Correlation between viscosity of molten Cu–Sn alloys and phase diagram

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Received 29 September 2005; received in revised form 30 October 2005; accepted 30 October 2005

Abstract

The dynamic viscosities of Cu–Sn alloys with different compositions were measured at the same superheat temperature using an oscillating-cup viscometer. It has been found that the viscosities of Cu–Sn melts increase with decreasing temperature and fit well with Arrhenius equation. At the same superheat temperature, it is found that the viscosity is higher around the phase of β (Cu5Sn), and the highest at Cu-25 wt%Sn. When the tin concentration is in the range of 20–40 wt%, the average rate of increasing viscosity with the decreasing temperature is faster, and the maximum appears at Cu-25 wt%Sn.

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PACS: 66.20.+d; 61.25.Mv

Keywords: Viscosity; Cu–Sn alloys; Phase diagram; Medium range order

1. Introduction

It’s well known that the viscosity of liquids, which is the reciprocal of the fluidity, is a measure of resistance to shear deformation. The viscosity of metallic melts is a very important thermophysical property in many industries as well as from the academic point of view. In the past 50 years, knowledge of viscosity has been widely accumulated. As to the temperature dependence of viscosity, Adam, Gibbs and Goldstein etc. brought forward their theories, respectively [1–3]. However, as metallic melts are considered, above-mentioned expressions can hardly provide an entirely satisfactory interpretation of their viscosity [4]. The viscosity of molten metals and alloys is a structural sensitive property, and the investigation on the correlation between the viscosity and the composition will be a theoretic guidance to develop Cu–Sn materials.

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. The liquid Cu–Sn system is a well-known system on account of the isotope substitution method was first applied in the neutron scattering experiments [5,6] and the medium-range order was discussed in the Ref. [7–11]. However, the relationship between viscosities with different compositions and phase diagram has not been involved in these studies. The main purpose of this work is to analyze the correlation between the viscosity and the phase diagram of Cu–Sn alloys.

2. Experimental procedure

The samples of alloys used in this work were prepared from pure ingot Cu (99.999 wt% pure) and pure ingot Sn (99.98 wt% pure). They were melted in a graphite clay crucible using a medium frequency induction electric furnace and cast ingots in a graphite mould.

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The device used to measure the viscosity of the melts is a torsional oscillation viscometer for high-temperature melts. The viscometer consists of a suspension system, an oscillation detection system and a heating system. The schematic view of the suspension and heating system inside the apparatus is shown in Fig. 1. When samples were placed in a vessel hung by a torsional suspension, and the vessel was set in oscillation about a vertical axis, the resulting motion was gradually damped on account of frictional energy absorption and dissipation within the melt. The viscosity of the liquid samples can be calculated by observing the decrement and the time period of the oscillations. The schematic view of the oscillation detection system is shown in Fig. 2. The mirror reflects incident light from a He–Ne laser and the light is focused as a small spot of about 0.1 mm diameter on the detector, which consists of phototransistors. Then the successive time intervals between the times when locus passes the detector are determined by using a data processing computer. The period of the oscillation and the logarithmic decrement were determined from the time intervals by means of an approximation algorithm. The kinetic viscosity data were calculated from the logarithmic decrement by Shvidkovskii’s equation [12]:

\[
v = \frac{I^2(\delta - T_0/\delta_0)^2}{\pi (Mr)^2 T W^2},
\]

where

\[
W = 1 - 3 \Delta - \frac{3}{8} \Delta^2 - a + (b - c\Delta) \frac{2\pi r}{H}.
\]

\[
\Delta = \delta/2\pi; I \text{ is the momentum of inertia of the suspended system; } \delta \text{ the logarithmic damping decrement, and } T \text{ the period time of the oscillations, the subscript 0 refers to an empty vessel; } M \text{ represents the mass of the liquid sample; } r \text{ is the radius of the vessel; } H \text{ is the height of the liquid sample in the vessel, and } a, b, c \text{ are constants; } n \text{ is the number of solid planes contacted horizontally by the liquid sample (i.e. in the case of a vessel having its lower end closed and its upper surface free, } n = 1, \text{ if the vessel encloses the fluid in top and bottom, } n = 2). \text{ The dynamic viscosity } \eta \text{ can be calculated using the following formula:}
\]

\[
\eta = \frac{nr}{\rho},
\]

where \( \rho \) is the density of sample.

After the chamber is cleaned to a vacuum of \( 2 \times 10^{-6} \) Pa, it is filled with high purity argon (99.999%) to \( 1.3 \times 10^5 \) Pa. The samples are placed in an Al₂O₃ crucible. During the process of measurement, the specimens of Cu–Sn alloy melts are heated to the same superheat temperature \( T_m + 200 \) K (\( T_m \) is the melting point of sample) and kept for 3 h at this temperature, then cooled down to the measured temperature. Measurements are made at every 20°C from the highest temperature to the melting point, respectively. Half an hour is waited and then viscosity is measured for three or four times at each temperature. The average value of data gained from three or four measurements are adopted. The data error of different measurements at the same temperature is no more than 3%. The viscosity experiments are repeated two times and the reproducibility is good. The reproducibility accuracy of the viscometer is better than 5%.

3. Results

Fig. 3 shows the viscosities of Cu–Sn alloy melts with different compositions (pure Cu, Cu-10, Cu-25, Cu-30.6, Cu-38, Cu-58.6, Cu-92.4, Cu-99.3 wt% Sn and pure Sn) as a function of the temperature during the cooling process and the fitted curves, respectively. It can be found that the viscosity of pure Cu is higher than the viscosity of pure Sn, and the viscosities of Cu–Sn melts increase with
decreasing temperature and fit to the Arrhenius equation [13] as in Eq. (4)

$$\eta = A \exp \left( \frac{E_v}{RT} \right)$$  \hspace{1cm} (4)

in which $\eta$ is the dynamic viscosity, $A$ is a pre-exponential factor, $E_v$ is the activation energy related to the motion of fluid units, $R$ is the gas constant and $A$ is a constant.

The fitted numerical parameters corresponding to different alloys are given in Table 1, where $R^2$ is the square of correlation coefficient, which reflecting the error of the Arrhenius relationship for the viscosities of Cu–Sn alloys. The fitted results show that the temperature dependence of the viscosity obeys Arrhenius relationship.

Fig. 4 shows the viscosity transitions of Cu–Sn alloy melts as a function of the tin concentration at the same superheat temperature. The comparison of the phase diagram with the viscosity curve of liquid Cu–Sn alloys at the melting point is shown in Fig. 5.

From the phase diagram it can be found that the liquidus of Cu–Sn alloy melts descend as the tin concentration increases. The viscosity curves at the melting point and the same superheat temperature rise compared with liquidus, and reach a maximum as the tin concentration is 25 wt%. Based on the gradient of every fitted curve in Fig. 3 and the distance among the viscosity curves in Fig. 4, it is found that the average rate of increasing viscosity with decreasing temperature is different. The average rate is faster when the tin content is in the range of 20–40 wt% and the maximum appears at 25 wt% as shown in Fig. 6.

4. Discussion

Nine samples with different tin contents were chosen according to the specific features of the phase diagram to illustrate variation of the viscosity on the composition. It can be found from Fig. 3 that the viscosities of Cu–Sn melts increase with decreasing temperature and the viscosity of pure Cu is higher than that of pure Sn at the same superheat temperature.

The viscosity of liquid melt is a function of the temperature. A well-known formula describing the temperature dependence of the viscosity of liquids is the Arrhenius equation as in Eq. (4). In present work, the temperature dependence of the viscosity of Cu–Sn melts obeyed the Arrhenius equation in the range of temperature above their melting points. The fitted numerical parameters corresponding to different alloys are given in Table 1. The results suggest that the experimental values are regular and trusty.

Viscosity, an apparent property of a fluid that resists flow, results from cohesion and molecular momentum exchange between fluid layers as it flows. In other words, the viscosity of a liquid is a measure of the resistance to shear deformation namely to the friction among atoms.

According to Eq. (5)

$$n = \frac{\rho V}{M},$$  \hspace{1cm} (5)
where $\rho$ is the density, $V$ is the volume, $M$ is the atomic weight and $n$ is the number of atoms it can be calculated that the atom numbers of pure Cu are about twice more than that of pure Sn in the same volume. The radii of atom Cu and Sn are close. The average distance between Cu atoms is less and the friction among atoms is larger accordingly. It also can be concluded from the value of $E_v$, which is the activation energy related to the motion of fluid units, of pure Cu and Sn in Table 1. Then it represents macroscopically that the viscosity of pure Cu is higher than the viscosity of pure Sn.

It is known that viscosity of liquid metals is a structural sensitive property. However, the values of viscosities are different from each other. This indicates that their structures in liquid are different.

As to structural properties, it is useful to take the structural orders into account. Elliott [14] defined three contiguous length scales; short range order (SRO) in the range of 0.2–0.5 nm, medium range order (MRO) in the range of 0.5–2.0 nm, and long range order (LRO) in the range of more than 2.0 nm.

According to the calculation results of the quantum mechanics [15], there exists a strong attraction between Cu and Sn atoms. Moreover, according to the binary phase diagram [16], the intermetallic compounds are formed during freezing when the tin content is in the range of 20–40 wt%. It can be concluded that the distribution of Cu and Sn atoms in melts is not microscopically random but forms some compound structure like Cu$_x$Sn$_y$. Those Cu$_x$Sn$_y$ atomic clusters are stable in the composition and structure, and may exist in molten metals of wide range composition. These cluster structures include Cu$_5$Sn, Cu$_{31}$Sn$_8$ and Cu$_3$Sn (i.e. the phase of $\beta$, $\gamma$ and $\delta$, respectively [16]), which exist in the Cu–Sn alloy melts when the tin concentration is in the range of 20–40 wt%.

The strongest compound formation ability is located at the phase that has the highest melting point [9,10]. Cu$_5$Sn has the highest melting point (799 °C) in the phase diagram, so its compound formation ability is strongest and inferentially the compound formation ability is stronger around Cu$_5$Sn in the Cu–Sn alloy system. The MRO is strengthened around Cu$_5$Sn in this system and strongest at Cu$_5$Sn, and then disappears when the tin concentration is more than 40 wt% [10]. Furthermore, under the same experimental conditions, there is not the MRO in pure metals whether near the liquid temperature or overheated to higher temperature [7,8].
According to the above statement, in Cu–Sn alloy melts, the MRO only exists when the tin concentration is in the range of 20–40 wt%, and strongest at Cu5Sn. The cluster diameter of the MRO is larger than that of the SRO and the friction among clusters is larger accordingly. So compared with liquidus in the phase diagram, the viscosity curves at the melting point and the same superheat temperature rise when the tin concentration is in the range of 20–40 wt% and the maximum occurs as the tin content is 25 wt%, i.e. at Cu5Sn, as shown in Fig. 4 and Fig. 5. It can be found from Table 1 that the change of \( E_v \), which is the activation energy related to the motion of fluid units, has the same orderliness as the change of viscosity. The value of \( E_v \) is higher when the tin concentration is in the range of 20–40 wt% and the maximum appears at 25 wt% (Cu5Sn). The change of \( E_v \) proves the change of viscosity on the other hand. The change of viscosity is in good accordance with the change of MRO, which implies that the viscosity has close relation to the structure of melt.

The MRO in general alloys will be strengthened when the melt is cooled to the liquidus temperature [17]. The transition of liquid structure, which the MRO appears and strengthens gradually with the decreasing temperature, will impact on the quick increase in viscosity. In contrast, the change of the viscosity slows down when there is no obvious change of liquid structure. Therefore, when the tin concentration is in the range of 20–40 wt%, the average rate of increasing viscosity with decreasing temperature is faster and the maximum appears in the Cu5Sn alloy as shown in Fig. 6. To sum up, the viscosity of liquid alloys is a structural sensitive property at an atomic scale.

5. Conclusions

1. The viscosities of Cu–Sn alloy melts with different compositions increase with the decreasing temperature. The viscosity curve dependence of the temperature obeys Arrhenius relationship.
2. The viscosity of pure Cu is higher than the viscosity of pure Sn at the same superheat temperature.
3. Compared with the phase diagram at the same superheat temperature, the viscosity curves rise around Cu5Sn, and are the highest at Cu5Sn; while the average rate of increasing viscosity with the decreasing temperature is faster when the tin concentration is in the range of 20–40 wt%, and the maximum appears at Cu-25 wt%Sn.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Project No. 50471052) and Natural Science Foundation of Shandong Province (Project No. Z2004F02).

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