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Liquid structure and viscosity of $In_{80}Cu_{20}$ alloy①

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Abstract: The structure and dynamic viscosity of $In_{80}Cu_{20}$ alloy melt in the temperature range from 600 ℃ to 1 000 ℃ were investigated by using a high-temperature X-ray diffractometer and a torsional oscillation viscometer. The experiments show that there exist medium range order (MRO) structures in $In_{80}Cu_{20}$ alloy melt in a low temperature range above liquidus. The MRO structures are weakened with increasing temperature and disappear when the temperature surpasses 800 ℃. The nearest interatomic distance r_1 and the coordination number N_s of $In_{80}Cu_{20}$ alloy melt decrease as temperature increases from 650 ℃ to 1 000 ℃. Thermal contraction of atom clusters can be found in the heating process. The viscosity of $In_{80}Cu_{20}$ alloy melt drops as temperature increases and meets with the exponential relation. No sudden change in structure occurs in the measured temperature range. DSC curve of $In_{80}Cu_{20}$ alloy during cooling process was measured. It is found that there is no noticeable variation of heat during cooling from 1 000 ℃ to 600 ℃, which testifies further that there is no sudden change in structure of $In_{80}Cu_{20}$ alloy melt.

Key words: $In_{80}Cu_{20}$ alloy; liquid structure; thermal contraction; atom clusters; viscosity
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1 INTRODUCTION

The structure and properties of liquid metals have a great impact on those of metallic solids obtained from solidification of melts[1]. It is worthy to study the structure of liquid metals. Viscosity is an important physical property of liquids and very sensitive to the change in structure[2]. By probing the viscosity of a liquid metal, a dynamic description of the structure of liquid metals was introduced, which has drawn much attention recently. Although many measurements on liquid structure and viscosity have been made over the last hundred years or more[3-7], metallic melts are less understood than their solids. So, it is necessary to investigate and measure the structure and viscosity of melts much more.

Alloys have been widely used in recent years. Gebhardt et al[8] studied the liquid structure of Ga-In alloys at different temperature above liquidus. WANG et al[9] measured the structure and viscosity of eutectic Ga-In alloy. Akinlade et al[10] investigated the bulk and surface properties of liquid In-Cu alloys. However, there are few reports on the liquid structure and viscosity of In-Cu alloys. In this work, the structure, dynamic viscosity and DSC curve of $In_{80}Cu_{20}$ alloy melt in the temperature range from 600 ℃ to 1 000 ℃ were measured by using a high-temperature X-ray diffractometer, a torsional oscillation viscometer and a differential heat-flow calorimeter. The temperature dependence on the structure and viscosity of $In_{80}Cu_{20}$ alloy melt were studied. The correlation of viscosity with structure was discussed on a basis of experimental results and theoretical analysis.

2 EXPERIMENTAL

The $In_{80}Cu_{20}$ alloy samples were prepared from high pure In (99.99%) and high pure Cu (99.99%) in graphite crucibles using a medium frequency induction furnace under vacuum atmosphere.

The $\theta-\theta$ liquid metal X-ray diffractometer used in this experiment was made by Metal Physics Institute of Ukraine National Academic. MoK_α radiation (λ= 0.071 nm) was reflected from the free surface of the specimen, and reached the detector through a graphite monochromator in the diffraction beam. The accuracy of the angle is 0.001°. Scanning angle ranges from 2θ= 5° to 90°. The magnitude of the wave vector Q ($Q = 4\pi\sin\theta/\lambda$) is from about 5 nm^{-1}

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to 120 nm^{-1}.

The specimen of $In_{80}Cu_{20}$ alloy is settled in the sample room after pretreatment and the sample room was vacuumized to about 2×10^{-6} Pa, then pure He (99.99%) is puffed to 1.3×10^{5} Pa. The specimen was heated to 1 200 ℃ in a crucible of the size 24 mm × 18 mm × 11 mm in this atmosphere and kept for 1 h at 1 200 ℃, then cooled down to the measured temperature. 20 min were waited before X-ray diffraction experiment. Measurements were made at 650, 700, 750, 800, 900, 1 000 ℃, respectively.

The scattering intensity measured was corrected, polarized and absorbed in the range of 0 – 110 nm^{-1} and the structure factor was obtained. The structure factor was then transferred into pair distribution function and radial distribution function by Fourier transformation. The nearest interatomic distance and the coordination number can be calculated. The coordination number were calculated using the equation as follows:

$$N_{min} = \int_{r_0}^{r_{min}} 4\pi r^2 \rho(r)\,dr \qquad (1)$$

where r_0, r_{min} are the nearest zero to the left and the first minimum to the right of the first peak of the RDF. More details of the data processing can be seen in Ref.[11].

The device used to measure the viscosity is a torsional oscillation viscometer made in Japan for high temperature melts. When a liquid is placed in a vessel hanged by a torsional suspension, and the vessel is set in oscillation about a vertical axis, the resulting motion is gradually damped on account of the frictional energy absorption and dissipation within the liquid. The viscosity of the liquid sample can be calculated by observing the decrement and the time period of the oscillations. Schvidkovskii's equation[12] is applied to the calculation of viscosity from the measured damping data. Schvidkovskii's equation has been used exclusively for absolute viscosity and provides accurate and reliable viscosity data. Viscosity was measured for three or four times at each temperature. The repetition of the data is fairly good. The data error of different measurements at the same temperature is not larger than 1%. The mean data of three or four measurements were adopted. All the measurements were carried out in a high purity vacuum of 2 × 10 Pa. During the process of the measurement, the specimen of $In_{80}Cu_{20}$ alloy was heated to 1 200 ℃ in an Al_2O_3 crucible and kept for 1 h at 1 200 ℃, then cooled down to the measured temperature. Half an hour is waited before measurement. Measurements were made at 600, 650, 700, 750, 800, 850, 900, 950, 1 000 ℃, respectively.

DSC curve of $In_{80}Cu_{20}$ alloy was measured with a differential heat-flow calorimeter (Netzsch DSC404) applying a method of comparison with sapphire as the reference standard. $In_{80}Cu_{20}$ alloy in the sample crucible used for the experiment is 40 mg. The sample was heated to 1 000 ℃ at a rate of 10 K/ min and then cooled down at the same rate. Thus, the curve during the cooling was obtained.

3 RESULTS AND DISCUSSION

3.1 Liquid structure of $In_{80}Cu_{20}$ alloy melt

The intensities and structure factors $S(Q)$ of $In_{80}Cu_{20}$ alloy melt at different temperatures are shown in Figs. 1 and 2, respectively. It can be found that the pre-peak occurs at values of scattering vector Q = 5 to 20 nm^{-1} in the structure factor of $In_{80}Cu_{20}$ alloy melt at 650, 700, 750 ℃. The occurrence of pre-peak suggests that there are the medium range order (MRO) structures in $In_{80}Cu_{20}$ alloy melt and there is correlation between the liquid and solid of $In_{80}Cu_{20}$ alloy. The height of the pre-peak in the melt decreases with increasing temperature. The pre-peak disappears when the temperature surpasses 800 ℃. The presence and the disappearance of the MRO structures in melt are a function of temperature, which is in agreement with the results of the study on Al-Fe, Al-Cu and Al-Ni alloys in Refs.[13, 14].

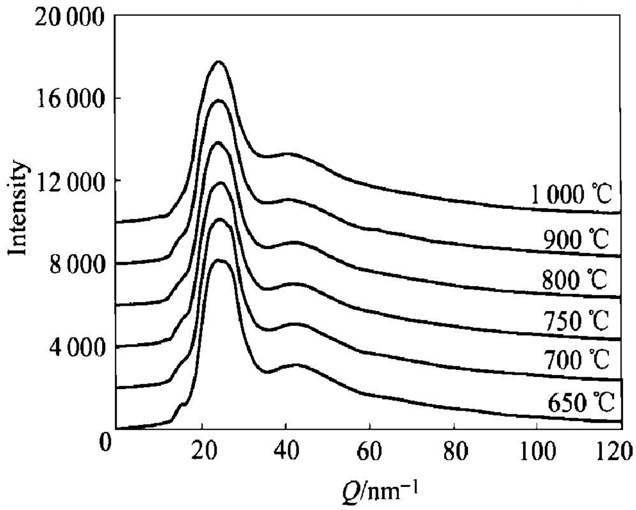

Fig. 1 Intensities of $In_{80}Cu_{20}$ alloy at different temperatures

The corresponding pair distribution function $g(r)$ and radial distribution function (RDF) are illustrated in Figs. 3 and 4, respectively. The nearest interatomic distance r_1 and the coordination number N_s can be calculated from $g(r)$ and RDF. r_1 is the position of the first peak of $g(r)$ and N_s is the area under the first peak of RDF.

Partial structural parameters of $In_{80}Cu_{20}$ alloy melt are listed in Table 1. In order to express clearly the temperature dependence on r_1 and N_s, as shown in Fig. 5. It can be seen that r_1 and N_s of $In_{80}Cu_{20}$ alloy melt decrease as temperature increases. It is concluded that the size of atom clusters of $In_{80}Cu_{20}$ alloy

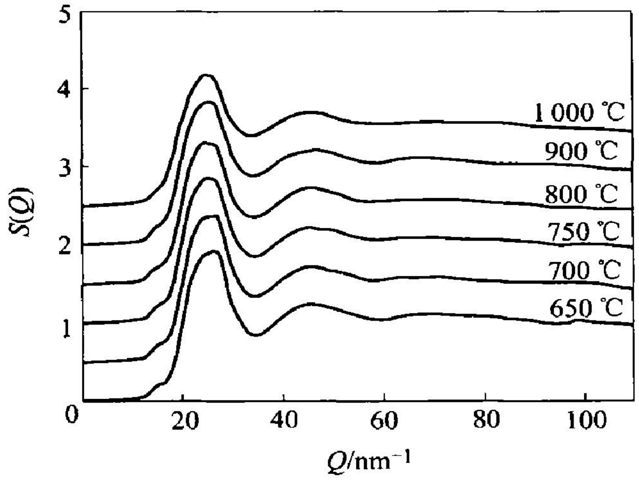

Fig. 2 Structure factors of $In_{80}Cu_{20}$ alloy at different temperatures

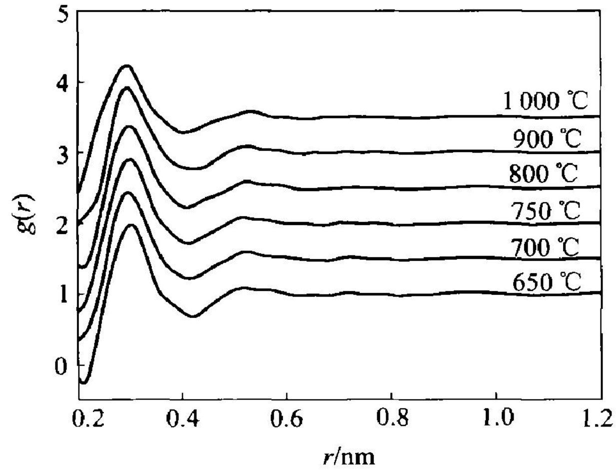

Fig. 3 Pair distribution functions of $In_{80}Cu_{20}$ alloy at different temperatures

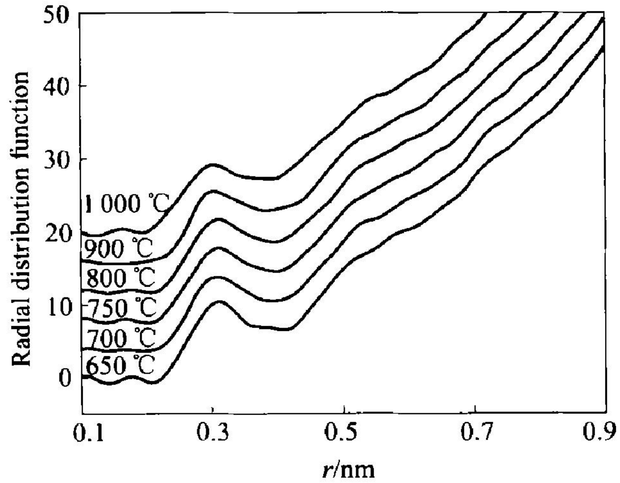

Fig. 4 Radial distribution functions of $In_{80}Cu_{20}$ alloy at different temperatures

melt decreases with increasing temperature, namely, the thermal contraction phenomenon of clusters occurs.

The thermal contraction phenomenon of clusters in In_{80} Cu_{20} alloy melt can be explained by the free

Table 1 Partial structural parameters of $In_{80}Cu_{20}$ alloy melt

t/ ℃	r_1/ nm	N_S	r_c/ nm	N	ρ_0
650	0.298 7	12.537	1.190	310	0.0462
700	0.295 9	11.934	1.085	234	0.0462
750	0.295 0	11.750	1.085	234	0.0462
800	0.294 3	11.638	1.085	234	0.0462
900	0.293 7	11.307	1.080	231	0.0462
1000	0.292 8	10.701	0.950	157	0.0462

r_c is correlated radius; N and ρ_0 denote the atom number in atom clusters and average number density of atoms, respectively.

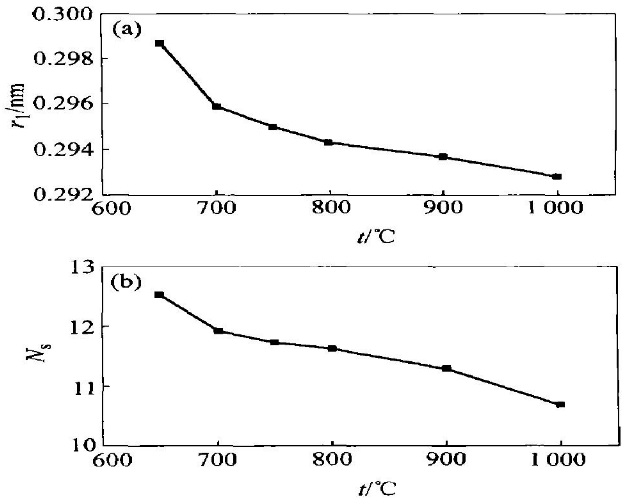

Fig. 5 Temperature dependence on r_1(a) and N_s(b) of $In_{80}Cu_{20}$ alloy

volume theory proposed by Eying[15]. Doolittle[16] thought that the free volume was the increased part of volume of liquid because of thermal expansion in the case of absence of phase transformation. Cohen[17] developed the free volume theory of liquid and used it to analyze the structure of liquid and correlative physical properties, such as viscosity, with the assumption that the redistribution of free volume does not consume local area free energy. In $In_{80}Cu_{20}$ alloy melt, as temperature increases, free volume expands and redistributes, and the vacancy concentration between clusters increases and results in the contraction of clusters.

With increasing temperature, the volume of $In_{80}Cu_{20}$ alloy melt expands, while the atom cluster contracts. What happens in the structure of $In_{80}Cu_{20}$ alloy melt is that big clusters split or reconfigure into more smaller clusters, due to enhanced thermal movement and increased atomic diffusivity. Clusters disperse in the large scale whereas the rearrangement of atoms within a cluster trends from loose structure into compact structure.

The change in the nearest interatomic distance r_1 is related to that of the coordination number N_s. It can be seen from Fig. 5 that the change in r_1 and N_s in the whole measured temperature is nearly the same and belongs to a kind of gradual change, implying that no sudden change in structure occurs in this temperature range in $In_{80}Cu_{20}$ alloy melt, which can also be found from the change of other parameters in Table 1.

3.2 Temperature dependence on viscosity of $In_{80}Cu_{20}$ alloy melt

Temperature dependence on viscosity of $In_{80}Cu_{20}$ alloy melt during the cooling process is shown in Fig. 6. The viscosity of $In_{80}Cu_{20}$ alloy melt decreases as temperature increases.

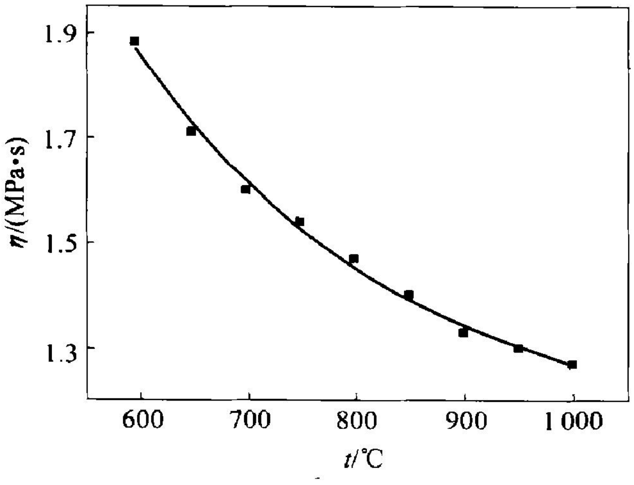

Fig. 6 Temperature dependence of viscosity(η) of $In_{80}Cu_{20}$

Exponential decay is made to the experimental values according to the following equation:

$$\eta = \eta_0 + A_1\exp(-t[t - t_0)/B_1] \qquad (2)$$

where η is viscosity; η_0 is a constant; t is temperature; A_1 and B_1 are constants relating to the type and composition of the alloys. The regression results are presented in Table 2 and Fig. 6. It can be seen that the variation of viscosity of $In_{80}Cu_{20}$ alloy melt versus temperature fits with the exponential relation. This suggests that the experimental values are regular and trusty.

The viscosity of liquid metals has close relation with the structure and the change in structure will result in the change in viscosity. Lihl[5] studied the viscosity of Al alloy and found that two abrupt decreases occurred at 775 ℃ and 875 ℃, respectively with a discontinuous decrease in coordination number. Sun[6] believed that the sudden change of viscosity of Al melt was due to the sudden change of liquid structure at about 780 ℃ and 950 ℃. Gui[7] measured viscosities of hypoeutectic and hypereutectic Al-Si alloy melt and believed that there existed three kinds of structure zones in Al-Si alloy melts because of the sudden changes in viscosity. In the case of $In_{80}Cu_{20}$ alloy melt, no anomalous variation of viscosity occurs in the temperature range from 600 ℃ to 1 000 ℃, suggesting that there is no sudden change in structure as temperature increases in $In_{80}Cu_{20}$ alloy melt.

Table 2 Parameters in exponential decay fitting Eqn. (2)

η_0/(MPa·s)	t_0/℃	A_1	B_1
1.131 8	600	0.737 3	241.885 4

3.3 DSC analysis of $In_{80}Cu_{20}$ alloy melt

The structural variation of substance often goes with the exchange of heat between the substance and environment. The embodiment in DSC curves is the existence of the endothermic peak or exothermic peak. QIN[18] found through DSC experiment of pure Sn that there was an obvious exothermic peak in the range from 884 ℃ to 1 210 ℃, suggesting that structural variation occurs at about 978 ℃ in the melt, which is well in accordance with the results of X-ray diffraction experiment. Fig. 7 displays the DSC curve of $In_{80}Cu_{20}$ alloy during the cooling process. It can be seen that there is no noticeable variation of heat during cooling process in $In_{80}Cu_{20}$ alloy melt, which testifies further that no sudden change in structure occurs with the changing temperature in $In_{80}Cu_{20}$ alloy melt.

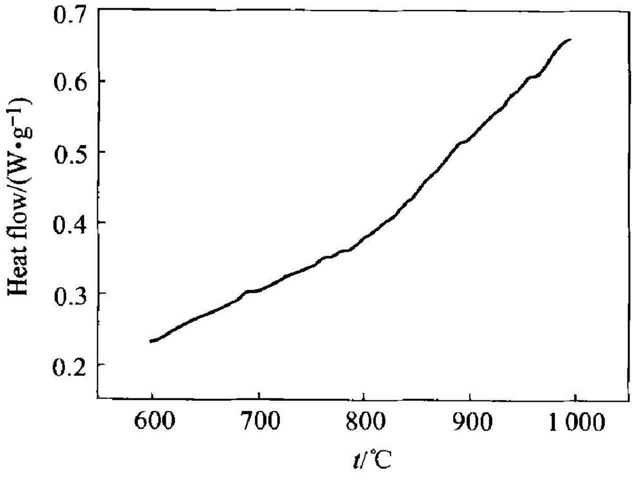

Fig. 7 DSC curve of $In_{80}Cu_{20}$ alloy during cooling process

4 CONCLUSIONS

1) There are medium range order (MRO) structures in $In_{80}Cu_{20}$ alloy melt in a low temperature range above liquidus. The MRO structures are weakened with the increasing temperature and disappear

when the temperature surpasses 800 ℃.

2) The nearest interatomic distance r_1 and the coordination number N_s of $In_{80}Cu_{20}$ alloy melt decrease as temperature increases from 650 ℃ to 1 000 ℃. Thermal contraction of atom clusters occurs in the heating process.

3) The viscosity of $In_{80}Cu_{20}$ alloy melt drops with increasing temperature and meets with the exponential relation in a wide temperature range from 600 ℃ to 1 000 ℃.

4) No sudden change in structure occurs as temperature increases in $In_{80}Cu_{20}$ alloy melt in measured temperature range.

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