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Surface and transport properties of Au–Sn liquid alloys

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Abstract

The present work is an experimentally based investigation of the applicability of the complex formation model (CFM) in the framework of statistical mechanical theory in conjunction with quasi-lattice theory (QLT) to describe the surface and transport properties of Au–Sn liquid alloys. Depending on melting temperatures, the surface tension of molten Au and Au–Sn alloys has been measured by the pinned-large drop method in the temperature range of $T = 1275$–1493 K. The calculations have been done with various objectives in view, i.e., to analyse existing thermodynamic data related to the peculiarities of the Au–Sn phase diagram, to use these data as the input for the interaction parameter calculations, to calculate the surface properties (surface tension and surface composition) and to compare the computed data with a new set of the surface tension experimental data as well as to predict the values of dynamic properties (chemical diffusion and viscosity). Some information on the structure of Au–Sn liquid alloys are given in terms of the microscopic functions (concentration fluctuations in the long-wavelength limit and chemical short-range order parameter).

Keywords: Equilibrium thermodynamics and statistical mechanics; Surface segregation; Surface tension; Surface thermodynamics (including phase transitions); Liquid surfaces; Gold; Tin; Alloys

1. Introduction

The compound-forming Au–Sn alloys are widely used in joining processes: as a subsystem of complex brazing alloys [1–3] or for diffusion bonding [4] in the field of precious gold alloys, as constituent of candidate materials for lead-free solders [5] as well as in the field of semiconductors [6].

The mixing behaviour of liquid alloys can be completely understood if their thermodynamics, structures and thermophysical properties are considered combining the theory with experiments.

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The thermophysical properties of Au–Sn liquid alloy system have been investigated by a quasi-lattice structural model for the chemical complexes (CFM) [7–9] as well as by the quasi-chemical approximation (QCA) for regular solution [10,11]. In this way the effect of short-range order phenomenon on the surface properties of Au–Sn liquid alloys can be estimated by the difference in the surface composition or surface tension calculated by the two models. The application of both approaches makes possible to study the ordering phenomena in the melts using the thermodynamic data on the heat of mixing, on the excess and integral Gibbs free energy of mixing as well as on the activity and, as result, to have an insight into the structure of liquid phase in terms of the microscopic functions.

The Au–Sn system has been studied by many authors [12–19]. The Au–Sn phase diagram [17–19] shows the presence of six intermetallic compounds in the solid state, $Au_{10}Sn$, Au_5Sn, AuSn, $AuSn_2$, $AuSn_4$ and ζ-phase of known structures [18,19], suggesting short-range ordering in the liquid phase [15,20]. The last assessment of the Au–Sn phase diagram [19] differs from the previous versions [17,18] in the phase composition ranges, probably due to still unclear, complex mixing behaviour in the Au-rich alloys.

The mixing properties of Au–Sn liquid alloys exhibit asymmetric behaviour around equiatomic composition [21], and for the temperatures ranging from 823 to 1473 K, the corresponding locations are between $C_{Sn} = 0.43$ and 0.45, respectively. Usually, the compound with the highest melting point persists in the liquid phase and the short-range ordered volume elements (associates or complexes) that are in prevalence have the same stoichiometry [7,9,21]. According to [18] the $Au_{10}Sn$ compound exists up to 798 K, but its compositional location, $C_{Sn} = 0.091$, is too far from those observed and thus, in the present work, the AuSn compound or δ-phase with melting point of $T = 692$ K [17,18] has been assumed as energetically favoured. The values of Hume–Rothery empirical factors such as size ratio ($V_{Sn}/V_{Au} \approx 1.62$), valency difference (=1 or =3) [22], electronegativity difference (=0.6) [23], electron concentration and solubility parameters support the compound forming tendency in this system. In order to reproduce quantitatively the thermodynamic and thermophysical quantities as well as the microscopic functions of Au–Sn liquid alloys, the complex formation model (CFM) [7,9,11] has been applied. The surface properties of Au–Sn melts have also been considered by the QCA for regular solution making possible to estimate the effects of short-range order phenomenon on these properties.

Preliminary inspection of the numerous surface tension literature data of liquid Au and Sn showed a considerable scatter, that is much more pronounced in the case of Sn [24]. The reported surface tension values at the melting point range from 1105 to 1185 mN/m and from 504 to 616 mN/m for liquid Au and Sn, respectively [24]. As concerns the surface tension of Au–Sn liquid alloys only few investigations have been reported [25–28]. The surface tension of Au–Sn alloys has been determined for different compositions and temperatures, so that it was also possible to find experimental data obtained under comparable conditions [25,27]. In the present work the pinned large drop method was used to determine the surface tension of liquid Au and Au–Sn alloys. The surface tension measurements of pure Au were performed between the melting point and 1413 K, while in the case of liquid Au–Sn alloys, surface tension was determined over the whole concentration range at the temperatures ranging from 1275 to 1493 K. In order to have a compatible data set, the surface tension reference data of Sn has been taken from Passerone et al. [29]. The interpretation of our new experimental results is given in the framework of CFM.

The microscopic behaviour of Au–Sn liquid alloys in atomic scale range has been analysed through macroscopic quantities such as thermodynamic functions using the Bhatia and Thornton formalism [30]. The microscopic functions, the concentration–concentration fluctuations in the long wavelength limit, $S_{cc}(0)$, and the Warren–Cowley short-range order parameter, α_1, [31] elucidate the nature of ordering and the degree of order in the melt, respectively. These functions are directly related to the dynamic properties, such