Viscosity Characteristic in Metallic Melts with Medium/Short-Range Order Structures *

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Viscosities and liquid structure of alloys $Cu_{75}Al_{25}$, $Cu_{87}Sn_{13}$ and Al-12.5%Si and pure metals Cu and Sn are investigated by using torsional oscillation viscometry and high temperature x-ray diffractometry. The viscosities of pure metals and eutectic alloy melts along with the short-range order structure are found to follow the Arrhenius law in a wide range of temperature above the liquidus. The breakpoints in Arrhenius plots emerge when the structures of alloy melts are transformed from the medium-range order structure to the short-range order structure. It has been found that the change of the viscosity of the metallic alloys is a characteristic of microstructure transformation in the related melts.

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Viscosity, an apparent property of a fluid that resists flow, results from cohesion and molecular momentum exchange between fluid layers when it flows. An intrinsic relation between the viscosity and the microstructure of a fluid is of great interest to practical applications[1,2] and theoretical studies.[3,4] A great deal of knowledge of viscosity in liquid matter has been accumulated for five decades. As to the temperature dependence of viscosity, Adam and Gibbs[5,6] proposed that the viscous flow process depends on the cooperative rearrangement of molecular units and the potential energy barrier associates with the rearrangement of these molecular units. The size of these units is a function of temperature and configurational entropy. However, Goldstein[7] suggested that the Adam and Gibbs theory could not account for the temperature dependence of viscosity of all liquids. Lacks[8] found that the temperature dependence of the viscosity changes from faster-than-Arrhenius to Arrhenius. As metallic melts are considered, these expressions can hardly provide an entirely satisfactory interpretation of their viscosity.[5]

It is known that viscosity of liquid metals is a structural sensitive property. The liquid structure is not homogenous but changeable with temperature. Zu and his co-workers[9,10] confirmed the existence of a first-order liquid–liquid phase transition in Pb–Sn melts and a temperature-dependent discontinuous structural change in In–Sn alloys. The structural changes occurred in liquid metals will definitely cause the changes of viscosity. However, experimental difficulties due to high temperature and high oxidation tendency have imposed restrictions on the quantity of data about the viscosity of metallic melts. The dependence of viscosity on structural order in metallic melts has not yet been found. In this Letter, we report the experimental results on viscosities and microstructures in metallic melts and discuss their close relation.

The sample of alloys used in this work was prepared from pure ingot Cu (99.999 wt.% pure), pure ingot Al (99.999 wt.% pure), pure ingot Sn (99.98 wt.% pure) and pure ingot Si (99.999 wt.% pure). The diffraction experiments were carried out in a $\theta - -\theta$-type high-temperature x-ray diffractometer. The diffraction beam of Mo K_α radiation with a wavelength of $\lambda = 0.07089$ nm was reflected from the free surface of the specimen and reached the detector through a graphite monochromator. After the chamber was cleaned to a vacuum of 2×10^{-6} Pa, it was filled with high purity helium (99.999%) to 1.3×10^5 Pa. The samples were placed in an alumina crucible of $30 \times 25 \times 8$ mm. Ta sheets served as the heating element. A laser calibrator was used to regulate the surface of specimen to a horizontal position. The scanning voltage of x-ray tube was 40 kV, the current 30 mA, exposure time 30 s, and scattering angle 2θ was from 5 to 90 deg. Based on the generalized Krogh–Moe–Norman method, the scattering intensity measured was then converted into the coherent scattering intensity per atom in an electron unit $I_a^{\rm coh}$. The other properties and error analysis of the diffractometer used here can be seen in Refs. [11,12].

The torsional oscillation viscometer for high-temperature melts was used for measuring the viscosity of the melts. The samples were placed in a vessel hung by a torsional suspension. The vessel was set in oscillation with respect to a vertical axis. The resulting motion was gradually damped on account of frictional energy absorption and dissipation within

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the melt. The kinetic viscosity of liquid samples was calculated according to the equation[13]

$$\nu = \frac{I^2(\delta - T\delta_0/T_0)^2}{\pi(MR)^2TW^2}, \quad (1)$$

where

$$W = 1 - \frac{3}{2}\Delta - \frac{3}{8}\Delta^2 - a + (b - c\Delta)\frac{2nr}{H}, \quad (2)$$

$\Delta = \delta/2\pi$; M represents the mass of the liquid sample; and a, b, and c are the constants; I is the momentum of inertia of the suspended system; R is the gas constant, r is the radius of the vessel; H is the height of the liquid sample in the vessel; δ is the logarithmic damping decrement; T is the period time of the oscillations; the subscript 0 refers to an empty vessel; and n is the number of solid planes, with which the liquid sample contacts horizontally (i.e. in the case of a vessel that has a lower closed end surface and the free upper surface, $n = 1$; if the vessel encloses the fluid in top and bottom, $n = 2$). The dynamic viscosity η was obtained by the formula $\eta = \nu\rho$ with ρ being the density of the sample. The accuracy for temperature measurement is in the range of 1–2 K.

The temperature dependencies of viscosities for $Cu_{75}Al_{25}$ and $Cu_{87}Sn_{13}$ alloys are shown in Fig. 1 and re-expressed in Fig. 2 in the form of Arrhenius plots, i.e. the natural logarithm of viscosity versus reciprocal temperature. As can be seen from Fig. 2, the relation $\ln\eta = f(10^3/T)$ does not obey the Arrhenius law. Breakpoints appear in the Arrhenius plots at about 1473 K for $Cu_{87}Sn_{13}$ and at about 1573 K for $Cu_{75}Al_{25}$, respectively. The total structure factors of liquid $Cu_{75}Al_{25}$ and $Cu_{87}Sn_{13}$ are demonstrated in Figs. 3 and 4. The main peaks of different temperatures are symmetric in those structure factors. It is noticed that a pre-peak emerges in front of each main peak on the structure factor curves below 1473 K for $Cu_{87}Sn_{13}$ alloy and 1573 K for $Cu_{75}Al_{25}$ alloy, respectively. Above the temperatures, these pre-peaks disappear. The presence and the disappearance of the pre-peak on the structure factors coincide well with the discontinuity of the Arrhenius plots for both the studied melts of alloys.

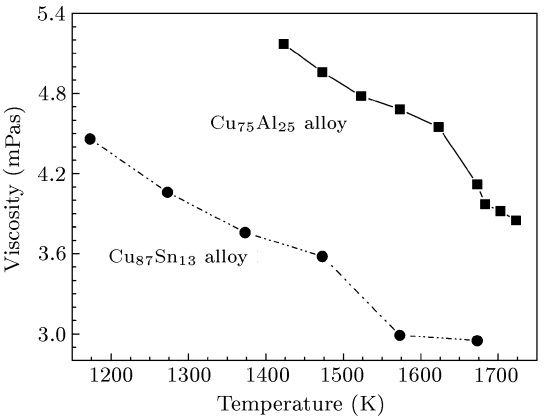


Fig. 1. Measured viscosities of $Cu_{75}Al_{25}$ and $Cu_{87}Sn_{13}$ alloys.

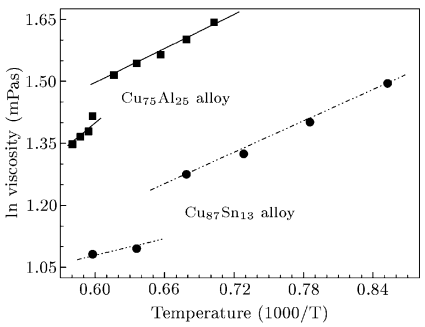


Fig. 2. Arrhenius plots of viscosity of liquid $Cu_{75}Al_{25}$ and $Cu_{87}Sn_{13}$ alloys.

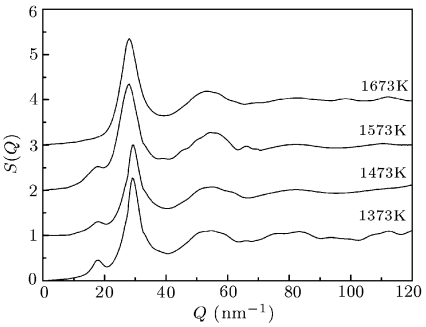


Fig. 3. Total structure factors of liquid $Cu_{75}Al_{25}$ alloy.

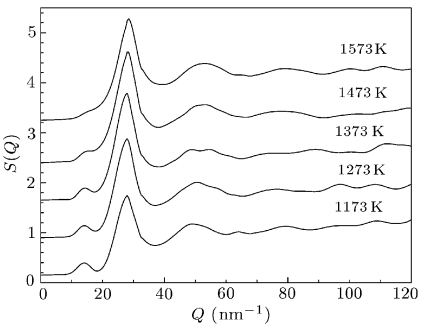


Fig. 4. Total structure factors of $Cu_{87}Sn_{13}$ alloy at different temperatures.

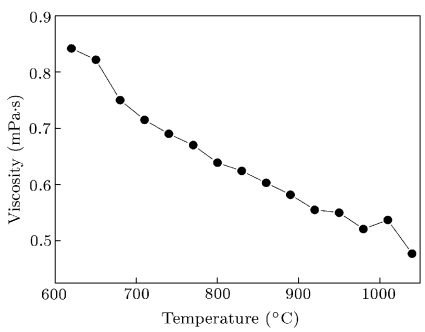


Fig. 5. Measured viscosities of Al-12.5% Si alloy.

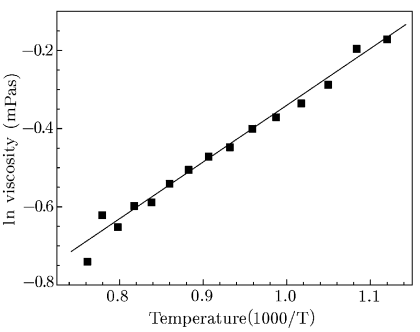


Fig. 6. Arrhenius plots of viscosity of Al-12.5% Si alloy.

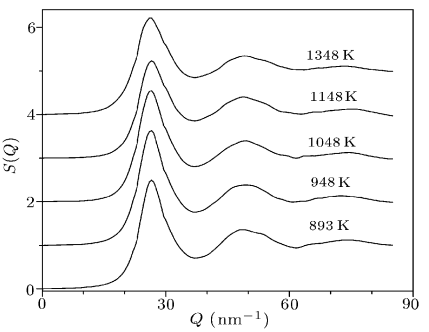


Fig. 7. Total structure factors of liquid Al-12.5% Si alloy.

For comparison, an eutectic alloy of Al–12.5% Si was investigated and the results of viscosities and Arrhenius plots are shown in Figs. 5 and 6. Different from the $Cu_{75}Al_{25}$ and $Cu_{87}Sn_{13}$ alloys, the temperature dependency of viscosity for the eutectic Al–12.5% Si alloy obeys the Arrhenius law well. The total structure factors of the eutectic the Al–12.5% Si alloy at different temperatures are shown in Fig. 7, in which no pre-peak can be observed.

For pure metals, Fig. 8 illustrates the total structure factors of Cu at different temperatures above its melting point. Figures 9(a) and 9(b) depict the total structure factor and pair correlation functions of Sn at different temperatures above the melting point. Arrhenius plots of viscosities of Cu and Sn are shown in Figs. 10 and 11, respectively.

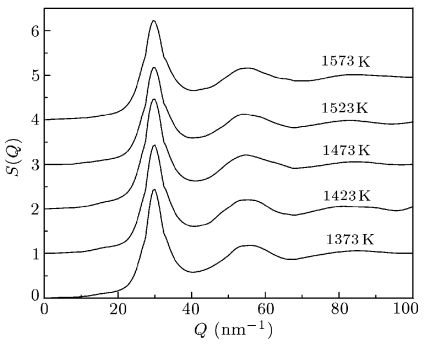


Fig. 8. Total structure factors of liquid Cu.

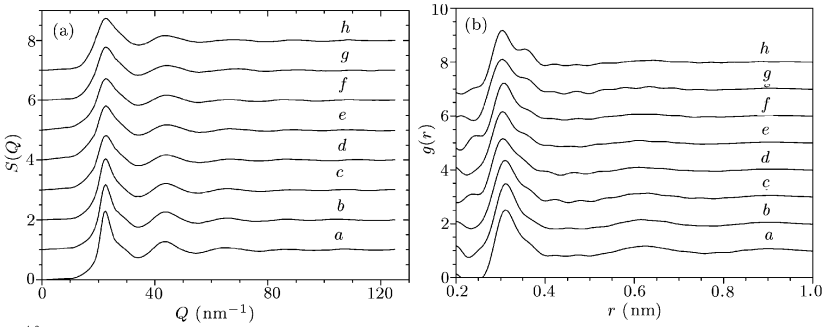


Fig. 9. Total structure factors and pair correlation functions of liquid Sn. Curves *a*–*h* represent the temperatures of 673, 873, 1073, 1473, 1573, 1773, 1873, and 1973 K, respectively. (a) Total structure factors. (b) Pair correlation functions.

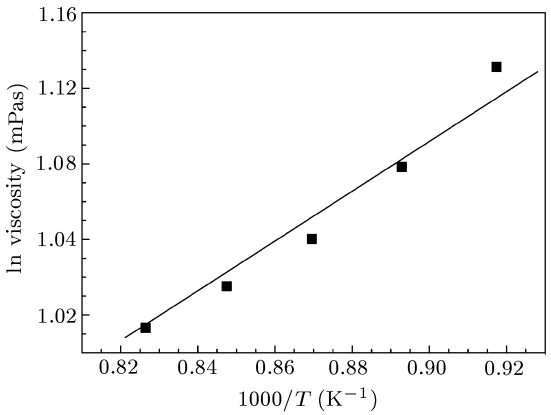


Fig. 10. Arrhenius plots of viscosity of liquid Cu.

The viscosity of liquid matter is a function of temperature. A well-known formula describing the temperature dependence of viscosity of liquids is the Arrhenius equation

$$\eta = A \exp\left(\frac{E_\nu}{RT}\right), \tag{3}$$

where A is a pre-exponential factor and E_v is the energy of activation for viscous flow. In this work, the temperature dependence of viscosity can be divided into two categories. One includes the eutectic alloy Al-12.5% Si and pure metals Cu and Sn which obey the Arrhenius equation in the range of temperature above their melting points. The other includes those alloys such as $Cu_{75}Al_{25}$ and $Cu_{87}Sn_{13}$ which have a more complicated structure. Considerable experimental results[9,10] implied that the structure of these melts might change discontinuously in a temperature range of hundreds of degrees above their liquidus. All of the viscosity data in this work are obtained under vacuum atmosphere, in order to avoid the influence of different atmospheres.[14,15]

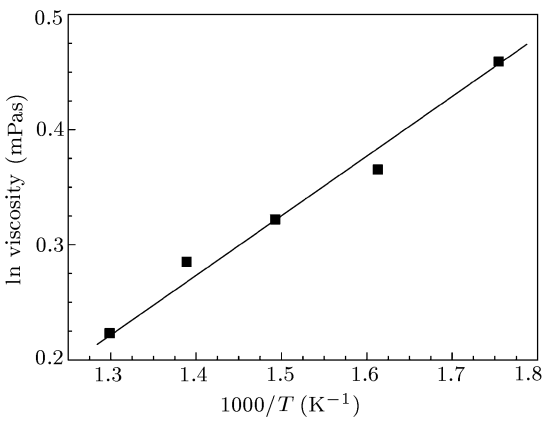


Fig. 11. Arrhenius plots of viscosity of liquid Sn.

For the structural properties, it is useful to take structural orders into account. Elliott[16] defined three contiguous length scales in amorphous: 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. The most characteristic signature of the medium-range order is the pre-peak in front of the main peak on the curve of the total structure factor, which is also referred to as the first sharp diffraction peak or the low Q structure.[16,17] The main peak on the curve of the structure factor is then known as the characteristic signature of the SRO structures.

It can be seen from Figs. 7–9 that, for pure Cu and Sn melts and eutectic Al–Si alloy melts, no pre-peaks appear on the curves of the total structure factors in the range of temperature above their melting points, i.e., only main peaks exist. The curve of the structure factors for the melt Sn is slightly different from that of the melt Cu, namely, in the case of Sn, it seems to be slightly asymmetric about the main peak. There is a small hump or shoulder to the right of the main peak in the curve of Sn, as shown in Fig. 9. The hump or shoulder on the pair correlation function is due to the residual covalent bonds of the solid in liquids. It is manifested that the SRO of tetrahedrons exists in the liquid.[10] Although the shoulder changes with temperature or the liquid–liquid phase translation occurs in melt Sn, the change is only limited to a structural size of SRO. Furthermore, the change in the structure of melt Sn does not bring the departure of viscosity from the Arrhenius plot as shown in Fig. 11. This indicates that no MRO structure exists in the molten alloys of the above-mentioned simple binary eutectic composition and pure metals. This suggests that the temperature dependence of viscosity in the systems which contain only SRO structures obeys the Arrhenius law.

The occurrence of pre-peaks is related to the formation of chemical compounds or chemical order structures. Moreover, according to the calculation results of quantum mechanics,[19] there exists a strong attraction between Cu and Sn atoms; the same also holds true to those of Cu and Al atoms. It can be concluded that the distribution of Cu and Sn atoms (Cu and Al atoms) in melts is not microscopically random but takes some compound structures such as Cu_xSn_y and Cu_xAl_y. Those Cu_xSn_y (Cu_xAl_y) atomic clusters, which are stable in composition and structure, may exist in a large scale of size in the melts. These atomic clusters contribute significantly to the formation of the pre-peak on the total structure factor curve in the $Cu_{75}Al_{25}$ and $Cu_{87}Sn_{13}$ alloys as shown in Figs. 3 and 4. In addition, the MRO structure changes with temperature. It exists in a lower range of temperature and disappears in a higher range of temperature above the melting point. The structural change from MRO to SRO should be responsible for the breakpoints in the Arrhenius plots of viscosities in the $Cu_{75}Al_{25}$ and $Cu_{87}Sn_{13}$ alloys as shown in Figs. 1 and 2.

The viscosity of liquid alloys is a structural sensitive property at an atomic scale. The changes of the liquid structure will result in the changes of viscosity. Using kinetic theory, Born and Green[20] derived an expression of the viscosity of liquids as a function of the pair correlation function and the pair interatomic potential:

$$\mu = \frac{2\pi}{15}\left(\frac{m}{kT}\right)^{1/2} n_0^2 \int_0^x g(r)\frac{\partial\phi(r)}{\partial r} r^4 dr, \qquad (4)$$

where m is the mass of the atoms, and k is Boltzmann's constant. Jonson *et al.* obtained some values of pure molten metals using Eq. (4). In calculating the values of viscosity, experimental data of pair distribution functions and pair potentials are required. The temperature dependence of viscosity upon this equation is still semi-quantitatively correct. From a theoretical point of view, however, the validity of Eq. (4) and the accuracy of the calculations of pair potentials need complete investigation.[20,21]

In conclusion, the viscosities of pure metals and eutectic alloy melts with only the short-range order structure follow the Arrhenius law in a wide range of temperature above the liquidus. The breakpoints in Arrhenius plots emerge as the structures of alloy melts is transformed from the medium-range order structure to the short-range order structure. The change of the viscosity of the metallic alloys is a characteristic of microstructure transformation in the related melts.

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