



## Bulk and surface properties of liquid Sb–Sn alloys

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### ABSTRACT

The mixing behaviour of liquid Sb–Sn alloys has been described in terms of energetics and structure through the study of their thermodynamic, surface, transport and structural properties by using the Complex Formation Model (CFM) in the weak interaction approximation and by postulating SbSn chemical complexes as energetically favoured. The new Sb–Sn surface tension experimental data, obtained by the pinned drop method at temperatures ranging from 513 to 1023 K, have been analysed in the framework of the CFM and compared with the calculated values as well as with the corresponding literature data. The structural characteristics of Sb–Sn melts are described by the two microscopic functions, i.e. the concentration fluctuations in the long-wavelength limit and the Warren–Cowley short-range order parameter.

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### 1. Introduction

The Sb–Sn binary alloys are recently used as high temperature solders, in particular a few Sn-rich compositions [1–3], while the Sb–Sn system has great importance as a subsystem of multicomponent lead free solders containing Ag, Cu, Au, Zn, Bi and In, used in the electronic industry for high temperature applications such as step soldering technology [4]. Among these, alloys from Sb–Sn–X (X = Cu, Ag, Bi) ternary systems have a wide range of fusible applications and are believed to be the most promising [1,5,6]. The addition of Sb results in a significant improvement of mechanical properties, enhancement of wetting, higher creep resistance and longer rupture time [2,5]. The presence of two intermetallic phases, i.e. the Sb<sub>2</sub>Sn<sub>3</sub>, and the SbSn, in the Sb–Sn system favours the formation of an intermetallic compound layer at the interface between liquid alloy and solid substrate (Cu and Ni), which is desirable to achieve a good metallurgical bond [1].

The Sb–Sn phase diagram has been assessed by many authors [3,7–11]. Although the numerous studies were carried out, the phase equilibria have not been established firmly. Analysis of the single SbSn phase ( $\beta$ -phase) showed disagreements concerning its structure; moreover, from emf measurements Vassiliev et al. [12] suggested the existence of four compounds, i.e.  $\beta$ ,  $\beta'$ ,  $\beta''$  and  $\beta'''$ . Knowledge about the energetics and the structure of a liquid alloy is a necessary prerequisite

to understand its mixing behaviour. The nature of interactions and structural re-adjustment of the constituent atoms in liquid alloys can be deduced by combining the theoretical modelling of observable indicators, such as the thermodynamic and the thermophysical properties and the corresponding experimental data [13–15].

The energetics of mixing of liquid Sb–Sn alloys has been analysed through the study of their thermodynamic functions and surface properties at 770 K using the quasichemical model for compound forming alloys and assuming an hypothetical AB<sub>2</sub> stoichiometry for clusters could be present in the melt [16], while in a subsequent investigation the same properties were studied at 905 K using four atom cluster model (FACM) and quasichemical approximation for regular alloys (QCA) [17].

Comparing the Gibbs energies of mixing of the two intermetallic phases [3,8], the SbSn phase ( $\beta$ -phase) results more stable indicating that in the liquid phase, chemical complexes with AB-stoichiometry are the most probable [18]. A compound formation tendency in the alloy melts can be “quantified” by the normalised form of the Gibbs free energy of mixing of the liquid phase at the equiatomic composition, expressed as  $G_M/RT$ . The values between  $-1$  and  $-2$  are the characteristic for weakly interacting systems. The curves describing the mixing properties of the Sb–Sn liquid phase are symmetric around the equiatomic composition and the values of  $G_M/RT \approx -1$  indicate that the interactions between Sb and Sn atoms in alloy melts can be considered to be weak in nature. Accordingly, the SbSn intermediate phase is assumed to be an energetically favoured compound, and thus, can be postulated that the Sb–Sn liquid phase will be rich in SbSn-clusters.

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The enthalpy of mixing [19–21] and the Sn-activities [12,22,23] measured at temperatures close to 905 K together with the data on the Gibbs free energy of mixing [3,8,11,12,19] were taken to calculate the interaction energies of liquid Sb–Sn alloys. All thermodynamic data indicate negative deviation from Raoult's law of ideality and substantiate the exothermic mixing effects in this system. Binary systems characterised by the presence of one or more intermetallic compounds in a solid state, exhibit in the liquid phase the associative tendency among the unlike constituent elements. The mixing properties of such molten alloys deviate from the regular solution behaviour and show a well-defined peak at one or more concentrations, which lie in the vicinity of the stoichiometric compositions of the intermetallic compounds [18]. The symmetric behaviour of the Sb–Sn mixing properties at the equiatomic composition is a result of weak exothermic effects and it can be only partially deduced from the Hume–Rothery empirical factors, such as size ratio ( $V_{Sb}/V_{Sn} \approx 1.07$ ), oxidation state difference ( $=1; =3$ ) [24] and electronegativity difference ( $\approx 0.09$ ) [25].

Accordingly, in the present work the CFM formalism in the weak interaction approximation assuming AB-stoichiometry has been applied to reproduce quantitatively the thermodynamic and the surface properties (surface tension and surface segregation), transport properties (diffusivity and viscosity) as well as the ordering phenomena (concentration fluctuations in the long-wavelength limit and the Warren–Cowley short-range order parameter) of the Sb–Sn melts [26].

The surface tension literature data of Sb and Sn reported by Keene [27] together with such data recently published by Mills and Su [28] exhibit significant scatter, particularly in the case of Sn. Although the applications of Sb–Sn alloys in joining processes are strongly related to the surface properties of their melts, the number of reported surface tension data is quite scarce [1,29]. In the present investigation the surface tension of five Sb–Sn alloys has been measured by the pinned drop method [30] over the whole temperature range from 1023 K to 50 K above their respective liquidus temperatures. The interpretation of the present experimental results is given in the framework of the CFM.

## 2. Experimental

### 2.1. Materials

Sb–Sn alloys were prepared from pure Sb ingots (99.999 wt.%, Newmet Koch) and Sn bar (99.9999 wt.%, Newmet Koch). Proper amount of pure elements were weighted and encapsulated inside quartz tube under argon atmosphere. The weight of each alloy sample was controlled to be around 3 g. The synthesis procedure and the thermal treatments on the samples were chosen according to the composition of the samples; these information are summarized in

**Table 1**  
Composition, synthesis procedure and thermal treatments of Sb–Sn alloys.

Sample n°	Nominal composition		Synthesis procedure and thermal treatments
	wt.%	at.%	
	Sb	Sn	
1	97.44	97.50	Induction melting and water quenching
2	84.67	85.00	Induction melting and water quenching.
3	69.46	70.00	Induction melting and water quenching.
4	52.06	52.70	Induction melting and water quenching. Annealed at 573 K for 30 min, at 498 K for 149 h and then water quenched.
5	19.59	20.00	Synthesis in furnace at 973 K for 120 min and water quenching. Annealed at 673 K for 23 h and then at 573 K for 23 h. Cooled inside the furnace.

**Table 1.** All ingots were checked by SEM/EDS analyses to ensure uniform structure and property composition.

### 2.2. Surface tension measurements

The surface tension measurements of five Sb–Sn alloys were performed by a variant of the large drop method [31], called pinned drop method [30], both based on the drop shape method. A liquid drop is placed on a flat, unwetted, solid support (sessile), or formed from a capillary (pendant) or placed on a cup (large) and its profile image is acquired. One of the advantages of the method is its non-invasive character. To improve the acquisition and elaboration of the drop profile, and thus the shape drop methods, computerised numerical calculations and computer-aided imaging techniques have been developed. The best results are obtained for non-wetting systems, i.e. those with a contact angle between the liquid drop and the solid support  $>90^\circ$ . This condition has been verified for a large number of metal-refractory systems, in particular the metal-oxide systems. In the case of a contact angle  $<90^\circ$ , a variant of the sessile drop method, called “the pinned drop” method is recommended. In this case the solid support is a special circular crucible with sharp edges. The design of the edges of the crucible blocks the triple line at an “apparent” contact angle that is much higher than the real one. A further advantage of the pinned drop method is that the axisymmetry of the drop can be imposed. The alloy specimens were prepared according to the procedure as described in Section 2.1. The experiments were performed in a horizontal furnace with Pt heating element, already described elsewhere [32].

The cleanliness of the environment was also assured by the high quality of the materials used and a systematic procedure of baking before each experiment. The apparatus enables working under a high vacuum (total pressure of  $10^{-4}$ – $10^{-5}$  Pa) or under controlled atmospheres such as high purity ArN60 (99.9999 %), as well as under reducing atmospheres of Ar-5 at.% H<sub>2</sub> mixture. The temperature, monitored by an S-type (Pt/Pt-10%Rh) thermocouple placed just below the specimen, was kept constant within  $\pm 2$  K. A solid-state electrode (POAS-Setnag®), with internal metal-oxide reference, kept at its optimal working temperature, allowed the oxygen partial pressure to be monitored inside the test chamber during the experiments.

Samples of Sb–Sn alloys of about 3 g were prepared and then mechanically abraded and chemically cleaned in an ultrasonic bath. Each sample was placed in a non-oriented monocrystalline alumina crucible ( $r = 5.5$  mm) [30]. The crucible with the sample was laid on an alumina holder sliding in the experimental apparatus. The surface tension measurements of Sb–Sn alloys were carried out by decreasing the temperature step by step (each 50 K) from 1023 K to 50 K above the melting temperature of the alloy sample. At each temperature the drop was allowed to equilibrate for a time of about 15–20 min. All measurements were performed under a fluxing atmosphere of high purity ArN60 (99.9999 %; mean flow rate  $q = 0.8 \cdot 10^{-6} \text{ m}^3 \text{ s}^{-1}$ ) with an oxygen content  $P_{O_2} \leq 10^{-2}$  Pa.

Resting on a perfectly levelled substrate, the sample drop was illuminated by an aligned light source and its image was captured by a CCD camera. The drop profile was acquired by a CCD camera and processed with ad hoc acquisition software (A.S.T.R.A.) [33] in LABview environment. This acquisition procedure allows real time surface tension measurements to be performed with an accuracy of  $\pm 0.1\%$  and at the same time the values of the other parameters (sample temperature and oxygen partial pressure) to be followed. In particular, the magnification factor is evaluated for each image utilised for the surface tension measurements. Each measured value showed a deviation of about  $\pm 2.5$  mN/m around the reported mean value.

After the experiment, the weight of solidified drop was checked with the aim to detect the loss of material eventually occurred. The metallographic examinations of the solidified sample were accomplished by optical microscopy and SEM/EDS analyses.

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