. Thermodynamic functions of double and triple intermetallides that are not available in the databases were calculated in [5]. Based on the results of thermodynamic modeling, a graph of the equilibrium composition of the condensed phase for the system Ar – 42 mass. %, Bi – 40.6 mass. %, Pb – 10 mass. %, Sn – 7.4 wt% Cd at P=10\(^5\) Pa (Figure 1).

**Figure 1.** Equilibrium composition of the condensed phase for the system Ar – 42 mass. %, Bi – 40.6 mass. %, Pb – 10 mass. %, Sn – 7.4 wt% Cd at P=10\(^5\) Pa.
Figure 1 shows that in addition to pure Bi, Pb, Sn, Cd, a metallic compound are present in significant amounts in the metal melt: BiPb, Sn3Bi, Pb3Bi4Sn4, PbSn, SnBi, PbSn3, Sn3Bi, Pb3Bi4.

The temperature dependences of the main components of the system are complex and not linear. A detailed description of the behavior of curves is presented in [9].

In the result of simula-

tion in metal melt Bi-Pb-Sn-Cd in the atmosphere of Ar are present: a) 15 metal compounds: BiPb, PbSn, SnBi, PbBi3Sn4, PbSn3, Bi2Sn3, Bi5Pb, CdSn, Sn3Bi, PbBi2Sn2, Pb3Bi4, Cd3Bi2, Bi1Pb3, Sn3Bi2; b) metals: Pb, Bi, Sn, Cd.

From the temperature dependence of the melt composition (Figure 1), it follows that at low temperatures, the metal melt contains a significant amount of compounds, the content of which decreases sharply with increasing temperature.

The equilibrium constants of thermal dissociation reactions are determined for 15 compounds present in the metal melt as a result of modeling (1–15):

1. \(2\text{Bi}_2\text{Sn}_3=\text{Bi}+\text{Sn}+2\text{SnBi}+\text{Sn}_3\text{Bi}\)
2. \(\text{BiPb}=\text{Bi}+\text{Pb}\)
3. \(2\text{Bi}_3\text{Pb}=5\text{Bi}+\text{Pb}+\text{BiPb}+\text{Pb}_3\text{Bi}+\text{Bi}_3\text{Pb}\)
4. \(2\text{Bi}_3\text{Pb}=13\text{Bi}+\text{Pb}+\text{BiPb}\)
5. \(2\text{Pb}_3\text{Bi}=5\text{Bi}+\text{Pb}+2\text{BiPb}+\text{Pb}_3\text{Bi}\)
6. \(2\text{Pb}_3\text{Bi}=\text{Bi}+5\text{Pb}+\text{BiPb}\)
7. \(2\text{PbSn}_3=5\text{Sn}+\text{Pb}+\text{PbSn}\)
8. \(\text{PbSn}=\text{Pb}+\text{Bi}\)
9. \(2\text{Sn}_3\text{Bi}=5\text{Sn}+\text{Bi}+\text{SnBi}\)
10. \(2\text{Sn}_3\text{Bi}=3\text{Sn}+\text{Bi}+2\text{SnBi}+\text{Sn}_3\text{Bi}\)
11. \(\text{SnBi}=\text{Sn}+\text{Bi}\)
12. \(\text{CdSn}=\text{Cd}+\text{Sn}\)
13. \(\text{Cd}_2\text{Bi}_3=3\text{Cd}+2\text{Bi}\)
14. \(\text{Pb}_3\text{Bi}_4\text{Sn}_4=2\text{Bi}+2\text{Sn}+3\text{Pb}+\text{BiPb}+\text{SnBi}+\text{PbSn}\)
15. \(3\text{PbBi}_2\text{Sn}_2=4\text{Bi}+4\text{Sn}+\text{Pb}+\text{BiPb}+\text{SnBi}+\text{PbSn}\)

The temperature dependence of the equilibrium constants of thermal dissociation reactions (1)–(15) is described by equation (16):

\[\ln K = \frac{A}{T} + B\]  

where A and B are individual constant coefficients characteristic of a given reaction, represented in table 1.

Figure 2 shows a summary graph of LnK values for double and triple metal compounds present as clusters in the melt of the Bi-Pb-Sn-Cd system in an Ar atmosphere at a pressure of \(10^5\) Pa. The dissociation temperature ranges of the studied clusters can be divided into three types: low-temperature (100–500 K), high-temperature, and thermally stable. The Pb3Bi compound thermally dissociates in the high-temperature region. The Pb3Bi4 compound thermally dissociates in the high-temperature region.

The number of compounds thermally dissociates over the entire temperature range without passing into a thermally stable state: PbSn3, Sn3Bi, Pb3Bi4Sn4, PbBi2Sn2.

For a number of compounds: Sn4Bi2, Bi2Sn3, PbBi3Sn4, the equilibrium is shifted towards the formation of the initial substances of metals and compounds: Sn, Bi, SnBi, Sn3Bi, BiPb, PbSn.
Table 1. Coefficients of equation (16) describing the equilibrium constants of reactions of thermal dissociation of a compound in a melt in an Ar atmosphere.

| Reactions                                           | \( A \)     | \( \Delta A \) | \( B \)    | \( \Delta B \) | \( \Delta T, K \) |
|-----------------------------------------------------|-------------|---------------|------------|---------------|------------------|
| \( 2Bi_2Sn_3 = Bi + Sn + 2SnBi + Sn_3Bi \)         | -2627.54    | 133.86        | -0.96      | 0.11          | 800-1800         |
| \( BiPb = Bi + Pb \)                                | -1370.98    | 55.73         | 2.31       | 0.04          | 1100-1700        |
| \( 2Bi_3Pb_3 = 5Bi + Pb + BiPb + Pb_3Bi + BiPb \)  | -7652.80    | 264.38        | 9.60       | 0.19          | 800-2400         |
| \( 2BiPb = 13Bi + Pb + BiPb \)                     | -17962.55   | 420.13        | 29.18      | 0.31          | 800-2400         |
| \( 2Pb_3Bi = 5Bi + Pb + 2BiPb + Pb_3Bi \)          | -35279.63   | 1966.88       | 24.67      | 0.98          | 1700-2400        |
| \( 2PbBi = Bi + 5Pb + BiPb \)                      | -8614.90    | 432.09        | 6.27       | 0.21          | 1800-2400        |
| \( 2PbSn = 5Sn + Pb + PbSn \)                      | -3936.05    | 18.98         | 7.51       | 0.02          | 500-2400         |
| \( PbSn = Pb + Bi \)                               | -1180.62    | 36.08         | 1.65       | 0.03          | 1000-2000        |
| \( 2SnBi = 5Sn + Bi + SnBi \)                      | -5114.89    | 99.13         | 9.69       | 0.09          | 600-2400         |
| \( 2Sn_2Bi = 3Sn + Bi + 2SnBi + Sn_3Bi \)          | 1150.96     | 65.42         | -15.39     | 0.06          | 800-1600         |
| \( SnBi = Sn + Bi \)                               | -1795.93    | 6.07          | 3.65       | 0.004         | 800-2000         |
| \( CdSn = Cd + Sn \)                               | -1375.51    | 33.68         | 1.67       | 0.03          | 600-1900         |
| \( CdBi_2 = 3Cd + 2Bi \)                           | -2918.73    | 132.413       | -19.41     | 0.11          | 900-1500         |
| \( Pb_2Bi_3Sn = 2Bi + 2Sn + 3Pb + BiPb + SnBi + PbSn \) | 11467.37   | 73.76         | -23.63     | 0.05          | 900-2400         |
| \( 3PbBi_2Sn = 4Bi + 4Sn + Pb + BiPb + SnBi + PbSn \) | -8105.32   | 101.97        | 14.92      | 0.08          | 800-2400         |

Figure 2. Summary graphs of \( \ln K \) values for double and triple compounds in an inert atmosphere Ar at a pressure of \( 10^5 \) Pa in the melt 42.0 Bi+40.6 Pb+10.0 Sn+7.4 Cd (wt %).
Conclusions
The paper presents the equilibrium composition of the condensed phase for the Bi-Pb-Sn-Cd system. New data have been obtained on the equilibrium constants of the thermal dissociation reaction for double and triple compounds in an inert atmosphere at a pressure of $10^5$ Pa in the melt 42.0 Bi+40.6 Pb+10.0 Sn+7.4 Cd (wt %).

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