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Correlation between the resistivity and the atomic clusters in liquid Cu-Sn alloys

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ABSTRACT

The liquid structure of $Cu_xSn_{100\text{-}x}$ ($x = 0$, 10, 20, 33, 40, 50, 60, 75, 80 and 100) alloys with atom percentage were investigated with resistivity and viscosity methods. It can be found from the resistivity data that the liquid $Cu_{75}Sn_{25}$ and $Cu_{80}Sn_{20}$ alloys had a negative temperature coefficient of resistivity (TCR), and liquid $Cu_{75}Sn_{25}$ alloy had a minimum value of $-9.24\ \mu\Omega\ cm\ K^{-1}$. While the rest of liquid Cu-Sn alloys had a positive TCR. The results indicated that the $Cu_{75}Sn_{25}$ atomic clusters existed in Cu-Sn alloys. In addition, the method of calculating the percentage of $Cu_{75}Sn_{25}$ atomic clusters was established on the basis of resistivity theory and the law of conservation of mass. The $Cu_{75}Sn_{25}$ alloy had a maximum volume of the atomic clusters and a highest activation energy. The results further proved the existence of $Cu_{75}Sn_{25}$ atomic clusters. Furthermore, the correlation between the liquid structure and the resistivity was established. These results provide a useful reference for the investigation of liquid structure via the sensitive physical properties to the liquid structure.

1. Introduction

The liquid structures have been a constant research focus in the field of physics and material science. In recent years, more attention was paid to melt structure due to the application of the liquid metal battery [1], liquid metal catalysts [2], thermoelectric materials [3] and self-driven liquid metal machine [4]. It has been proved through experimental data that the liquid structure can significantly affect the solidified structure and properties directly. Therefore, it is of scientific and engineering significance to study the liquid structure and application of alloy melts.

Electrical resistivity and viscosity acted as two sensitive physical properties to the melt structure and can reflect the transport properties of electrons and atoms, respectively. It has been confirmed though the majority of research work that the resistivity and viscosity methods are applicable to the investigation of liquid structure, as there is close relationship between the physical property and liquid structure [5–8]. Especially, the resistivity can reflect the information of melt structure from a more microcosmic angle in a real time. The resistivity and viscosity data are also effective for estimating the local structure of liquid alloys: short-range order and medium range order [9–11]. In addition, the percentage of atomic clusters in the melt can be calculated on the basis of the resistivity [12]. Therefore, resistivity and viscosity methods are widely used to investigate the liquid structure.

Cu–Sn alloys are applied extensively in material, machine and industry fields, etc. because of their interesting mechanical, electrical and chemical properties. The Cu–Sn alloy system shows excellent properties due to its characteristic of the intermetallic compounds [13]. The liquid Cu–Sn system was first applied in the neutron scattering experiments on account of the isotope substitution method [14]. The existence of the medium-range order was proved in liquid Cu-Sn alloys [15]. However, the relationship between resistivity and local structure has not been involved in these studies. The main purpose of this work is to analyze the correlation between the resistivity and the atomic clusters.

The liquid structures of Cu–Sn alloys were investigated using X-ray diffraction, neutron diffraction and reverse Monte Carlo model. The results showed that the whole concentration range can be separated into three intervals corresponding to four types of clusters [16]. It was confirmed that the existence of the micro-inhomogeneous structure and $Cu_{75}Sn_{25}$ atomic cluster in liquid Cu-Sn alloys. In the solid state, Cu–Sn

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alloys exhibit a number of intermetallic phases. The structure-sensitive physical properties such as the viscosity and the electrical resistivity show a non-monotonous composition dependence with maxima at the compound level [5]. Assuming that the interactions between the atoms in these alloys are basically unchanged when heating to the liquid state, one can expect signs of cluster formation should be similar to the corresponding intermetallic phases in the liquid state.

In order to further investigate the composition dependence of the atomic clusters in liquid alloys, the resistivities of liquid Cu–Sn alloys were measured over the entire concentration range. In addition, the composition dependence of temperature coefficient of resistivity was carefully analyzed to establish the correlation between the liquid structure and the physical properties. The results can provide a good reference for the investigation of liquid structure via resistivity method.

2. Materials and methods

The Cu-Sn alloys were prepared from Cu block and Sn block with a high purity of 99.999 wt.%. In order to ensure the uniformity of the composition, the raw materials were melted in a graphite clay crucible using a medium frequency induction electric furnace and casted into a graphite mold. The cast alloys were subsequently treated via the following processes. Firstly, each cast alloy was re-melted under 99.999% argon gas in the electrical resistance furnace and assisted by intelligent control system to ensure that the temperature error below 5 K. Secondly, the melt was stirred uniformly and held for 30 min at the temperature of 200 K above liquidus temperature. Finally, the melt was poured into a quartz tube for resistivity test and poured into an alumina crucible with an internal diameter of 25 mm for the measurement of viscosity.

The resistivity was measured by the DC four-probe method. The main parts of instrument for resistivity measurement were described in our previous work [17]. The constant current, flowing from one current electrode to the other, was provided by a PF66M constant-current source. The voltage drop between two potential electrodes and temperature were measured by a Keithley 2182A nanovoltmeter. The experimental data was obtained by an automatic computer acquisition system. In addition, the DC current-reversal technique was used to cancel the extra potentials which maybe come from the connection points and temperature fluctuations in the test. Moreover, in order to minimize the deviation of the cell size and systematic errors of measurement, the cells are made of quartz with quite small thermal expansion. In addition, the shape factor of cell was calibrated using the liquid mercury with a known resistivity of 95.8 μΩ cm [18]. During testing, tungsten wires with a diameter of 0.8 mm were employed as current and potential electrodes, the sample was under the shielding of flux argon gas (99.999%), and the data was collected during cooling.

A torsional oscillation viscometer of high-temperature melt was adopted to measure the viscosity of Cu-Sn system melts [19–21]. The samples were held in a sealed Al_2O_3 cylindrical crucible suspended on a Mo wire. The torsion oscillation was damped by the friction between the inner walls of the crucible with the melt. The dynamic viscosity of the liquid sample can then be obtained. To eliminate the error induced by temperature fluctuation, each data point was obtained after the temperature was held for about 20 min before measurement.

3. Results and discussion

3.1. Temperature dependence of resistivity

Fig. 1 showed the temperature dependence of resistivity (termed ρ-T curve) for the liquid Cu-Sn alloys with varied compositions during cooling. It need to be noted that resistivity of copper was obtained by linear extrapolation of the resistivity of liquid copper. It can be seen that the resistivity increased linearly with increasing temperature for pure Sn, pure Cu, $Cu_{10}Sn_{90}$, $Cu_{20}Sn_{80}$, $Cu_{33}Sn_{67}$, $Cu_{40}Sn_{60}$, $Cu_{50}Sn_{50}$ and $Cu_{60}Sn_{40}$ alloys. These liquid alloys had a positive temperature coefficient of resistivity (TCR). Intuitively, TCR is the slope of ρ-T curve. It can be determined using the linear fitting method that the values of TCR are 19.52, 8.62, 19.43, 18.62, 16.72, 15.32, 11.60, and 6.76 μΩ cm K^{-1}, respectively. Nevertheless, $Cu_{75}Sn_{25}$ and $Cu_{80}Sn_{20}$ alloys had negative temperature coefficients of resistivity. The values of TCR are −9.24 and −8.00 μΩ cm K^{-1}, respectively. In addition, it can be deduced that there are at least two liquid Cu-Sn alloys, the TCR of which were zero in the temperature range from liquidus to 1350 K. This kind of material is called the material with constant electrical resistivity. Assuming that there is no strong interaction between Cu atom and Sn atom and no Cu-Sn clusters exists in liquid Cu-Sn alloys, all liquid Cu-Sn alloys should have positive temperature coefficients of resistivity. However, this is contrary to the experimental results. Therefore, there is Cu-Sn clusters with strong chemical combination in liquid Cu-Sn alloys investigated.

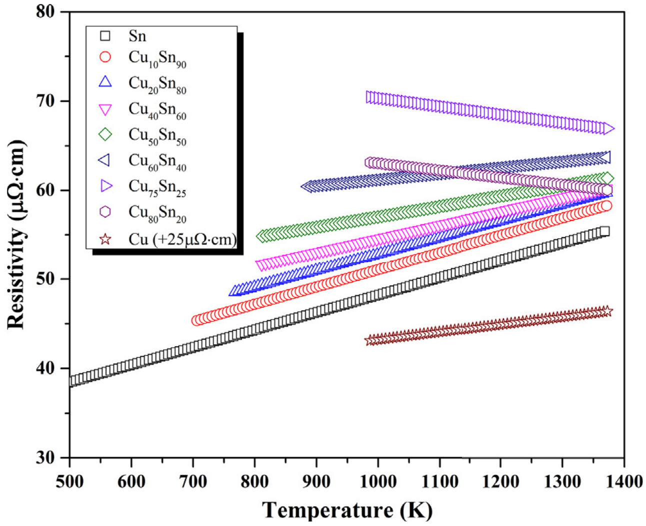

Fig. 1. Temperature dependence of resistivity for liquid Cu-Sn alloys at the cooling rate of 5 K/min.

In order to further analyze the features of Cu-Sn clusters, subsequent analyses were performed using electrical conductivity instead of resistivity. The conductivity σ can be expressed as following equation.

$$\sigma = n\mu e \tag{1}$$

where n, μ and e are the electron concentration, the mobility of electron and the electric charge of a single electron, respectively. It can be seen from Eq. (1) that the conductivity just relies on the electron concentration and the mobility of electron because of the constant value of e. The conductivity of liquid alloys decreases with the increase of temperature due to the enhancement of electron scattering intensity or the decrease of mobility. This means that the mobility of electron increases with increasing temperature in liquid alloys. Therefore, the increase of conductivity originates from the increase of the electron concentration. The increase of electron concentration can be attributed to the cleavage of covalent bonds or ionization of atoms. Because higher energy is required for the second ionization, atoms are difficult to ionize again in the range of the experimental temperatures. Thus, the cleavage of covalent bonds led to the increase of electron concentration and conductivity. This indicated that the Cu-Sn clusters with covalent bonds exist in liquid Cu-Sn alloys and the size of Cu-Sn clusters gradually decreases with increasing temperature. Cu-Sn clusters can exist in liquid Cu-Sn alloys in wide temperature range, indicating that the closer to the center of clusters atoms on the clusters is, the stronger the covalent bond is.

For $Cu_{10}Sn_{90}$, $Cu_{20}Sn_{80}$, $Cu_{33}Sn_{67}$, $Cu_{40}Sn_{60}$, $Cu_{50}Sn_{50}$ and $Cu_{60}Sn_{40}$ alloys, the resistivity increased with the increasing temperature. Compared with $Cu_{75}Sn_{25}$ and $Cu_{80}Sn_{20}$, the increase of resistivity can be