Electrical conductivity of liquid Sn-Ti-Zr alloys

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Abstract. Electrical conductivity of liquid binary Sn-Ti, Sn-Zr and ternary Sn-Ti-Zr alloys on the Sn-rich side was studied in a wide temperature range above the liquidus. Admixtures of Ti and Zr affect considerably the electrical conductivity of liquid Sn. The melting-solidification temperatures were determined. The conductivity results are interpreted in the context of the s-d hybridization model.

1. Introduction

The Sn-Ti-Zr system is of technical importance for active brazing filler metals [1, 2], and a detailed knowledge of thermophysical and structure-sensitive properties, in particular, of these molten alloys prior to solidification is very important for the development of materials with predicted properties. Typical filler metals for diamond brazing contain active elements such as Ti or Zr in order to wet the diamond or other ceramic materials. Brazing processes also need accurate information on thermodynamic data and phase diagrams of the binary subsystems. Sn-Ti and Sn-Zr binaries were studies repeatedly [2-4], but discrepancies in reported intervals of solubility at higher temperatures, the structure of intermetallic compounds and their thermal expansion, in particular near the liquidus line on the Sn rich side still remain. The components of the Sn-Ti and Sn-Zr systems show a substantial difference in melting temperatures. Therefore, the addition of a refractory element affects a drastic increase of the liquidus line, and even a negligible error in the alloy composition can provoke a serious error in determination of the solidification onset. Because of this peculiarity and the experimental difficulties the data on structure-sensitive properties of these systems in the liquid state are scarce and contradictory. Recently the liquid binary Sn-Ti and Sn-Zr alloys with a high Sn content (from 75 to 100 at.%) were studied [5]. It was revealed that the Ti and Zr admixtures influence vastly the structure-sensitive properties of the liquid Sn, namely, reduce the electrical conductivity and increase substantially the viscosity. In this work we present new results for the electrical conductivity of liquid binary and ternary Sn-Ti-Zr liquid alloys measured over a wide temperature interval above the liquidus.

2. Experimental

The electrical conductivity was measured by a contact method in accordance with the 4-point scheme as described elsewhere [6]. The samples were placed into the measuring cells manufactured of BN

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ceramics in the form of vertical cylinders with an operating cavity height of 60 mm. The graphite electrodes for the current and potential measurements were inserted into the wall of the container along its vertical axis. The potential electrodes were provided with WRe-5/20 thermocouples. The experiments were performed under Ar gas pressures up to 10 MPa. The resultant error of the electrical conductivity determination did not exceed 2%. The electrical conductivity measurements were performed for liquid binary and ternary alloys. The alloys given in Table 1 were prepared by arc-melting of pure elements. The liquidus temperature was determined from the deviation from the linear decrease of the electric conductivity with decreasing temperature as shown in Figure 1. This graphical determination resulted in a estimated error of ± 10K.

| Comp. | Sn_{65}Ti_{35} | Sn_{65}Ti_{45} | Sn_{65}Zr_{35} | Sn_{65}Ti_{26.25}Zr_{8.75} | Sn_{65}Ti_{26.25}Zr_{75} |
|-------|----------------|----------------|----------------|---------------------------|-------------------------|
| T_{Liq} [K] | 1420 ± 10 | 1675 ± 10 | 1690 ± 10 | 730 ± 10 | 860 ± 10 |
| Comp. | Sn_{75}Ti_{12.5}Zr_{12.5} | Sn_{65}Ti_{17.5}Zr_{17.5} | Sn_{65}Ti_{26.25}Zr_{8.75} | Sn_{65}Ti_{26.25}Zr_{75} | -- |
| T_{Liq} [K] | 1090 ± 10 | 1400 ± 10 | 1410 ± 10 | 1550 ± 10 | -- |

3. Results and Discussion
The measured temperature dependencies of conductivity, $\sigma(T)$, for binary melts together with conductivity of pure Sn for comparison are presented in figure 1. The data for pure Sn are in agreement with those reported earlier [5]. Transition from the solid to the liquid state is accompanied by an abrupt decrease of conductivity, which is specific for each composition and corresponds to the melting onset. Cooling of the molten alloy is accompanied by the gradual conductivity increase, which becomes more drastic in the solidification region. The melting and solidification processes are accompanied by a hysteresis, indicating an existence of a certain “melting-solidification” temperature range. While the liquidus temperature fits well to available phase diagram data of the binary systems [7], the “solidus” temperature is far too high. This might be caused by the formation of a continuous layer of the primary precipitating intermetallic phase, causing a short-cut between the measurement electrodes. This in turn would result in measurement of this layer only, instead of the partially liquid alloy. Additions of the Ti or/and Zr lead to a decrease of the temperature coefficient of conductivity $\sigma(T)/dT$ in the high-temperature region corresponding to liquid phase. Moreover, $\sigma(T)/dT$ tends to zero at high content of the Ti or/and Zr admixtures.

![Figure 1](image1.png)

**Figure 1.** Electrical conductivity as a function of temperature of liquid Sn_{65}Ti_{35} (1-heating, 2-cooling), Sn_{75}Ti_{12.5}Zr_{12.5} (3-heating, 4-cooling), Sn_{65}Zr_{35} (5-heating, 6-cooling) alloys

![Figure 2](image2.png)

**Figure 2.** Electrical conductivity as a function of temperature of liquid Sn_{65}Ti_{12.5}Zr_{12.5} (1-heating, 2-cooling), Sn_{65}Ti_{17.5}Zr_{75} (3-heating, 4-cooling), Sn_{65}Ti_{12.5}Zr_{12.5} (5-heating, 6-cooling), Sn_{65}Ti_{17.5}Zr_{17.5} (7-heating, 8-cooling) alloys
The slope of $\sigma(T)$ curve for Sn$_{65}$Ti$_{35}$ changes twice at 1370-1380 K and at ~1433 K indicating the range of melting. After heating the sample up to 1550 K, it was held for 1 hour and then cooled. The cooling curve shows a deviation from the linearity (start of solidification) corresponding to the liquidus temperature, $T_L$, at about 1420 K. The slope of $\sigma(T)$ curve for Sn$_{65}$Ti$_{35}$ changes at about 1610 K. The next curve bend is observed at about 1660-1680 K. Further heating is accompanied by a linear conductivity decrease in the liquid state. The sample was held for 1 hour at 1750 K and then cooled. A kink indicating start of solidification appeared at about 1675 K. A first kink of $\sigma(T)$ curve for Sn$_{65}$Zr$_{35}$ is observed at about 1650 K and the second at 1700 K. After 1 hour stage at 1800 K and further cooling a kink indicating the liquidus appeared at 1690 K.

The $\sigma(T)$ dependence of ternary Sn-Ti-Zr melts, where Ti and Zr admixtures present at equal ratio, as well as the conductivity of pure Sn are presented in figure 2. As is seen, the conductivity of Sn$_{65}$Ti$_{26.25}$Zr$_{8.75}$ decreases with heating. A slope of $\sigma(T)$ curve slightly changes approaching to 700 K indicating start of melting. The next curve bend is observed at about 750 K. The sample was held for 1 hour at 850 K and than cooled. A kink indicating $T_L$ appeared at about 730 K.

A slope of $\sigma(T)$ curve for Sn$_{65}$Ti$_{26.25}$Zr$_{8.75}$ changes approaching to 840 K indicating start of melting (figure 2). The next curve bend is observed at about 890 K. Heating in the liquid state is accompanied by a negligible conductivity decrease. The sample was held for 1 hour at 1000 K and then cooled. $T_L$ was determined as 860 K. Contrary to Sn$_{65}$Ti$_{26.25}$Zr$_{8.75}$, the melting-solidification hysteresis is more pronounced. Similar hysteresis was also observed for Sn$_{75}$Ti$_{12.5}$Zr$_{12.5}$ ($T_L = 1090$ K) and Sn$_{65}$Ti$_{17.5}$Zr$_{17.5}$ alloys ($T_L = 1400$ K).

The electrical conductivity vs. temperature of ternary Sn$_{65}$Ti$_{26.25}$Zr$_{8.75}$ and Sn$_{65}$Ti$_{8.75}$Zr$_{26.25}$ liquid alloys is presented in figure 3. A general run of $\sigma(T)$ curves and the hysteresis are very similar to those revealed in the above described binary and ternary alloys. $T_L$ was determined as 1410 K and 1550 K, correspondingly.

Contrary to the stepwise conductivity changes in pure metals during the liquid-solid transition, the extended conductivity increase during solidification is explained by a gradual precipitation of the solid phases between liquidus and solidus temperature. The later is peculiar to the systems with substantial difference in melting temperatures of the components.

The electrical conductivity of simple liquid metals is well described by the Ziman equation [8] which makes use of pseudopotentials and structure factors. Serious difficulties are encountered in the case of 3d transition metals. The point is that d-electrons heavily distort the density of states and the free electron approximation in its classic form is not quite correct.

The interpretation in terms of phase shifts, proposed by Friedel [9], provides only semiquantitative agreement with experiment [10]. The Ti and Zr dopants belong to transition metals with partially filled
d shells. The d states in such solutes can be described using the Friedel–Anderson scheme, central to which is the concept of virtual bound states. This picture is substantiated by experimental data for transition metal impurities in liquid Al [11] and Sn [12].

The electrical conductivity of a liquid alloy is expressed as [13]:

$$\sigma = \frac{n_e e^2 L_0}{\hbar k_f}$$

(1)

where $\hbar$ is the Planck constant, $n_e$ is the electron density, $e$ is the electron charge, $L_0$ is the mean free path of conduction electrons, $k_f$ is the Fermi wave number.

It is clear that the change of conductivity in Sn-Ti, Sn-Zr and Sn-Ti-Zr alloys can be attributed to the changes in the parameters $n_e$ and $L_0$. The later is due to the structure changes, which may include the altering of the nearest neighbour distance, the first coordination number, as well as the relaxation time of s-d resonance scattering. The contribution of these parameters to the total conductivity can be very different. $n_e$ can lead either to an increase or to a decrease of conductivity, whereas a decrease of $L_0$ due to the s-d resonance scattering always results in a decrease of conductivity as it occurs if Ti or/and Zr are added to liquid Sn.

4. Summary
The electrical conductivity of liquid binary Sn-Ti, Sn-Zr and ternary Sn-Ti-Zr alloys on the Sn-rich side was studied in a wide temperature range above the liquidus. Admixtures of Ti and Zr affect considerably the electrical conductivity of liquid Sn. The results are interpreted in the context of the s-d hybridization model. The temperature ranges of the melting-solidification processes and the liquidus temperatures were determined.

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