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Electrical conductivity, thermoelectric power and viscosity of liquid Sn-based alloys

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Abstract Shear viscosity of liquid Sn–Ag, Sn–Cu and Sn–Ag–Cu eutectics from melting temperature up to 1100 K and their electrical conductivity and thermoelectric power up to 850 K have been investigated. The electrical properties of liquid Sn with additions of Fe and Ni have also been studied. It is shown that small amounts of metal admixtures affect noticeably the behavior of the physical properties of liquid Sn.

Introduction

The most suitable alloys selected for replacement of the traditional lead-tin solders by a solder material free of lead seem to be Sn-based eutectics containing Ag or/and Cu [1–4]. Sn–Ag and Sn–Cu are the attractive candidates due to their good mechanical properties. The main benefits of the Sn–Ag–Cu eutectic are a lower melting temperature compared with the Sn–Ag and Sn–Cu and its distinguished wetting behavior without loosing strength. However, the selection of a lead-free solder requires a careful and comprehensive study of various physical properties of the candidate alloys. It would be the best to find an alloy that can provide the same results, which are presently accustomed with the lead-tin solders. In this connection, basic investigations of the physical properties of liquid Sn-based alloys are of prime importance.

Solder joints in the electronic devices are electrical as well as structural connections. They should provide the lowest possible electrical resistance between mounted electronic components and the substrate. At the same time, the values of the thermoelectric power, which usually appear at the points of electric junctions between different materials, is to be low. The solder's fluidity influences its wetting capability, hence knowledge of the viscosity is important. Finally, increasing influence of the computational modeling in technological processes generates a higher demand for accurate values of the physical properties of applied materials.

Experimental studies of various eutectic systems in liquid state showed that at the temperatures much higher than the eutectic one they exhibit large concentration inhomogeneities, which are not represented on the phase diagrams [5]. It is a question how the physical properties of the molten alloys vary with the temperature? Therefore, investigations of the electrical conductivity (σ), thermoelectric power (S), and shear viscosity (η) of liquid $Sn_{96.2}Ag_{3.8}$, $Sn_{98.7}Cu_{1.3}$ and $Sn_{94.9}Ag_{3.8}Cu_{1.3}$ eutectics (all compositions in at.%) have been performed in a wide temperature range in the present work.

The influence of Fe and Ni admixtures on the physical properties of liquid Sn has also been studied. This is important because these elements may be used for improvement of the technological and operating performances of Sn-based solders (wetting, interaction with Fe- or Ni-based constructional materials etc.). For example, the Sn–Ag–Cu alloys with minor additions of Ni showed a substantially better creep resistance at lower stresses [4].

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Experimental

Viscosity measurements

The viscosity measurements were carried out in a computer-controlled oscillating-cup viscosimeter [6]. Using the modified Roscoe equation, the $\eta(T)$ was calculated from the logarithmic decrement and the period of oscillations [7]. The proper amounts of the components (99.99 Ag, 99.99 Cu, 99.99 Sn) were initially melted in evacuated and sealed quartz ampoules. Before making an experiment a cavity of the cylindrical BN crucible with internal diameter of 20 mm was filled with a sample. A vacuum in the chamber and the sample outgassing were carried out with the vacuum pump working continuously. The experiments were performed in an atmosphere of 90% Ar + 10% H_2 after initially pumping out the working volume of the furnace in order to avoid the sample oxidation.

The compositions of samples having a mass of about 70 g were accurate to ± 0.02 wt.%. Each sample was weighed before and after the measurements, and no loss of mass was observed. A homogeneous temperature field ($\Delta T \approx \pm 0.3$ K) in the range of absolute values up to 1100 K was created inside a furnace. The temperature was measured with a Pt/PtRh thermocouple arranged just below the crucible. The heating and cooling rate was 120 K/h. The viscosity data were obtained with an accuracy of ~5%.

Electrical conductivity and thermoelectric power measurements

The σ(T) and $S(T)$ were measured by the 4-point contact method [8]. The samples prepared from pure Ag (99.99), Cu (99.99), Fe (99.98), Ni (99.99) and Sn (99.99) were inside the BN cells in the form of vertical cylinders with an operating cavity height of 60 mm and an inner diameter of 3 mm. 6 graphite electrodes, 2 for the current and 4 for the potential measurements, dividing the cell in several sections with 10 mm length, were inserted into the cell wall along its vertical axe. The potential electrodes were provided with WRe-5/20 thermocouples. This permitted simultaneous determination of the temperature as well as the measurement of σ and S in one run. Moreover, the cell construction allowed eliminating analytically jamming and noise signals arising due to contact wires as well as a systematic device deviation. The experiments were performed under Ar atmosphere. The sample compositions were accurate within 0.02 wt.%. The resultant error of σ is ~2%, and that of S is ~5%.

Results and discussion

The dynamic viscosity of liquid Sn and $Sn_{96.2}Ag_{3.8}$, $Sn_{98.7}Cu_{1.3}$ and $Sn_{94.9}Ag_{3.8}Cu_{1.3}$ alloys as a function of temperature, $\eta(T)$, is presented in Fig. 1. The experimental data for pure Sn are in a good agreement with those reported earlier [6, 9].

The viscosity increases exponentially with cooling and the temperature dependences $\eta(T)$ for all investigated alloys can be rather well described by the Arrhenius equation:

$$\eta(T) = \eta_0 \exp\left(\frac{E_A}{RT}\right) \quad (1)$$

where η_0 is a constant (mPa s), R is the gas constant (J mol^{-1} K^{-1}), T is the absolute temperature (K), E_A is the flow activation energy (J mol^{-1}). As an example, the Arrhenius plot for Sn is shown in Fig. 1. The values of η_0 and E_A for the studied alloys are given in Table 1.

It is also seen from Fig. 1 that Ag or Cu (or both) increase the viscosity of liquid Sn by 4–8%. Such increase of the viscosity with addition of a small quantity of solute is in agreement with the experimental data on other dilute binary alloys (1–5% increase η with addition of 1 at.% solute [10]) as well as with the theoretical estimations (7–8% increase η with addition of 1 at.% solute [11]).

One of commonly used theoretical descriptions is based on the correlation between the viscosity and interchange energy, which can be expressed through the enthalpy of mixing [12]. In this case, viscosity of a real melt is:

$$\eta = \eta^{id} + \Delta\eta \quad (2)$$

where η^{id} is an ideal viscosity and $\Delta\eta$ is an excess viscosity. Assuming that the activation energy of a viscose flow is additive, for the viscosity of a two-component ideal system can be written:

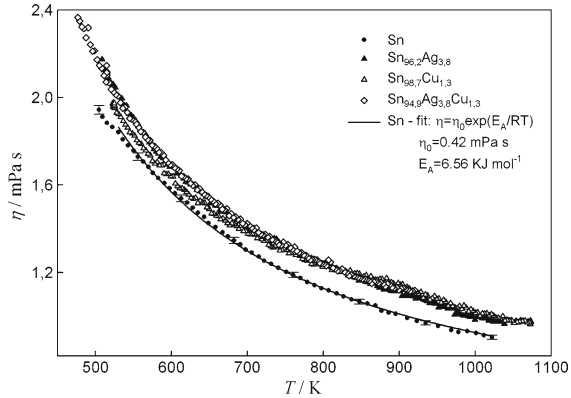

Fig. 1 Viscosity as a function of temperature for liquid Sn and $Sn_{96.2}Ag_{3.8}$, $Sn_{98.7}Cu_{1.3}$, $Sn_{94.9}Ag_{3.8}Cu_{1.3}$ eutectic melts

Table 1 Fitting parameters to the Arrhenius function for viscosity of liquid Sn and $Sn_{96.2}Ag_{3.8}$, $Sn_{98.7}Cu_{1.3}$, $Sn_{94.9}Ag_{3.8}Cu_{1.3}$ eutectic melts plotted in Fig. 1

Composition	η_0 (mPa s)	E_A (kJ mol^{-1})
Sn	0.42	6.56
$Sn_{96.2}Ag_{3.8}$	0.47	6.41
$Sn_{98.7}Cu_{1.3}$	0.51	5.84
$Sn_{94.9}Ag_{3.8}Cu_{1.3}$	0.48	6.26

$$\ln \eta^{id} = x_1 \ln \eta_1 + x_2 \ln \eta_2 \quad (3)$$

where η_1 η_2, x_1, x_2 are the viscosities and concentrations of the melt components 1 and 2, respectively.

The excess viscosity $\Delta\eta$ is given by:

$$\Delta\eta = -2(x_1\eta_1 + x_2\eta_2)\frac{\Delta H}{RT} \quad (4)$$

The sign of the excess viscosity depends only upon that of the integral enthalpy of mixing ΔH. It has been shown that $\Delta\eta$ tends to become negative as the difference in atomic size increases [10]. Viscosity is expressed in terms of some basic physical quantities (ionic radius, mass of an atom, coefficient of activity) and consists of the hard and soft parts of the friction constant for viscous movements of atoms. It was shown that the hard part tends to become less negative as the difference between ionic radii increases. On the other hand, the soft part tends to become positive as the difference between the mass of atoms increases. A model proposed in Ref. [11] is similar, but the integral enthalpy of mixing is taking into account only in the soft component. The increase of the viscosity of liquid Sn with additions of Ag or Cu observed in Fig. 1 correlates with the theoretical predictions derived with the relationship between the excess viscosity and integral enthalpy of mixing [10].

The experimental temperature dependences of the electrical conductivity for liquid Sn and Sn-based alloys with small additions of Ag, Cu, Fe and Ni are presented in Fig. 2. For a comparison, electrical conductivity of pure Sn measured in [13] is also shown and a good agreement between our measurement and these results is observed.

The electrical conductivity of all studied melts decreases gradually with heating. The temperature dependences can be well fitted by linear functions of type: $\sigma(T) = \sigma_0 - \frac{d\sigma}{dT}T$ Table 2 gives the parameters of linear fits for the experimental data plotted in Fig. 2.

It is interesting that the results of this study show that the absolute value of the electrical conductivity of liquid Sn is increased by ~5% when 3.8 at.% of Ag is added and by ~1 per cent when 1.3 at.% of Cu is added. The measurements in the present work were repeated several times and in all cases the results were similar to those shown in Fig. 2. In general, electrical conductivity of a liquid metal

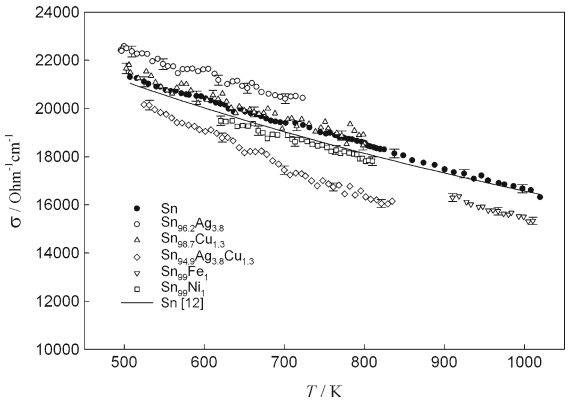

Fig. 2 Electrical conductivity as a function of temperature for liquid Sn, $Sn_{96.2}Ag_{3.8}$, $Sn_{98.7}Cu_{1.3}$, $Sn_{94.9}Ag_{3.8}Cu_{1.3}$, $Sn_{99}Fe_1$, and $Sn_{99}Ni_1$

Table 2 The temperature dependences of the electrical conductivity for the studied liquid alloys: linear fits to the experimental data plotted in Fig. 2

Composition	$\sigma(T) = \sigma_0 - \frac{d\sigma}{dT}T$ (Ohm^{-1} cm^{-1})	
	σ_0 (Ohm^{-1} cm^{-1})	$\frac{d\sigma}{dT}$ (Ohm^{-1} cm^{-1} K^{-1})
Sn	26029	9.4
$Sn_{96.2}Ag_{3.8}$	27176	9.5
$Sn_{98.7}Cu_{1.3}$	26201	9.4
$Sn_{94.9}Ag_{3.8}Cu_{1.3}$	27305	13.8
$Sn_{99}Fe_1$	25173	9.8
$Sn_{99}Ni_1$	25057	8.9

is decreased when foreign atoms are introduced to the melt [10]. According to the earlier experimental works, conductivity of Sn decreases with additions of Ag or Cu [14–16]. One should however note that (i) in these works the binary Sn alloys containing not less than 10 at.% Ag or Cu were investigated; (ii) a difference between the electrical resistivity of pure Sn and $Sn_{90}Ag_{10}$ ($Sn_{90}Cu_{10}$) is negligibly small; (iii) it has been revealed experimentally that in the case of a liquid system composed of polyvalent components, the electrical resistivity is decreased when small quantity of an element with lower resistivity is added [10]; and (iv) the estimations made with the nearly free electron model (NFL) in [17] predict firstly slight decrease of the electrical resistivity when Ag or Cu is added to Sn and only beginning from 30–40 at.% of Ag (Cu) the resistivity is increased. Thus our measurements should not obviously be an artefact.

Additions of both Cu and Ag in amounts needed for the ternary eutectic Sn–Cu–Ag lead to a decrease of the electrical conductivity by ~5% as compared with pure Sn. The electrical conductivity of liquid Sn is decreased by ~2.5% when 1 at.% of Ni is added and by ~5.5% when 1 at. % of Fe is added. This agrees with the theoretical predictions of the NFL model [17] as well as with other investigations.

A decrease of the electrical conductivity by ~1% with addition of 1 at. % Ni and by ~3% with addition of 1 at.% Fe was revealed experimentally in [18].

The experimental temperature dependences of the thermoelectric power are presented in Fig. 3. The thermoelectric power of liquid Sn is about −1 to −2 μV/K and remains practically constant over the whole studied temperature range. The absolute values for liquid Sn well agree with the results reported in [13]. The thermoelectric power of Sn-Ag and Sn-Cu eutectics is kept at the level of −5 μV/K to −7 μV/K. It is noteworthy that an increase of the absolute values of the thermoelectric power of Sn with small additions of Ag is predicted by the theoretical calculations [19]. However the experimental results [19] showed a disagreement with the theory. We are not aware for experimental data for the thermoelectric power of liquid Sn with small Ag or Cu additions.

The temperature behavior of the thermoelectric power of the ternary Sn–Ag–Cu eutectic is not linear dependent. $S(T)$ of liquid $Sn_{94.9}Ag_{3.8}Cu_{1.3}$ is kept at the level of approx. −20 μV/K after melting up to 680 K, then between 680 and 700 K it changes to −10 μV/K, and remains nearly constant with a further heating. The thermoelectric power of liquid Sn is also increased in absolute values when small quantities of Fe or Ni are added. This agrees with the changes reported in [20] but our absolute values of $S(T)$ are about of order higher.

Doping of eutectic melts by minor admixtures with a narrow *d*-band like Al, Ga, Ni, Bi, Cu was studied in [21] and it was suggested that the *s–d* interaction is of considerable importance in the charge transfer processes. The 3*d* orbital in Fe and Ni is well localized and can lead to resonance with the *s* conduction electrons [22]. We suggest that such an *s–d* resonance scattering causes the conductivity decrease in our case. As the density of states (DOS) of the melt is formed by DOS of pure Sn and of the admixture (3*d* states of Fe or Ni), the common DOS at the Fermi level increases. The thermoelectric power is determined as the energy derivative of DOS, thus absolute values of the thermoelectric power of $Sn_{99}Fe_1$ and $Sn_{99}Ni_1$ melts is higher than that of pure Sn.

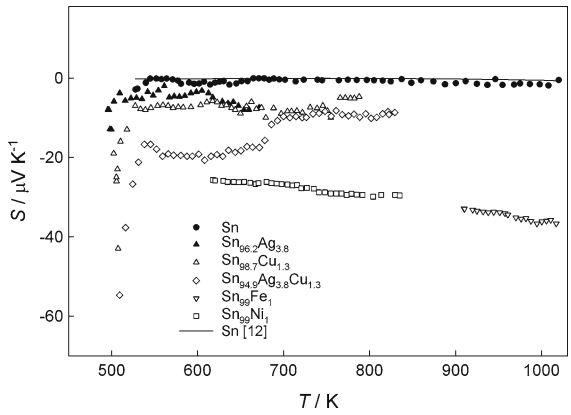

Fig. 3 Thermoelectric power as a function of temperature for liquid Sn, $Sn_{96.2}Ag_{3.8}$, $Sn_{98.7}Cu_{1.3}$, $Sn_{94.9}Ag_{3.8}Cu_{1.3}$, $Sn_{99}Fe_1$, and $Sn_{99}Ni_1$

Conclusions

The experimental study of the dynamic viscosity, electrical conductivity and thermoelectric power of liquid Sn and Sn-based alloys with Ag, Cu, Fe and Ni showed that these properties are very sensible to very small quantities of admixture elements. It is established that (i) dynamic viscosity of liquid $Sn_{96.2}Ag_{3.8}$, $Sn_{98.7}Cu_{1.3}$ and $Sn_{94.9}Ag_{3.8}Cu_{1.3}$ alloys is about 4–8% higher than the viscosity of pure Sn; (ii) addition of Ag (3.8 at.%) or Cu (1.3 at.%) to Sn increases the absolute value of the electrical conductivity while addition of both elements (Ag and Cu) to Sn leads to a decrease of the electrical conductivity; small additions (1 at.%) of Fe and Ni also decrease the electrical conductivity of liquid Sn; iii) additions of Ag, Cu, Fe or Ni to Sn increase the absolute values of the thermoelectric power.

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