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Correlation between viscous-flow activation energy and phase diagram in four systems of Cu-based alloys

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Activation energy is obtained from temperature dependence of viscosities by means of a fitting to the Arrhenius equation for liquid alloys of Cu–Sb, Cu–Te, Cu–Sn and Cu–Ag systems. We found that the changing trend of activation energy curves with concentration is similar to that of liquidus in the phase diagrams. Moreover, a maximum value of activation energy is in the composition range of the intermetallic phases and a minimum value of activation energy is located at the eutectic point. The correlation between the activation energy and the phase diagrams has been further discussed.

1. Introduction

Cu-based alloys are applied extensively in material, machine, electricity, and especially in the field of functional composite materials because of their excellent mechanical, electrical and chemical properties. Much attention has been paid to the physical properties and structures of Cu-based alloys. It is well known that the characteristic of liquid metals or melts will have a strong impact on the qualities of the final materials [1]. Recently, some studies have investigated the particular structures and corresponding properties of several Cu-based alloy systems, e.g. Cu–Sb, Cu–Sn, Cu–Ge and Cu–Si, through the measurements of dynamic viscosity, electrical resistivity, diffusion coefficients, and so on [2–6].

Activation energy, in viscous activation picture, as an energy barrier for the movement of atom in liquids, was experimentally proposed by Glasstone [7]. For strong liquid, it has been found that activation energy is temperature independent [8,9]. For some metals, the activation energy of different melts has a linear relationship with the corresponding melting points [10]. In addition, it has been revealed that the activation energy is proportional to the high-frequency shear modulus by studying the viscosity of glass-forming molecular liquids [11]. In the present work, we will investigate the relationship between the activation energy and phase diagram of Cu-based alloys.

2. Materials and methods

Samples of Cu-based alloys used in the present work were prepared from ingot Cu (99.999 wt%), Sb (99.98 wt%) and Te (99.98 wt%). They were melted in a graphite clay crucible using a medium frequency induction electric furnace and cast ingots in a graphite mould.

The measurements of viscosity were carried out using an oscillating cup viscometer. The torsion oscillation of a cylindrical crucible suspended on a wire is damped by the friction with the melt. Based on the Shvidkovskii equation [12], the viscosity of the liquid can be calculated from the periodic time and the logarithmic damping decrement of the harmonic oscillation. After the chamber was cleaned with a vacuum of 7×10^{-6} Pa, it was filled with high purity argon (99.999%) of 1.1×10^{5} Pa [13]. Samples are placed in an Al_2O_3 crucible and heated at a rate of 4 K/min to 300–400 K above the liquidus temperature. After maintaining for 3 h at the given temperatures, the samples were cooled down to the experimental temperatures with a rate of 4 K/min and held for 1 h before each measurement. The viscosity measurements were repeated four times at each temperature and at least ten temperature points above the liquidus temperature were taken for each alloy system. The error bar of data was no more than ±3% at the same temperature in different measurements.

In a wide temperature range above the liquidus temperature T_L, the viscosity behavior of the melts generally obeys the Arrhenius equation [14]:

$$\eta=\eta_0\exp(E_v/RT) \tag{1}$$

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where η_0 is a pre-exponential constant, which is associated with the nature of the liquid, R is the molar gas constant and E_v is the viscous-flow activation energy.

3. Results

Viscosity data for the melts of Cu–Sb and Cu–Te are obtained through the oscillating cup viscometer. Fig. 1 shows that the viscosities of Cu–Sb alloys with different compositions increase with decreasing temperature according to the Arrhenius-type empirical equation. Moreover, the analogous viscosity trend with temperature can also be revealed in the Cu–Te alloys, as shown in Fig. 2. The fitting parameters of Cu–Sb and Cu–Te alloy systems are shown in Tables 1 and 2, respectively, where R^2 is the square of correlation coefficient, which reflects the error of the Arrhenius relationship for the viscosities of Cu–Sb and Cu–Te systems. The fitted results show that the temperature dependence of the viscosity obeys the Arrhenius relationship well.

Figs. 3 and 4 show the viscosities of Cu–Sb and Cu–Te alloys as a function of the atomic concentrations at the same superheated temperature, respectively. In comparison with the phase diagrams [15], it can be seen from Fig. 3 that the maximum of viscosity of Cu–Sb system is located at 25 at% Sb, corresponding to the range of β-Cu–Sb intermetallic phase in the solid state. Fig. 4 shows the maximum of viscosities of Cu–Te system located at 36.5 at% Te, corresponding to the range of $Cu_{2-x}Te$ (β-Cu–Te) in the solid state.

Values of activation energy for the melts of Cu–Sb, Cu–Te, Cu–Sn [5] and Cu–Ag [16] systems have been summarized. The phase diagrams coupled with the corresponding activation energy curve with concentration are listed and compared in Fig. 5 for each system. It can be observed that the changing trend of activation energy curves with concentration similar to that of liquidus in both compound forming systems (Cu–Sb, Cu–Te and Cu–Sn systems) and simple eutectic systems (Cu–Ag system). Interestingly, activation energy reaches a minimum at eutectic point for all alloys mentioned above and the maximum of the activation energy covers the range of the intermetallic phases for all compound forming systems. Fig. 5(a) shows the maximum of activation energy located at Sb-content of 25 at%, corresponding to the range of β-Cu–Sb phase in the solid state. Fig. 5(b) shows the maximum of activation energy of Cu–Te system is

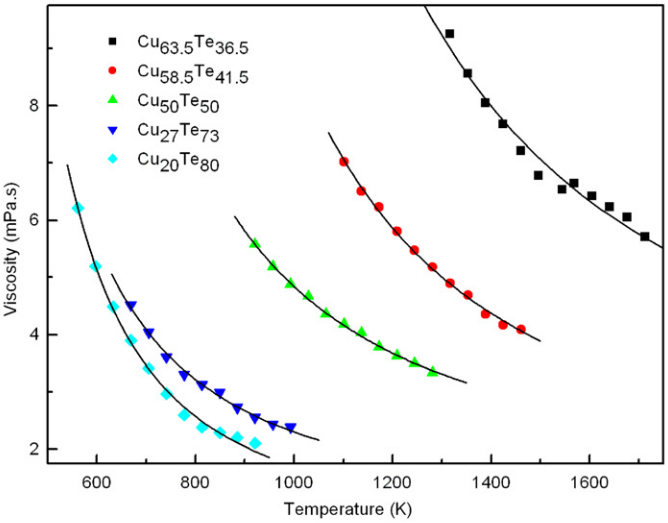

Fig. 2. Temperature dependence of viscosities of molten Cu–Te alloys during cooling process. Solid lines are the Arrhenius plots.

Table 1
Parameters of the viscosity fitted by the Arrhenius equation in Cu–Sb system.

Alloys	η_0 (mPa s)	$\Delta\eta_0$ (mPa s)	E_v/R (K)	$\Delta(E_v/R)$ (K)	R^2
$Cu_{84.5}Sb_{15.5}$	1.32	0.03	1574.5	28.2	0.994
$Cu_{81}Sb_{19}$	1.75	0.10	1229.8	62.6	0.968
$Cu_{75}Sb_{25}$	1.27	0.03	1658.9	24.6	0.997
$Cu_{67}Sb_{33}$	1.13	0.04	1479.1	34.7	0.993
$Cu_{45}Sb_{55}$	1.43	0.05	845.7	34.8	0.976
$Cu_{37}Sb_{63}$	1.25	0.04	803.2	28.4	0.983
$Cu_{25}Sb_{75}$	0.98	0.05	861.6	52.9	0.951

Table 2
Parameters of the viscosity fitted by the Arrhenius equation in Cu–Te system.

Alloys	η_0 (mPa s)	$\Delta\eta_0$ (mPa s)	E_v/R (K)	$\Delta(E_v/R)$ (K)	R^2
$Cu_{63.5}Te_{36.5}$	1.25	0.11	2601.8	126.9	0.976
$Cu_{58.5}Te_{41.5}$	0.75	0.03	2464.9	44.4	0.997
$Cu_{50}Te_{50}$	0.93	0.02	1649.4	22.5	0.998
$Cu_{27}Te_{73}$	0.60	0.03	1340.0	33.8	0.995
$Cu_{20}Te_{80}$	0.33	0.02	1654.7	33.4	0.996

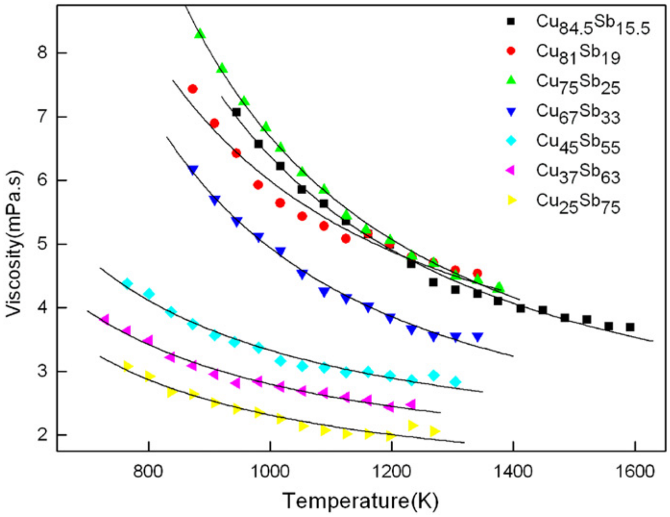

Fig. 1. Temperature dependence of viscosities of molten Cu–Sb alloys during cooling process. Solid lines are the Arrhenius plots.

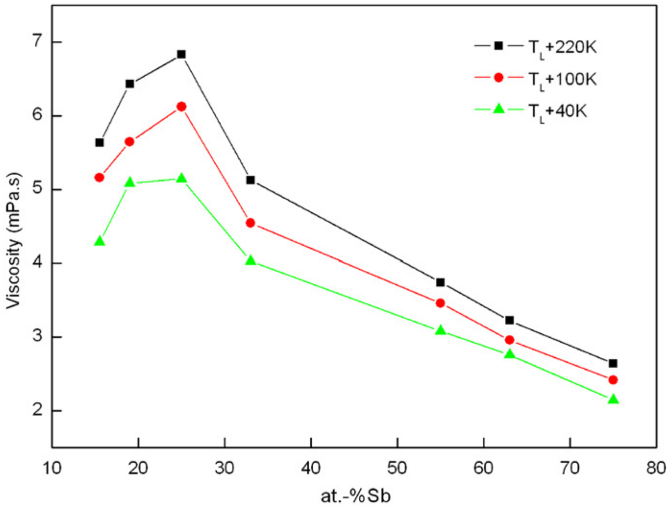

Fig. 3. Experimental viscosities of Cu–Sb alloy melts at the same superheated temperature.

located at a Te-content of 36.5 at%, corresponding to the range of $Cu_{2-x}Te$ (β-Cu–Te) in the solid state. Fig. 5(c) indicates that the maximum of activation energy is located at $Cu_{84.9}Sn_{15.1}$ alloy, corresponding to the range of β-Cu–Sn of solid state in Cu–Sn system. Strikingly, the value of activation energy at the range of the intermetallic phases is much larger than that at the range of eutectic and near-eutectic composition.

As shown in Fig. 6, the values of E_v exhibit a general linear relationship with the T_L in an individual alloy system for the Cu-based alloys. Expressed in algebraic form, the relationship is

$$E_v = a \times T_L + b \tag{2}$$

The fitting parameters a and b for different systems are showed in Table 3, where R is the correlation coefficient, which reflects the relevance of the values of activation energy and liquidus temperature. Based on Fig. 6 and Table 3, it can be found that different categories of Cu-based alloys have different slope and different relevance of E_v and T_L.

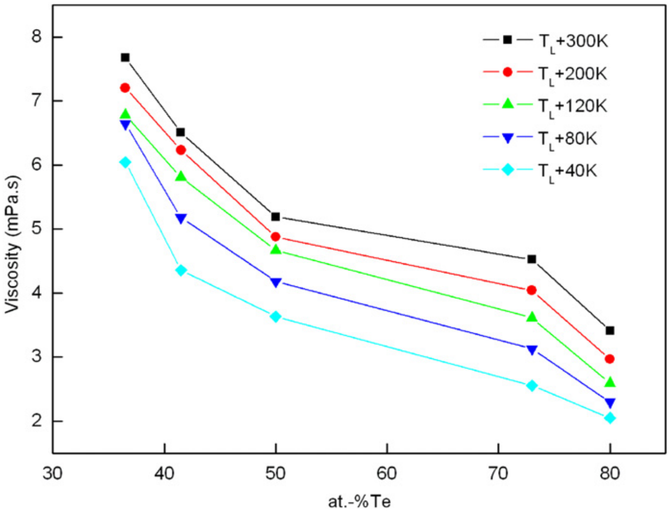

Fig. 4. Experimental viscosities of Cu–Te alloy melts at the same superheated temperature.

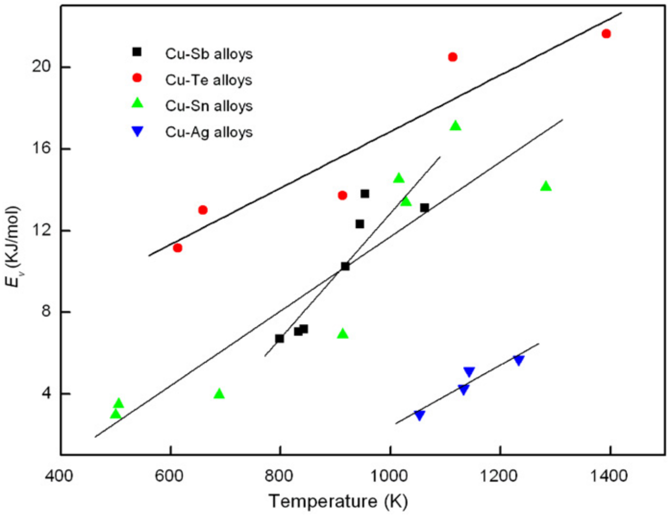

Fig. 6. Activation energy vs liquidus temperatures for different Cu-based alloys.

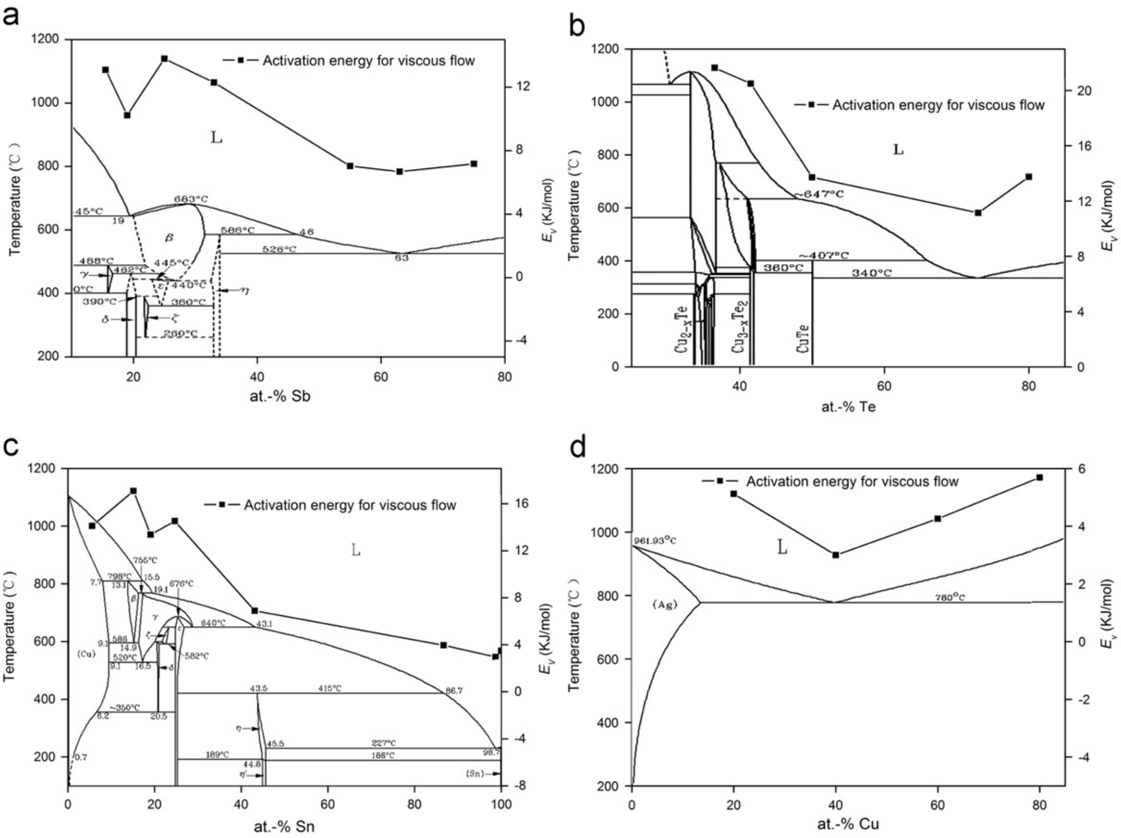

Fig. 5. Comparison of the phase diagram with the activation energy curve of liquid Cu–Sb system (a), Cu–Te system (b), Cu–Sn system (c) and Cu–Ag system (d). Symbols stand for the fitting data, and the solid lines are guides to the eye.

Table 3
Fitting parameters according to Eq. (2) for different systems.

Alloys	*a*	*b*	*R*
Cu–Sb system	0.0306	– 17.7	0.8992
Cu–Te system	0.0133	3.7	0.9344
Cu–Sn system	0.0183	– 6.5	0.9083
Cu–Ag system	0.0150	– 12.6	0.9463

4. Discussion

It is believed that the change of activation energy is related to the microstructure of liquid. In the intermetallic-containing alloy systems, some clusters of unlike atoms can be formed in the liquid at the range of intermetallic phases owing to the strong interplay between the electronic and the atomic structure [4,17]. According to the studies of the liquid structure of Cu–Sn, Cu–Ge, Cu–Sb, Cu–Te, Fe–Al and Fe–Si alloys [4,18–26], it has been revealed that the clusters of unlike atoms exist. Simple eutectic alloys of Cu–Ag system are micro-homogeneous in the liquid state similar to their solid state [27]. In the light of the heat by mixing the liquid copper alloys, it has been also proved that the liquid copper alloys containing electron compounds of complex crystal structures in solid state have some atoms associating into small groups of atoms similar to the type A_mB molecules and are bound by a sort of covalent. While in a simple eutectic structure, atoms are randomly arranged in the liquid alloys [28,29]. Clusters of unlike atoms, which correspond to the solid structure of compound, cause the atoms to move from one position to another more difficultly on account of enhancing interaction of atoms [27]. Thus the clusters of unlike atoms induce E_v to increase significantly [29]. Within each interval melts, it will constitute two kinds of clusters. The variation of composition within a certain region does not influence the existence of clusters in a certain type, but only change their volume [3,18]. Accordingly, the volume fraction of the unlike atom clusters is bigger at the range of intermetallic phases. It means that the influence of the unlike atom clusters on the activation energy of eutectic alloys or near-eutectic alloys is not as strong as that on the activation energy of Cu-rich alloys containing intermetallic phase in Cu–Sb, Cu–Te and Cu–Sn systems. Thus the maximum of the activation energy covers the composition range in which the intermetallic compounds will exist in the solid state. And the value of activation energy at the range of the intermetallic phases is much larger than that at the range of eutectic and near-eutectic composition. In the case of the liquid copper alloys (i.e. Cu–Sb, Cu–Ge, Cu–Sn and Cu–In), it is also observed that the heat of mixing exhibits a deep valley in the heat of evolution in the ranges of the intermetallic phases [28]. The maximum of viscosity at the same superheated temperature is located at the same composition as the activation energy in Cu–Sb and Cu–Te systems, respectively. On the other hand, these results have also proved the influence of the unlike atom clusters in liquids.

For the eutectic alloy, there exist no dominant correlations of atomic bonds in the eutectic liquid alloy. And thus, the clusters show a continuous and random fluctuation in the liquids [27]. Obviously, the interaction between atoms is weak in the liquid eutectic alloys, which induces activation energy to reach a minimum at the eutectic point in all systems. Liquidus temperature is relative to the atomic bonds. Accordingly, the general similarity of the shape of activation energy curves to that of liquidus can be observed. The maximum of electrical resistivity of molten Cu–Sb alloys is located at an Sb-content of 25 at%, while the minimum of electrical resistivity of molten alloys is located at eutectic point [30]. It can be reasonable to conclude that the clusters in liquid have influenced properties of liquid.

The correlation radius of clusters in liquids r_c is influenced by clusters of unlike atoms [27,31]. Fig. 7 shows that the viscosity η in liquid $Al_{100-x}Cu_x$ ($x=18$, 25 and 35) alloys [32] shows linear characteristic with the correlation radius, r_c [33] at the same temperature. The correlation between r_c and viscosity of melts indicates that viscous behavior of melts is related with the clusters of unlike atoms in liquid intuitively.

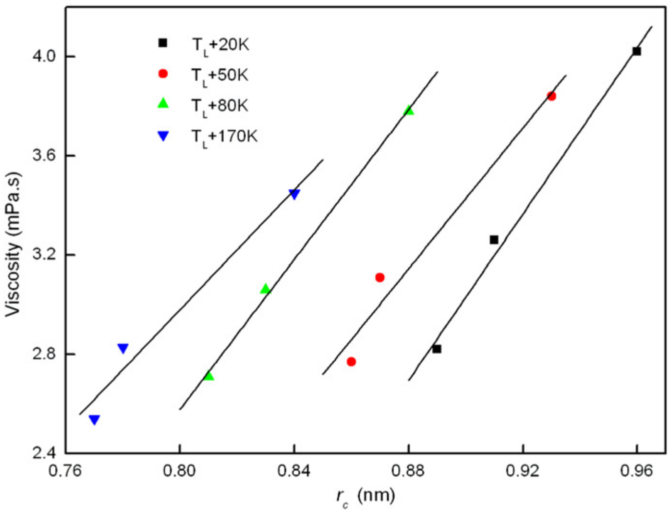

Fig. 7. Viscosity η in liquid $Al_{100-x}Cu_x$ ($x=18$, 25, 35) alloys as a linear function of correlation radius r_c at the same temperature. Solid lines are fitting curves. Experimental data are taken from Refs. [32,33].

Table 4
Equilibrium lattice parameters for different Cu_xTe structures. The numbers in parenthesis are experimental data [34].

x	Structure	a_0 (Å)	b_0 (Å)	c_0 (Å)
2	Trigonal	8.24	8.24	7.13
1.5	Tetragonal	7.79	7.79	6.03
1	Orthorhombic	3.18	3.88	6.88

Correlation radius r_c is influenced by the structure of solid state [33]. It is thought that the activation energy is related to the structure of solid state in nature. The lattice parameters of Cu–Te alloys with Te content between 33 and 50 at% are listed in Table 4 [34]. Obviously, the unit cell of the Cu_2Te cluster is larger than that of $Cu_{1.5}Te$ cluster, and the latter is larger than the unit cell of the CuTe cluster. The change of E_v with Te content increasing has the same tendency as that of the unit cell volume in Cu–Te system. The correlation between E_v and lattice parameters in Cu–Te system proves that the structure of solid state is related to activation energy.

The crystal structures of some elements or space configuration of the solid state persist in the liquid state [10]. It is deemed that the different slope in Fig. 6 is responsible for different atomic structure and space configuration. Moreover, because of the complicated structure configuration in Cu-rich composition range for Cu–Sn and Cu–Sb system in solid state, their relevance of E_v and T_L in Table 3 is much lower. While for simple eutectic Cu–Ag system, the relevance of E_v and T_L is the highest. This fact indicates that activation energy is related to the structure of solid state.

5. Conclusions

Viscosities of Cu–Sb and Cu–Te alloys with different compositions increase with decreasing temperature. The temperature-related viscosity curves obey the Arrhenius relationship.

It is found that the changing trend of activation energy curves with concentration is similar to that of liquidus in Cu–Sb, Cu–Te, Cu–Sn and Cu–Ag systems. Moreover, a maximum of activation energy covers the ranges of the intermetallic phases for all compound forming systems and a minimum of activation energy is located at the eutectic point for all alloys. According to the discussion of the correlation between the activation energy and the phase diagrams, it is deemed that activation energy is related to clusters of unlike atoms and the structure of solid state.

Acknowledgements

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