THERMODYNAMIC PROPERTIES OF ALLOYS OF THE BINARY Sb-Yb AND Bi-Yb SYSTEMS

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The alloys of antimony and bismuth with lanthanides (Ln) have quite broad sphere of use: as magnetic, thermoelectric materials; in the process of selective extraction of lanthanides from the mixture of their salts. Also, from the theoretical point of view, ot is interesting to elucidate the ionic, covalent and metallic contributions into the interaction energy in these alloys, which may depend significantly on the valence of the lanthanide. We need to say that compounds in these systems, especially Ln_3E_4 (E = Sb, Bi), are very stable and refractory, compared to their components. In the case of the systems Sb-Yb and Bi-Yb, the melting temperatures of such compounds are not far from the boiling points of Sb(Bi) and well above the boiling point of Yb. This provides the question on searching indirect methods of synthesis of such compounds and on investigating their physico-chemical properties. Thermodynamic modeling plays an important role here, but it is impossible to conduct with necessary precision until some minimal experimental information is obtained.

There are two concentration ranges ($0<x_{Yb}<0.4$ и $0.9<x_{Yb}<1$) for both these systems, where the alloys are low-melting. This gave us an opportunity to investigate the mixing enthalpies of melts of the Sb-Yb system at 960-1150 K and Bi-Yb at 1040-1270 K for the first time, using the isoperibolic calorimetry technique. The obtained results are presented in the figure.

For the purpose of modeling the thermodynamic properties of liquid and solid alloys of the Sb-Yb and Bi-Yb systems, and particularly for extrapolation of the mixing enthalpies of melts into the range of high temperatures and interstitial concentrations ($0.4<x_{Yb}<0.9$), we used the model of ideal associated solutions (IAS), considering the possibility of formation of associates YbE and Yb_2E (E = Sb, Bi). It was also necessary to account for the data known for these systems from literature – phase diagrams and standard enthalpy of formation of the SbYb compound. It became clear that we can obtain good agreement with the literature data for the Sb-Yb systems. Noticeably, in 2012 Chinese researchers conducted an assessment of the thermodynamic properties of the Sb-Yb system by means of Calphad method, though the mixing enthalpies of melts calculated by them appeared to be 1.5-2 times less exothermic than the ones obtained by us. Thus, the set of data used by those authors was insufficient for precise assessment.

For the Bi-Yb system, we only managed to obtain limited agreement with the phase diagram, although some its features were doubted by other authors, too.

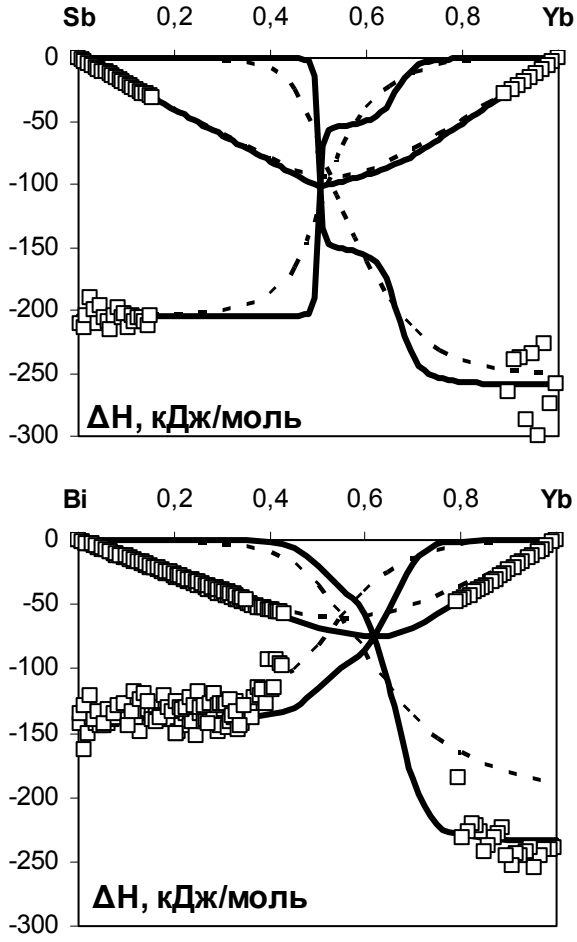

Fig. 1 Partial and integral mixing enthalpies of melts of the Sb-Yb system at 960-1150 K and Bi-Yb at 1040-1270 K: □ – experimental; IAS model: ——— – at 1100 K, and - - - – at 1600 K