The structural change of Cu-Sn melt

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With the high-temperature viscometer and magnetic susceptibility measurement device designed by our group, the viscosity and the magnetic susceptibility of the $\text{Cu}_{65}\text{Sn}_{35}$ melt were measured during the cooling process. An anomalous change can be found in the curves of viscosity and magnetic susceptibility at a certain temperature. The structure of the melt was studied by the high-temperature X-ray diffractometer. The anomalous change also can be found in the pair distribution function, correlation radius, and coordination number at the approximate temperature, which shows the microstructural change of the $\text{Cu}_{65}\text{Sn}_{35}$ melt. From the results, it was confirmed that the Cu_6Sn_5 compound occurs in the melt, which leads to the structural change of the melt.

Cu-Sn alloy, melt, structure

1 Introduction

The Cu-Sn alloy is an important industrial alloy, which is widely used in areas of machinery, materials, war industry and so on^[1]. It can be used as shape memory materials for its excellent shape memory performance. At the same time, the Cu-Sn alloy is inexpensive, pollution-free and steady in the air, so it is good cathodic material for batteries. The Cu-Sn alloy is also a fine leadless solder alloy. Now the result of X-ray diffraction in liquid melts has validated the correlation of structure in liquid and solid states. So the study of structure in Cu-Sn melt can supply an important academic guide for exploitation of excellent industrial Cu-Sn alloy.

There are mainly two means to get the information of the structure in liquid metals. One is an indirect way which analyzes sensitive physical properties (such as resistivity^[2], viscosity^[3], magnetic susceptibility^[4], surface tension^[5]) to study the change of the structure in melt. The other is a direct way, viz. X-ray diffraction^[6], neutrons diffraction^[7], EXAFS^[8] and so on. Besides these ways, there are also computer simulation methods, such as Monte Carlo (MC) and Molecular Dynamic (MD)^[9].

In this paper, the viscosity and magnetic susceptibility of the liquid $\text{Cu}_{65}\text{Sn}_{35}$ are measured

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during the cooling process. Combined with the result of the high temperature X-ray diffraction of the liquid $\text{Cu}_{65}\text{Sn}_{35}$ melt, its structural change is discussed.

2 Experimental procedures

The experimental materials were 99.999% Cu and 99.9% Sn. The Cu-Sn alloy was prepared in the vacuum arc furnace.

The viscosity was measured by a RHEOTRONI C VIII torsional oscillation viscometer for high-temperature melts made by Tokyo industry kabuskiki kaisha of Japan. The principle is to measure the vibration damping factor, by which the viscosity is calculated according to the equation between the vibration damping factor and the viscosity. The concrete principle about the equipment and the coherent parameters can be seen in ref. [10].

The magnetic susceptibility of the melt was measured by the equipment designed by our group (patent number: 03112473.9). The principle of this equipment is the electromagnetic induction law. The induction voltage was measured, and the direct ratio can be found between the induction voltage and the magnetic susceptibility of the sample. So the change tendency of the magnetic susceptibility of the sample can be obtained from the change of induction voltage. The detailed information about the equipment can be found in ref. [11]. This equipment can measure the change of susceptibility of the sample during the cooling process, and it is low cost and better than the Faraday balance.

The liquid metal X-ray diffractometer used in this work was made by Metal Physics Institute of Ukraine National Academy. The main parameters are shown as follows: Mo $K\alpha$ radiation (the wave length is $\lambda = 0.071$ nm), the range of scanning angle (2θ) is $5-90^\circ$ and the accuracy of the angle is 0.001° , the precision of sampling time is 0.001 s and the precision of temperature is $\pm 5^\circ\text{C}$. The highest temperature is 1800°C . The sample was measured during the cooling process.

3 Results and discussion

The viscosity is the exhibition of the migratory ability of atoms, which reflects the atomic binding forces. It is one of the sensitive physical properties of melt. The change of sensitive physical properties is the macroreflection of the structural change in melt. So it is an important method to study the structure of melt by measuring its viscosity.

The viscosity of the $\text{Cu}_{65}\text{Sn}_{35}$ melt during the cooling process is shown in Figure 1. From this figure, it can be found that the viscosity increases with the decreasing temperature, which can be expressed by Arrhenius equation^[12]:

$$\eta = A \exp\left(\frac{\varepsilon}{kT}\right), \quad (1)$$

$$A = h / v_m,$$

where η is the viscosity, h is the Planck's constant, k is the Boltzmann constant, v_m is the flow unit (ions, atoms or clusters) volume, ε is the viscous activation energy and T is the absolute temperature.

The viscosity was fitted by the equation $y = y_0 + A_1 \cdot \exp(-(x-x_0)/t_1)$. The exponential relationship can be seen between the viscosity and the temperature on the whole. But there is an obvious discontinuous point between $870^\circ\text{C} - 920^\circ\text{C}$. This point divides the curve of viscosity into two segments: low temperature zone and high temperature zone. The changes of viscosity are different

Figure 1 The change of viscosity of the $\text{Cu}_{65}\text{Sn}_{35}$ melt during the cooling process.

clearly in the two temperature zones around the discontinuous point.

The logarithm was adopted at both sides of eq. (1), and eq. (2) can be got as follows:

$$\ln \eta = \ln A + \frac{\varepsilon}{k} \cdot \frac{1}{T}. \quad (2)$$

From eq. (2), the linear correlation can be seen between $\ln \eta$ and $1/T$. From the fitted linear curves between $\ln \eta$ and $1/T$, v_m and ε can be obtained by calculation, which are shown in Table 1.

Table 1 The flow unit volume and the viscous activation energy in different temperature zones

	Low temperature zone	High temperature zone
ε (eV)	0.13244	0.03076
v_m (10^{-25} cm^3)	8.6468	3.2015

From Table 1, it can be seen that the values of flow unit volume and the viscous activation energy in the low temperature zone are much larger than that in the high temperature zone. It suggests that the movement of a bigger flow unit need more energy to overcome the stricture of the surrounding atoms.

The magnetic susceptibility change reflects the change of the electronic state in melt, and the structural change can be seen from the electronic state change. So the magnetic susceptibility is one of the sensitive properties of the melt structure.

The curve of the reciprocal of magnetic susceptibility of the $\text{Cu}_{65}\text{Sn}_{35}$ melt with temperature is shown in Figure 2. From the figure, it is clear that the magnetic susceptibility increases with the increasing temperature, which is opposite to the Curie law. Luck^[13] also found this change of magnetic susceptibility in the melt of $\text{Al}_{65}\text{Cu}_{20}\text{Co}_{15}$ and $\text{Al}_{70}\text{Ni}_{15}\text{Co}_{15}$. It is an important exhibition of the chemical short range in the compound forming the liquid system, which suggests that the degree of order in the melt strengthens with the decreasing temperature. So the discontinuous change at about 850°C in the curve of the magnetic susceptibility reciprocal of the $\text{Cu}_{65}\text{Sn}_{35}$ melt is inferred to be caused by the change of the structure of the chemical short range.

The changes of viscosity and magnetic susceptibility indicate an abnormal change of the structure in the $\text{Cu}_{65}\text{Sn}_{35}$ melt at certain temperature. The minute difference of discontinuous temperature using two methods may be caused by different measurements. In order to verify the

structural change in the melt, the experiment of the high temperature X-ray diffraction was carried out and the parameters of the structure were obtained. The correlated radius is shown in Figure 3 during the cooling process.

In fact the melt is not completely disordered and there are ordered structures in a certain scope, viz. the short range order. When the temperature decreases, the ordered structure of melt will be reinforced. The correlation radius reflects the degree of order in the melt. From Figure 3, it can be seen that the correlation radius increases abruptly during 800°C—880°C and the degree of order increases, which indicates the structural change of the melt. With the liquid X-ray diffraction experiment of the Cu-Sn alloy, Xue^[14] found that the structural transition from the short range order to the medium range order disappears during 22.6at.%—44.5at.%Sn. Though there is a structural change in the Cu₆₅Sn₃₅ melt, the prepeak representing the medium range order cannot be seen during the X-ray diffraction experiment. It seems that no medium range order structure can be found in the Cu₆₅Sn₃₅ melt. Bernal^[15,16] ever presented the geometric model including several construction units. And he pointed out that there are different short range order structures according to the different compound modes of different construction units. With the change of temperature, the abrupt change in the construction unit with a high degree order or in its relative value will lead

Figure 2 The reciprocal of magnetic susceptibility of the Cu₆₅Sn₃₅ melt during the cooling process.

Figure 3 The change of the correlation radius of the Cu₆₅Sn₃₅ melt with temperature.

to the discontinuous change of the structure in melt. From the conclusion, it is inferred that the structural change in $\text{Cu}_{65}\text{Sn}_{35}$ melt is due to the forming of the higher degree short range order structure by realignment of construction units, but not due to the transition from the short range order to the medium range order.

There are three bonded pairs Cu-Sn, Sn-Sn, Cu-Sn in the melt. Shimoji^[17] pointed out that foreign atoms get together prior to the like atoms in the Cu_6Sn_5 melt. Combining the experiment results and the phase diagram of the Cu-Sn alloy, we inferred that the abnormal change of the structure in the $\text{Cu}_{65}\text{Sn}_{35}$ melt is caused by the occurrence of the solid-like compound structure for the aggregation of Cu-Sn foreign atoms with the decreasing temperature. Before the structural transition, more electrons with higher energy in the high temperature zone can overcome the atomic stricture to get the free state, which leads to the higher magnetic susceptibility. Atoms interact with electrons. The increase of free electrons leads to the smaller interaction and the minor viscosity. So the melt can flow much more easily. When the temperature decreases to the critical value, the structure changes abnormally. The Cu-Sn atoms get together by the valence electrons interaction and form the solid-like compound structure, which leads to the decrease of free electrons and the abrupt change of magnetic susceptibility. At the same time, the bigger atom cluster occurs owing to the increase of foreign atoms interaction. The viscosity increases abruptly and the melt is much more difficult to flow. The correlation radius reflects the size of the cluster in the melt. From the change of the correlation radius, it is clear that the size of the cluster increases clearly when the temperature decreases to the low temperature zone from the high temperature zone, which is in accordance with the change of the flow unit volume obtained from the viscosity.

The pair correlation function and coordination number of the melt are shown in Figures 4 and 5, respectively. In Figure 4, it is visible that a shoulder peak occurs on the right of the first peak when the temperature decreases to 800°C . And the coordination number increases suddenly during $800^\circ\text{C} - 880^\circ\text{C}$ as shown in Figure 5. It suggests the structural change in the melt. The meaning of the pair correlation function is the probability of occurrence of one atom at the distance r departing from the reference atom. The first peak of the pair correlation function presents the position of the first coordination layer. From the meaning of the pair correlation function, the shoulder peak on the right of the first peak at 800°C indicates that the first peak is composed of two coordination layers, viz. the main and secondary coordination layers. The positions of the main and secondary coor-

Figure 4 The correlation function of the $\text{Cu}_{65}\text{Sn}_{35}$ melt with temperature.

Figure 5 The coordination number of the $\text{Cu}_{65}\text{Sn}_{35}$ melt with temperature.

dination layers can be obtained by splitting the first peak of the pair correlation function at 800°C , and then they are compared with the position of the coordination layer in the solid Cu_6Sn_5 phase. The result is shown in Table 2.

Table 2 The coordination layer position of the solid Cu_6Sn_5 phase and the $\text{Cu}_{65}\text{Sn}_{35}$ melt

Solid Cu_6Sn_5 phase				$\text{Cu}_{65}\text{Sn}_{35}$ melt (800°C)	
Reference atom a (1/3,2/3,1/4)		Reference atom b (0,0,0)		Main coordination layer (nm)	Secondary coordination layer (nm)
First coordination layer (nm)	Second coordination layer (nm)	First coordination layer (nm)	Second coordination layer (nm)		
0.2728	0.3493	0.2728	0.4192	0.2745	0.3490

From this Table, it can be found that the position of the main coordination layer of the $\text{Cu}_{65}\text{Sn}_{35}$ melt is very close to that of the first coordination layer of reference atoms a or b in the solid Cu_6Sn_5 phase. And the position of the secondary coordination layer of the $\text{Cu}_{65}\text{Sn}_{35}$ melt is nearly the same with that of the second coordination layer of reference atom a in the solid Cu_6Sn_5 phase. From the results, it is considered that the structure of the melt at the nearest neighbor distance is almost the same with that of Cu_6Sn_5 intermetallic compound while the structure at hypo-neighbor distance is approximate.

The solid Cu_6Sn_5 phase is the NiAs type structure that has two occupied atoms a and b, either of which has two atoms in a crystal cell. The occupied atoms a and b have 6 and 8 nearest neighbor coordination numbers, respectively. And the secondary coordination numbers of a and b are both 6. The average coordination number of the solid phase can be obtained by eq. (3):

$$N = N_1 \times \frac{N_a}{N_a + N_b} + N_2 \times \frac{N_b}{N_a + N_b}, \quad (3)$$

where N_a , N_b is the atoms number of two occupied atoms in a crystal cell; N_1 , N_2 is their coordination atoms number, respectively. After calculation, it can be obtained that the average coordination number of the first coordination layer is 7 and that of the second coordination layer is 6. So the total coordination number of the solid Cu_6Sn_5 phase is 13, which is very close to the coordination number of the $\text{Cu}_{65}\text{Sn}_{35}$ melt 12.93 (Table 3).

From comparison of the position of the coordination layer and the coordination number in the $\text{Cu}_{65}\text{Sn}_{35}$ melt and the solid Cu_6Sn_5 intermetallic compound, it can be concluded that the structural change of the melt is caused by the occurrence of the solid-like Cu_6Sn_5 intermetallic compound

Table 3 The coordination number of the solid Cu_6Sn_5 phase and the $\text{Cu}_{65}\text{Sn}_{35}$ melt

Reference atoms	Solid Cu_6Sn_5 phase		The coordination number of the $\text{Cu}_{65}\text{Sn}_{35}$ melt (800°C)
	Coordination number of the first coordination layer	Coordination number of the second coordination layer	
Occupied atom a (1/3,2/3,1/4)	6	6	12.93
Occupied atom b (0,0,0)	8	6	
Average value	7	6	

during 800°C—880°C.

4 Conclusions

(1) The curves of the viscosity and the magnetic susceptibility of the $\text{Cu}_{65}\text{Sn}_{35}$ melt all have the discontinuous point in the similar temperature range, which suggests the structural change of the melt during this temperature range.

(2) With the high temperature X-ray diffraction experiment, the correlation radius and the pair correlation function both have a sudden change during 800°C—880°C. The position of the coordination layer and the coordination number of the melt at 800°C are close to those of the solid Cu_6Sn_5 phase. From the analysis, it can be concluded that the structural change of the $\text{Cu}_{65}\text{Sn}_{35}$ melt is due to the occurrence of the solid-like Cu_6Sn_5 intermetallic compound.

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