Viscosities and their correlations with structures of Cu–Ag melts*

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The viscosities of a series of Cu–Ag melts in a temperature range from 1473 K to nearly liquid temperatures are measured by using an oscillating viscometer. At the same temperature, the value of viscosity increases first with silver content increasing, and reaches a maximum value at the eutectic component $Cu_{40}Ag_{60}$, then decreases. All the temperature dependences of the viscosities of Cu–Ag melts conform with the Arrhenius equation. The parameters of correlation length D of the studied Cu–Ag melts are calculated according to the experimental results of x-ray diffraction. The temperature dependence of correlation length D shows an exponential decay function, which is similar to the Arrhenius equation. Based on the values of viscosities and correlation length D, a direct correlation between viscosity and liquid structure is found for the investigated Cu–Ag melts through comparative analysis.

Keywords: viscosity, liquid structure, correlation length

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1. Introduction

Viscosity, one of the main atomic transport properties, is considered to be most important not only from practical considerations, such as the applications in processing, chemical and metallurgical industries, but also from the theoretical point of view as a "structure sensitive" property.[1,2] As one of the most important properties of melts, the viscosities of molten metals and alloys are studied extensively by many experimental and calculational methods.[3] Because of experimental difficulties, systematic investigation of alloy viscosity at elevated temperatures is rather limited.[4] Many physical models expressed by different characteristic parameters based on quantum mechanics and statistic mechanics have been established.

Since the viscosity is seen as a "structure sensitive" property,[1] there must be some correlations between viscosity and structural characteristics. Born and Green[5] proposed an expression of the viscosity of liquid as a function of the pair correlation function $g(r)$ and the pair interatomic potential $\phi(r)$

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

where m is the mass of the atom, k is the Boltzmann constant, and n_0 is the average density. Based on Brownian motion, Zwanzig *et al.*[6] and Rice and Allnatt[7] proposed a similar equation

$$\eta = \frac{n_0 mkT}{2\zeta} + \frac{\pi\zeta}{15kT} n_0^2 \int r^3 \left[\frac{\mathrm{d}\phi(r)}{\mathrm{d}r}\right] g(r)\psi_2(r)\mathrm{d}r, \qquad (2)$$

where ζ is the friction coefficient, and ψ_2 the boundary condition function for a finite differential equation. The Born–Green and Kirkwood–Rie models set up the correlations between viscosity and structure, and can obtain good results in some mono-atomic liquid metals, but some calculated results are not satisfied.[8] In addition, it is usually difficult to accurately estimate the pair interatomic potential $\phi(r)$. Its validity still needs to be investigated.

In the aspect of experimental study, Sun[9] found that the component with a more intense pre-peak (a peak on the left of the main peak of structure factor $S(Q)$) has the bigger viscosity value for Al–Cu melt. In our previous studies on In–Sn[10] and Cu–Sn[11] melts, viscosity and some structural parameters, such as the correlation radius r_c, and the coordination number N_1, have the same abnormal change range with temperature. All the studies can only reflect the viscosity changing qualitatively. To date, a direct correlation between liquid structure and viscosity quantitatively through an experimental method has not been set up.

In this study, the viscosities of $Cu_{100-x}Ag_x$ (x = 20, 40, 60, 80, at.%) melts are investigated by an oscillating viscometer for high temperature melts. By comparing with our previous structural investigations through an x-ray diffraction method,[12] the correlation between viscosity and liquid structure is investigated and discussed.

2. Experimental materials and procedures

The samples for viscosity and x-ray diffraction measurements were prepared by melting from pure ingots of Cu, Ag (99.99% in purity) in a vacuum inductive furnace. The samples were cooled into ingots in the furnace, and then were

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processed into a sample of 25 mm×18 mm×8 mm for x-ray diffraction experiments, and a sample of 28 mm×48 mm for viscosity measurements.

The viscosity measurements were performed by using an oscillating viscometer for high temperature melts. The corundum crucible was used. The detailed process of measurement can be seen elsewhere.[13,14] The kinematic viscosity obtained by the logarithmic damping decrement of a melt can be calculated by the following Schvidkovskii equation:[15]

$$\nu = \frac{I^2(\delta - T\delta_0/T_0)^2}{\pi(mR)^2 T\omega^2}, \tag{3}$$

$$\omega = 1 - \frac{3}{2}\Delta - \frac{3}{8}\Delta^2 - a + (b - c\Delta)\frac{2nR}{H}, \tag{4}$$

where $\Delta = \delta/2\pi$, a, b, c are constants, m is the mass of the liquid sample, I is the momentum of inertia of the suspended system, R is the radius of the vessel, H is the height of the liquid sample in the vessel, δ is the logarithmic damping decrement, and T is the period time of the oscillations, while the subscript 0 refers to an empty vessel, n 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, $n = 1$, if the vessel encloses the fluid top and bottom, $n = 2$). The dynamic viscosity η can be calculated from the following formula:

$$\eta = \nu\rho, \tag{5}$$

where ρ is the density of the sample.

X-ray diffraction measurements were carried out using a high temperature θ–θ type diffractometer. The detailed process of measurement can be seen in Ref. [12]. The scattering intensity measured in arbitrary units was converted into the coherent scattering intensity per atom in an electron unit $I_{\rm eu}^{\rm coh}(Q)$ by using the generalized Krogh–Moe–Norman method.[16,17] Compton scattering was corrected by using the values given by Cromer and Mann[18]

$$I_{\rm eu}^{\rm coh}(Q) = \langle f^2\rangle + \langle f\rangle^2 \int_0^\infty 4\pi r^2[\rho(r) - \rho_0]\frac{\sin(Qr)}{Qr}\,{\rm d}r, \tag{6}$$

where f is the scattering factor, ρ (r) is the radial density function, and ρ_0 is the average density. Then the Ashcroft–Langreth structure factor $S(Q)$ can be obtained from the scattering intensity as the following function:[19,20]

$$S(Q) = \frac{I_{\rm eu}^{\rm coh}}{\langle f^2(Q)\rangle}, \tag{7}$$

$$\text{with}\quad \langle f^2(Q)\rangle = \sum_j c_j f_j^2(Q), \tag{8}$$

where c_j is the mole fraction, and $f_j(Q)$ is the total atomic scattering factor of the j-th component in the alloy. The detailed processing and error analysis of the x-ray diffractometer used in this work are described somewhere else.[21,22]

3. Results and discussion

Figure 1 shows the temperature dependences of the viscosity of equilibrium liquids for the Cu–Ag alloys. It can be seen that at the same temperature the viscosity increases with increasing Ag content till the eutectic component $Cu_{40}Ag_{60}$ and then decreases in the Cu–Ag melts. The data as a function of temperature can be expressed by Arrhenius equation:

$$\eta = \eta_0 \exp\left(\frac{E_{\rm a,V}}{RT}\right), \tag{9}$$

where η_0 is a constant depending on the nature of the liquid, $E_{\rm a,V}$ is the activation energy for viscous flow, R the gas constant, and T the temperature. By fitting the discrete data in Fig. 1, the values of η_0 and $E_{\rm a,V}/R$ of the four Cu–Ag melts can be obtained. The eutectic $Cu_{40}Ag_{60}$ alloy has a maximal value of η_0 (2.340) and the minimum value of $E_{\rm a,V}/R$ (609.952). The detailed results are shown in Table 1.

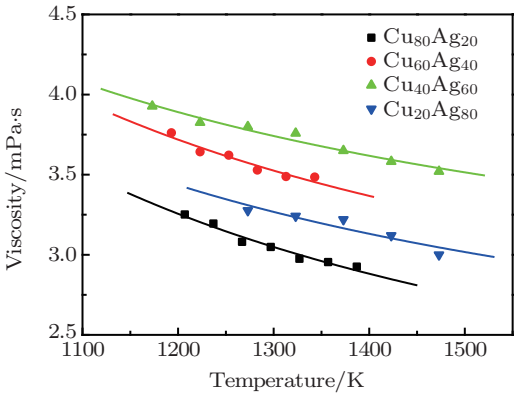


Fig. 1. (color online) Temperature dependences of viscosities of Cu–Ag melts (the lines are fitted by Arrhenius equation).

Table 1. Parameters η_0 and $E_{\rm a,V}/R$ of the Cu–Ag melts fitted by Arrhenius equation.

Alloys	η_0/mPa·s	$(E_{\rm a,V}/R)$/K
$Cu_{80}Ag_{20}$	1.384	1026.311
$Cu_{60}Ag_{40}$	1.857	833.179
$Cu_{40}Ag_{60}$	2.340	609.952
$Cu_{20}Ag_{80}$	1.797	777.376

Many efforts have been made to study the correlation between viscosity and liquid structure. Based on the Born and Green formula (Eq. (1)), Morioka[23] put forward a dense gas-like model of viscosity for liquid metals. Mi *et al.*[24] studied the correlation between viscosity and liquid structure of aluminum by the molecular dynamics simulation. Mi *et al.* studied the kinematic viscosity of magnesium[2] and Mg–9Al[24] melts and their relationship with the microstructure. However, as mentioned above, the direct quantitative correlation between liquid structure and viscosity in a wide range of temperature is not found experimentally due to the complexity of liquid structure and the instability of viscosity measurement, especially for the alloy melts.

To find a direct correlation between viscosity and structure, the structural parameters such as the mean nearest neighbor distance r_1, the correlation radius r_c, the atom numbers N_c, etc. are all investigated thoroughly. They all show a "saltation pattern", i.e., the parameters keep stable in a temperature range and an abrupt change arises at the critical temperature, which is different from the continuous temperature dependence of viscosity. Therefore, other parameters should be introduced. In the study of solids, the half-height-width of the Bragg peak of x-ray diffraction can be used to estimate the microcrystalline size. For the amorphous material, usually the correlation length D (or named the size of structural unit) is used to estimate the size of ordered domain, it can be calculated from the following equation:[25,26]

$$D \approx \frac{2\pi}{\Delta Q}, \tag{10}$$

where ΔQ is the half-height-width of the first peak of $S(Q)$.

Figure 2 shows the temperature dependences of the correlation length D of the studied Cu–Ag melts. It can be seen that the discrete data follow an exponential function changing with temperature. The solid lines in Fig. 2 are fitted by the Arrhenius equation

$$D = D_0 \exp\left(\frac{E_{a,D}}{RT}\right), \tag{11}$$

where D_0 is a constant, and $E_{a,D}$ the activation energy for structural evolution. By fitting the discrete data in Fig. 2, D_0 and $E_{a,D}/R$ of the four Cu–Ag melts can be obtained. The detailed results are shown in Table 2.

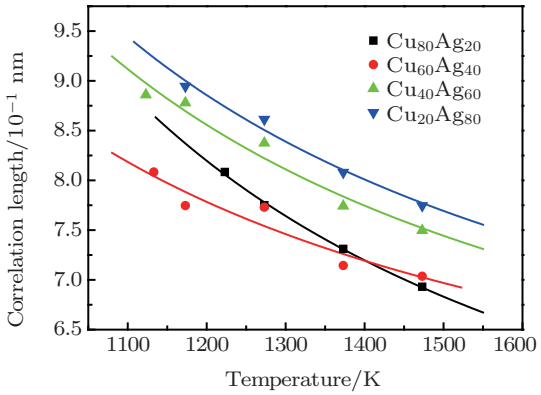


Fig. 2. (color online) Temperature dependences of correlation length of Cu–Ag melts (the lines are fitted by the Arrhenius equation).

Table 2. Parameters D_0 and $E_{a,D}/R$ of the Cu–Ag melts fitted by the Arrhenius equation.

Alloys	$D_0/10^{-1}$ nm	$(E_{a,D}/R)$/K
$Cu_{80}Ag_{20}$	3.295	1093.500
$Cu_{60}Ag_{40}$	4.477	663.586
$Cu_{40}Ag_{60}$	4.333	802.262
$Cu_{20}Ag_{80}$	4.379	845.168

The viscosity η and correlation length D both show Arrhenius-type temperature dependence, i.e., an exponential variation with temperature. This provides a chance to investigate the direct correlation between liquid structure and viscosity quantitatively. At the first, a linear scaling adjustment between η and D is employed as[27]

$$\eta = aD + bT + c, \tag{12}$$

where a, b, and c are constants. This relation is similar to the linear function between the size of average atomic cluster d_S and kinematic viscosity ν of magnesium and Mg–9Al melts in Refs. [2] and [24]. Although this simple equation can reflect a good correlation between η and D, the fitted constants (a, b, c) are stochastic without any physical interpretation. To set up the direct correlation between liquid structure and viscosity, a correlation factor k (in 10^{-1} mPa·s·nm^{-1}) is introduced, which can make the units of η and D unified. The data of kD–η are investigated. Encouragingly, kD–η also shows an exponential function varying with temperature when the value of k is 1, which is shown in Fig. 3. The solid lines in Fig. 3 are fitted by the Arrhenius type equation

$$kD - \eta = \alpha \exp\left(\frac{\beta}{RT}\right), \tag{13}$$

where $k = 1$, α and β are constants. The fitted results of α and β/R for the four Cu–Ag melts are shown in Table 3.

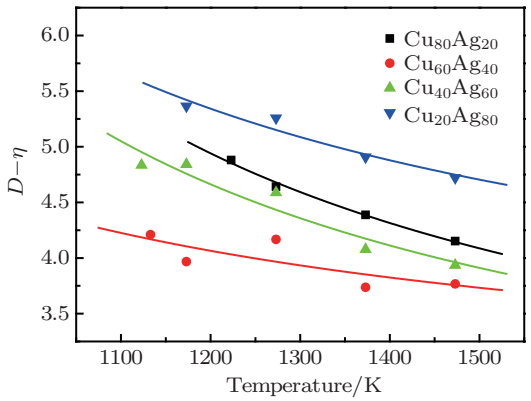


Fig. 3. (color online) Temperature dependences of kD–η ($k = 1$) of Cu–Ag melts (the lines are fitted by the Arrhenius type equation).

Table 3. Parameters α and β/R of the Cu–Ag melts fitted by the Arrhenius type equation.

Alloys	α/mPa·s	(β/R)/K
$Cu_{80}Ag_{20}$	1.914	1138.299
$Cu_{60}Ag_{40}$	2.654	511.521
$Cu_{40}Ag_{60}$	1.982	1027.579
$Cu_{20}Ag_{80}$	2.587	888.104

To make parameters α and β have certain physical significances rather than the fitted values, the data in Tables 1–3 are compared carefully. Parameters α and β can be expressed as

$$\alpha = kD_0 - \eta_0, \tag{14}$$

$$\beta = \frac{E_{a,D}^2}{E_{a,V}}, \tag{15}$$

then parameter α has the same unit (mPa·s) as η_0 and parameter β has the same unit (J·mol^{-1}) as $E_{a,D}$ or $E_{a,V}$. The calculated parameters kD_0–η_0 ($k = 1$), $E_{a,D}^2/(RE_{a,V})$ and the errors with α and β/R are shown in Table 4. It can be seen that the data of kD_0–η_0 ($k = 1$) are close to α with a maximum error 1.276% for $Cu_{60}Ag_{40}$ alloy. The data of $E_{a,D}^2/(RE_{a,V})$ are slightly bigger than β/R with a maximum error 3.465% for $Cu_{20}Ag_{80}$ alloy. In order to see the accuracies of the calculated parameters, the calculated curves of kD–η are shown in Fig. 4. The calculated data (curves) show a little deviation from the discretely experimental data due to the slightly bigger data of $E_{a,D}^2/(RE_{a,V})$ than β/R.

Table 4. Calculated parameters kD_0–η_0 ($k = 1$), $E_{a,D}^2/(RE_{a,V})$ and the errors with α, β/R.

Alloys	kD_0–η_0	Error/% $\left\lvert\frac{\alpha-(kD_0-\eta_0)}{\alpha}\right\rvert \times 100\%$	$E_{a,D}^2/(RE_{a,V})$	Error/% $\left\lvert\frac{\beta/R-E_{a,D}^2/(RE_{a,V})}{\beta/R}\right\rvert \times 100\%$
$Cu_{80}Ag_{20}$	1.911	0.137	1165.088	2.353
$Cu_{60}Ag_{40}$	2.620	1.276	528.513	3.322
$Cu_{40}Ag_{60}$	1.993	0.582	1055.205	2.688
$Cu_{20}Ag_{80}$	2.582	0.171	918.873	3.465

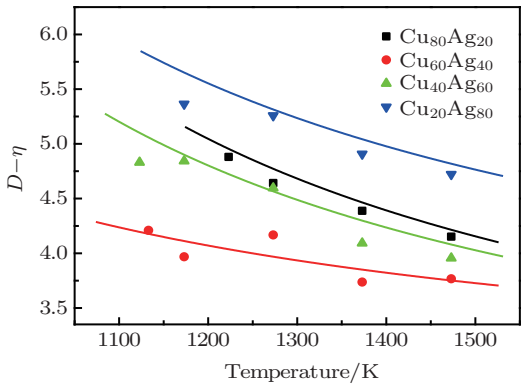


Fig. 4. (color online) Temperature dependences of kD–η ($k = 1$) of Cu–Ag melts (the lines are calculated from Eq. (13) with $\alpha = kD_0$–η_0, $\beta = E_{a,D}^2/E_{a,V}$).

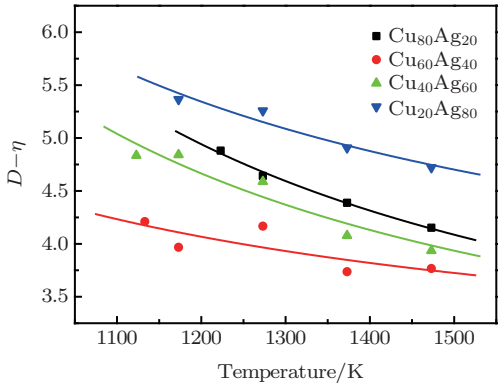


Fig. 5. (color online) Temperature dependences of kD–η ($k = 1$) of Cu–Ag melts (the lines are fitted by Eq. (13) with $\alpha = kD_0$–η_0).

If kD–η ($k = 1$) curves are calculated from Eq. (13) with fixing $\alpha = kD_0$–η_0 ($k = 1$), fitting β/R or fixing $\beta/R = E_{a,D}^2/(RE_{a,V})$, and fitting α, then the better match between the calculated kD–η ($k = 1$) curves and the discrete data points can be obtained. The corresponding results are shown in Figs. 5 and 6, and also in Table 5. Based on the above analyses, the correlation between viscosity and liquid structure of Cu–Ag melt, expressed by Eqs. (13)–(15), is reasonable in the consideration of experimental errors of viscosity (less than 2%) and liquid structure measurement (less than 5%).

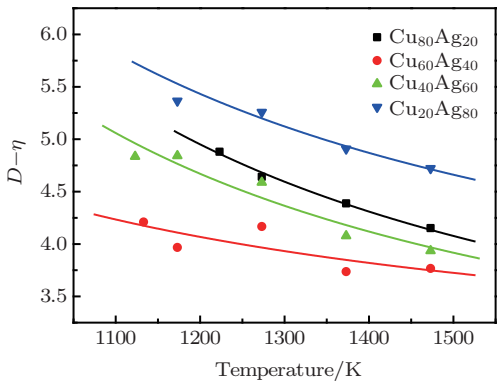


Fig. 6. (color online) Temperature dependences of kD–η ($k = 1$) of Cu–Ag melts (the lines are fitted by Eq. (13) with $\beta = E_{a,D}^2/E_{a,V}$).

Table 5. Fitted β/R with fixing $\alpha = kD_0$–η_0 ($k = 1$), fitting α with fixing $\beta = E_{a,D}^2/E_{a,V}$, and their errors with β/R and α.

Alloys	Fitted (β/R)/K	Error/% $\left\lvert\frac{(\beta/R)-\text{fitted}(\beta/R)}{(\beta/R)}\right\rvert \times 100\%$	Fitted α/mPa·s	Error/% $\left\lvert\frac{\alpha-\text{fitted}(\alpha)}{\alpha}\right\rvert \times 100\%$
$Cu_{80}Ag_{20}$	1140.098	0.158	1.875	2.013
$Cu_{60}Ag_{40}$	527.596	3.143	2.619	1.336
$Cu_{40}Ag_{60}$	1020.385	0.700	1.938	2.184
$Cu_{20}Ag_{80}$	890.312	0.249	2.526	2.339

4. Summary

The viscosities of Cu–Ag melts are investigated by an oscillating viscometer. Combined with the structural results obtained by the x-ray diffraction method, the correlation between viscosity and liquid structure is investigated. The results of this work will enhance the understanding of the correlations between dynamic properties and liquid structure of alloy melts. Some conclusions from the present study are summarized as follows.

(i) Temperature dependences of the viscosities of Cu–Ag melts conform with the Arrhenius equation. The eutectic component $Cu_{40}Ag_{60}$ alloy has the biggest viscosity in all the investigated Cu–Ag melts, and has a maximal value of η_0 (2.340) and a minimum value of $E_{a,V}/R$ (609.952).

(ii) Each of the temperature dependences of the correlation length D of the studied Cu–Ag melts shows an exponential decay function, which is similar to the Arrhenius equation.

(iii) Based on analyses of the experimental data of viscosity and correlation length D, a direct correlation between them is found. It can be expressed as $\eta = kD – \alpha \exp(\beta/RT)$ with $k = 1$, $\alpha = kD_0 – \eta_0$, and $\beta = E_{a,D}^2/E_{a,V}$.

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