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Thermodynamic stability of liquid Ag–polyvalent metal alloys

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Abstract

Thermodynamic stability, taking account of the electronic and ionic structures in liquid Ag–polyvalent metal alloys, has been discussed in comparison to other monovalent–polyvalent metal alloys. Liquid Ag–Zn, Ag–Ga, Ag–In and Ag–Sn alloys show some ordered states as seen in their $S_{CC}(0)$, and have different electronic and ionic structures in Ag- and polyvalent metal-rich regions, respectively. $S_{CC}(0)$ of liquid Ag–Pb and Ag–Tl alloys has shown the tendency to phase separation. © 1998 Elsevier Science B.V.

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1. Introduction

Thermodynamic properties of matters are macroscopic quantities although they result from the accumulation of the microscopic behavior of atomic scale range. Thermodynamic properties of simple liquid metals have been investigated by various theoretical and experimental approaches [1–3]. Structure factor $S(q)$ of liquid metals in the long-wavelength limit, for example, relates to compressibility, which can be obtained from the density-fluctuation theory [1]. In liquid binary alloys, Bhatia and Thornton [4] (B–T) have derived some important relations between the microscopic fluctuations and the thermodynamic quantities. Their relations include partial structure factors in the long-wavelength limit, and are used to quantitatively represent the ordering of liquid alloys.

As an extension of B–T theory, March et al. [5] have derived a relation between the electron density fluctuation in the long-wavelength limit and the thermodynamic data. Tamaki [6] and his co-workers have, furthermore, extended this idea to quantitatively obtain the charge transfers from thermodynamic data. The charge transfer in binary liquid alloys between unlike atoms often shows a strong indication of the stable order or chemical short-range order.

Several liquid noble metal–polyvalent metal alloys, which are the so-called Hume-Rothery alloys in their solid states, have a characteristic behavior with respect to electrical conductivity and magnetic susceptibility [2,7,8]. Hume-Rothery and Raynor [9,10] have classified the structural stability of intermetallic com-

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pounds in terms of the electron-to-atom ratio, *e/a*. According to Mott and Jones [11,12], Hume-Rothery compounds were classified in terms of the electron-to-atom ratio under a nearly free electron model and their stabilities could be retained until the Fermi surface of the conduction electrons contacted the Brillouin zone.

Arai et al. [13] have suggested that alloys of liquid noble metal and polyvalent metal satisfy a rule similar to that satisfied by Hume-Rothery phases in their solid states, in addition to their concentration–concentration fluctuations. It was, therefore, confirmed that the nature of liquid Ag–polyvalent alloys could be explained in terms of the relation between the concentration–concentration fluctuation in the long-wavelength limit $S_{CC}(0)$ and the electronic density of states.

In the present paper, we have investigated the thermodynamic stability of liquid Ag–polyvalent metal alloys in view of microscopic scale such as the potential difference, the atomic size ratio and the electronic state.

2. $S_{CC}(0)$ of liquid Ag–polyvalent metal alloy

In the fluctuation theory of liquid binary alloys, the relations between fluctuations and thermodynamic properties can be demonstrated by considering a grand canonical ensemble [6]. We can obtain the mean square fluctuation of a number of particle $\langle(\Delta N)^2\rangle$, the correlation between the two fluctuations ΔN and $\Delta c\langle(\Delta N\Delta c)\rangle$ and the mean square fluctuation of the concentration $\langle(\Delta c)^2\rangle$, under a given volume as follows

$$\begin{aligned}
\langle(\Delta N)^2\rangle &\equiv \overline{N}\left\{\rho_0 k_B T\chi_T + \overline{N}k_B T\delta^2\left(\frac{\partial^2 G}{\partial c^2}\right)_{p,T,N}\right\}\\
\langle\Delta N\Delta c\rangle &\equiv -\overline{N}k_B T\delta\Big/\left(\frac{\partial^2 G}{\partial c^2}\right)_{p,T,N} \qquad (1)\\
\langle(\Delta c)^2\rangle &\equiv \frac{1}{\overline{N}}\left\{\overline{N}k_B T\Big/\left(\frac{\partial^2 G}{\partial c^2}\right)_{p,T,N}\right\}
\end{aligned}$$

where $\delta = V^{-1}(\partial V/\partial c)_{p,T,N}$, $\overline{N}$ is the averaged number of particles in volume V, ρ_0 the number density, k_B the Boltzmann constant, T the temperature, χ_T the isothermal compressibility, G the Gibbs free energy per particle and c the concentration. The Bhatia–Thornton partial structure factors in the long-wavelength limit are defined as

$$\begin{aligned}
S_{NN}(0) &= \frac{\langle(\Delta N)^2\rangle}{\overline{N}}\\
S_{NC}(0) &= \langle\Delta N\Delta c\rangle \qquad (2)\\
S_{CC}(0) &= \overline{N}\langle(\Delta c)^2\rangle
\end{aligned}$$

And we have

$$\begin{aligned}
S_{CC}(0) &= \overline{N}k_B T\Big/\left(\frac{\partial G^2}{\partial^2 c}\right)_{p,T,N}\\
S_{NC}(0) &= -\delta S_{CC}(0) \qquad (3)\\
S_{NN}(0) &= \frac{\overline{N}}{V}k_B T\chi_T + \delta^2 S_{CC}(0)
\end{aligned}$$

$S_{CC}(0)$ is easily converted to the excess stability of alloys, *ES*, defined by Darken [14] as follows:

$$\frac{RT}{S_{CC}(0)} = ES + \frac{RT}{c(1-c)} \qquad (4)$$

where R is the gas constant. So far, the $S_{CC}(0)$ defined by Bhatia and Thornton is a good clue to investigate the ordered state in the atomic configuration, because that of an ideal mixture is exhibited by $c(1-c)$, while $S_{CC}(0)$ of an alloy with an ordered state tends to zero or shows the minimum values at the concentration of compound formation. The curve of $S_{CC}(0)$ [6] derived from the EMF data for E is expressed in terms of the following relation for liquid Ag–polyvalent metal alloys,

$$S_{CC}(0) = -\frac{RT}{zF}\frac{1-c}{(\partial E/\partial c)_{p,T}} \qquad (5)$$

where z is the valence number of Ag, c the atomic fraction of Ag in the alloy and F the Faraday constant.

Figs. 1 and 2 show the $S_{CC}(0)$'s of several Ag–polyvalent metal alloys in their liquid states[2]. As shown in Figs. 1 and 2, liquid alloys such as Ag–Zn, Ag–Ga, Ag–In and Ag–Sn have two minima in $S_{CC}(0)$ which indicate the existence of two short-range

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[2] $S_{CC}(0)$ has been calculated from the results of EMF measurements [15,16]. The calculated results are very sensitive to EMF data which have been measured at different temperatures. In liquid alloys, ordered states are strongly dependent on temperature. Therefore, the magnitude of the ordered state is not discussed at the present stage.

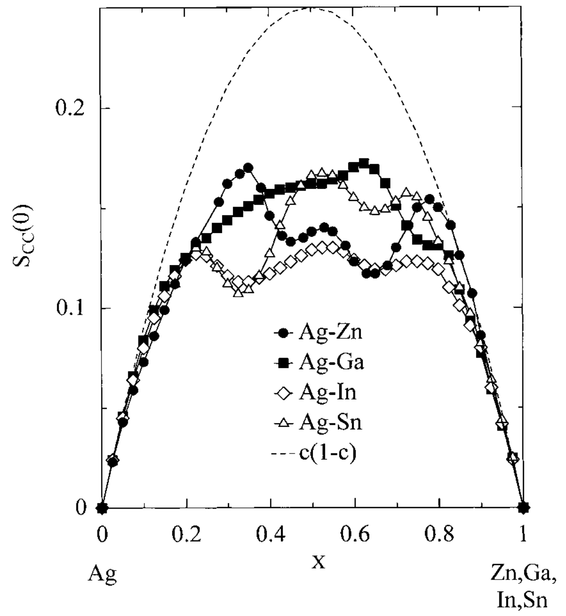

Fig. 1. The $S_{CC}(0)$ of liquid Ag–Zn, Ag–Ga, Ag–In and Ag–Sn. The dotted line shows the $S_{CC}(0)=c(1-c)$ of ideal mixture. X represents the atomic fraction of polyvalent metal in the alloy.

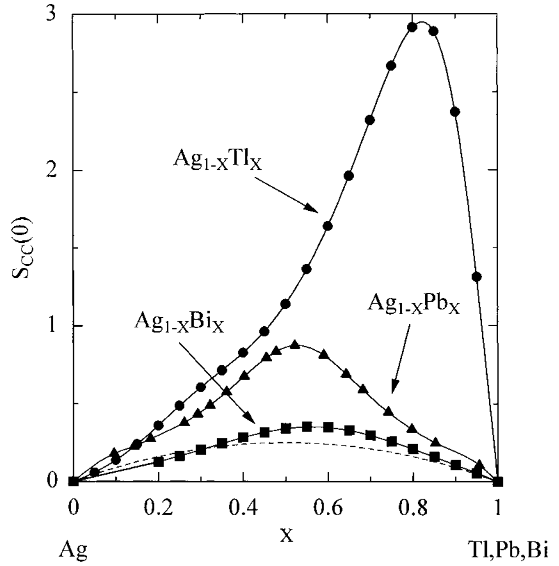

Fig. 2. The $S_{CC}(0)$ of liquid Ag–Tl, Ag–Pb and Ag–Bi.

ordered states. On the other hand, $S_{CC}(0)$'s of liquid Ag–Tl, Ag–Pb and Ag–Bi alloys do not show any indication of short-range ordering.

Hume-Rothery and Raynor [9,10] have indicated that alloys form a stable phase when the size ratio for the constituents is less than ca. 1.4. This is the reason why noble metal–polyvalent metal alloys have a restriction in their solubilities in the solid state. The ratios of the radii for pure liquid polyvalent metals to that for pure liquid Ag(Cu, Au) are shown in Table 1. These radii are estimated from the half value of the first peak position of the pair distribution function $g(r)$ [17]. In Ag–heavy metal alloys, such with Tl, Pb and Bi, the ratio has a relatively large value near 1.4. Therefore, these alloys do not have any ordered states. However Ag–In and Ag–Sn with a large value indicate some ordering.

Table 1
The atomic-size ratio and the potential difference of liquid Cu–, Ag– and Au–polyvalent alloys

Alloy	Atomic size ratio	Potential difference in 10^{-2} eV
Cu–Zn	1.04	6.66
Cu–Ga	1.10	5.96
Cu–Ge	1.10	—
Cu–Cd	1.21	—
Cu–In	1.26	5.45
Cu–Sn	1.26	5.28
Cu–Hg	1.19	7.52
Cu–Tl	1.28	5.40
Cu–Pb	1.30	3.48
Cu–Bi	1.32	5.22
Ag–Zn	0.93	5.73
Ag–Ga	0.98	5.03
Ag–Ge	0.98	—
Ag–Cd	1.08	—
Ag–In	1.13	4.52
Ag–Sn	1.13	4.35
Ag–Hg	1.07	6.59
Ag–Tl	1.14	4.47
Ag–Pb	1.16	2.55
Ag–Bi	1.18	4.29
Au–Zn	0.94	8.33
Au–Ga	0.99	7.63
Au–Ge	0.99	—
Au–Cd	1.09	—
Au–In	1.13	7.12
Au–Sn	1.13	6.95
Au–Hg	1.07	9.19
Au–Tl	1.15	7.07
Au–Pb	1.16	5.15
Au–Bi	1.18	6.89

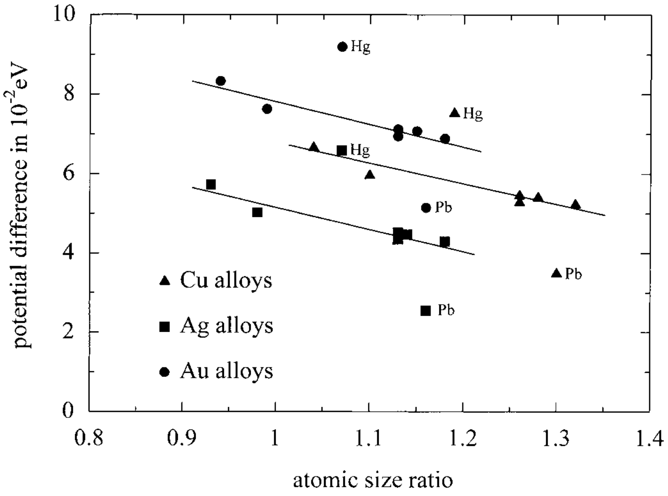

Fig. 3. The relation between the atomic-size ratio and the potential difference of liquid Cu–, Ag– and Au–polyvalent metal alloys.

Hume-Rothery has found another condition for the formation of stable phases, such as when atoms have a large difference in their electronegativities. However, the electronegativity is not an absolute, but a relative property. In view of the microscopic scale, the difference of electronegativity corresponds to that of atomic potential. If there is some potential difference between atoms, the electron transfer appears to truncate the potential difference. Waseda and Suzuki [18] have calculated pair potentials of several pure metals from experimental results by the Born–Green approximation. The potential differences estimated from their calculations are tabulated in Table 1. As shown in this table, there is no distinct difference between the values of ordered and non-ordered states. In Fig. 3, the atomic-size ratio is plotted vs. the potential difference for liquid Cu–, Ag– and Au–polyvalent metal alloys. These alloys have a linear relation except for Cu–Hg, Ag–Hg and Au–Hg and Cu–Pb, Ag–Pb and Au-Pb alloys. At the present stage, it is not understood why noble metal–Hg and noble metal–Pb alloys deviate from this relation. However, this linear relation between the atomic-size ratio and the potential difference indicates that an alloy with a small atomic-size ratio gives rise to a large amount of charge transfer. A large charge transfer causes partial ionic bonds or compound formation at certain concentrations. As shown in this figure, it is possible that the stable state due to the ionic bonding occurs in the systems with a smaller radius of polyvalent metal compared to that of noble metal. The charge transfer yielded by this difference gives a considerable change in the density of states. Therefore, it is necessary to obtain further information on the electronic states of the ordered stable state.

Magnetic susceptibility measurement gives us some information of the electronic states of liquid alloys. The total magnetic susceptibilities χ_{obs} of liquid metals can be generally given as the sum of the diamagnetic susceptibility χ_{ion}, due to the ions, and the paramagnetic susceptibility χ_{ele}, due to the conduction electrons.

$$\chi_{\mathrm{obs}} = \chi_{\mathrm{ele}} + \chi_{\mathrm{ion}} \qquad (6)$$

χ_{ele} is closely related to the density of states at the Fermi energy [3].

The alloys in Fig. 1 show a kind of short-range ordering for both, Ag and polyvalent metal-rich side. In the first place, we consider the stability of the ordered state in Ag-rich side. Arai et al. [13] have investigated the electronic states of liquid Ag–Zn, Ag–Ga, Ag–In and Ag–Sn alloys by magnetic susceptibility measurement. From the concentration dependence of the density of states at the Fermi energy, it is found that there is a pseudogap in the density of states for these alloys. These results suggest that the shape of the density of states for pure liquid Ag remains like that of the rigid-band model, even if some amount of

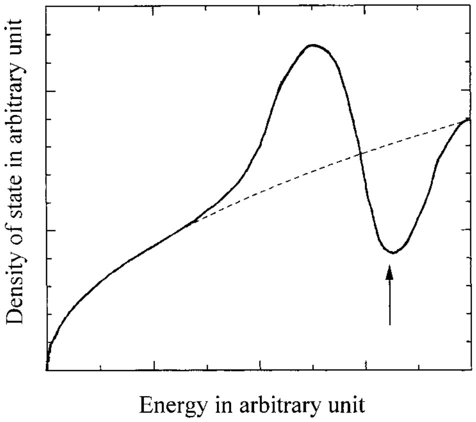

Fig. 4. A schematic diagram of the density of states with a pseudogap. An arrow indicates the pseudogap.

polyvalent metal is added into liquid Ag metal. A schematic diagram of the density of states with a pseudogap is shown in Fig. 4. This figure illustrates the density of states for pure liquid Ag [19]. In the case of liquid Ag–In, the Fermi energy reaches the pseudogap at 30% In concentration. The local structure of liquid Ag–In changes at this concentration [20]. Hence, the density of states for liquid Ag–polyvalent alloys having an ordered state is expected to change at a concentration in Ag-rich region, where the Fermi energy approaches the pseudogap. This mechanism, leading to the restriction in the solubility of polyvalent metals, corresponds to the Hume-Rothery rule in the solid state.

For liquid Ag–In, the neighboring atoms are mainly like the ones on the Ag-rich region in contrast to the case of In-rich side in which unlike atoms are nearest neighbors [20]. The charge transfer easily occurs among the neighboring unlike atoms, and gives a stable state. This stable state remains until 30% In in the In-rich region is reached.

As shown in Fig. 2, the liquid Ag–Bi system exhibits an almost ideal behavior, but liquid Ag–Tl and Ag–Pb have a considerable tendency of phase separation with increasing concentration of polyvalent metals. The density of states in pure liquid Ag changes by the addition of small amounts of Bi and Pb [13]. The valence electrons in such heavy atoms have a relativistic effect and, therefore, the alloying behavior with Ag metal is somewhat different to that of light metals such as In and Sn.

3. Comparison of other liquid monovalent–polyvalent metal alloys

It is worthwhile to study the $S_{CC}(0)$'s of various liquid noble metal–polyvalent metal alloys in interpreting the short-range order. Fig. 5 displays $S_{CC}(0)$'s of liquid Cu–Pb, Ag–Pb and Au–Pb alloys estimated from thermodynamic data [12,21]. Liquid Cu–Pb shows a distinct phase separation, while liquid Au–Pb has some short-range order. In the case of liquid noble metal–Zn and –Sn alloys, the concentrations and the magnitudes of the short-range order are quite different as shown in Figs. 6 and 7.

Au metal in the liquid state is characterized by ordering with almost all polyvalent metals due to a strong attractive interaction between Au and polyvalent metals. Terzieff et al. [22] have measured the magnetic susceptibility of liquid Au–In in which the observed $d\chi/dT$ shows negative values in the Au-rich region. This result means that the density of states of liquid Au behaves like that of liquid Ag. On the other hand, the magnetic susceptibility data and $S_{CC}(0)$ of liquid Cu–Sn [8] indicate the existence of some short-range order in the Cu-rich region. But $d\chi/dT$ does not show any negative values. It implies that the change by alloying differs for the density of states at Fermi

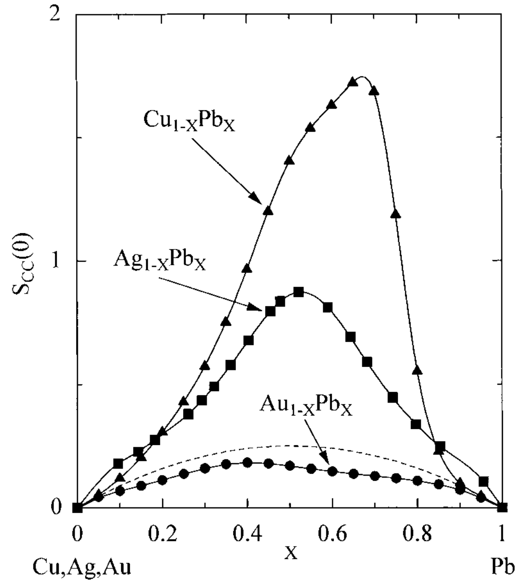

Fig. 5. The $S_{CC}(0)$s of liquid Cu–Pb, Ag–Pb and Au–Pb alloys.

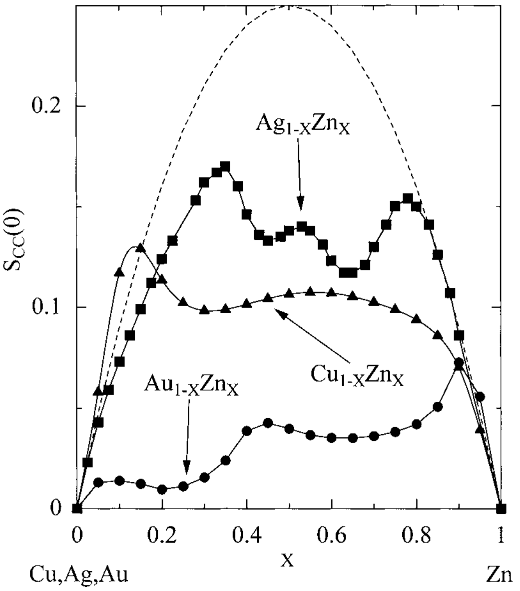

Fig. 6. The $S_{CC}(0)$s of liquid Cu–Zn, Ag–Zn and Au–Zn alloys.

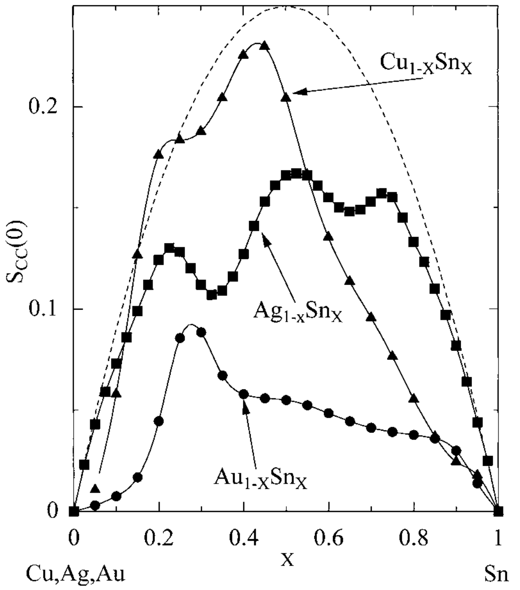

Fig. 7. The $S_{CC}(0)$s of liquid Cu–Sn, Ag–Sn and Au–Sn alloys.

energy of liquid Cu from those of liquid Ag and Au. This difference may be caused by a difference in the *s–d* hybridization. This is expected to give the short-range order at different concentrations as seen in Figs. 6 and 7.

Tamaki [6] and his co-workers have developed an interesting method to obtain the charge transfer of liquid Na–polyvalent metal alloys using Thomas–Fermi screening length and partial structure factors in the long-wavelength limit. He discussed the electron distribution and ionic local order of liquid Na–Sn and Na–Pb as typical examples. The partial structure factors in the long-wavelength limit of these alloys have been reported, based on the measured data of $S_{CC}(0)$, the density and compressibility data. The estimated charge transfer and local ordering in these alloys have also reported and showed some characteristic features. In liquid Na–Sn, the charge is transferred from Na to Sn atoms for all composition ranges. In the dilute limit of the Pb concentration, the charge is also transferred from Na to Pb atoms, but from Pb to Na atoms in Pb-rich region. On the Na-rich side, both Na–Sn and Na–Pb systems have the same behavior for the charge transfer. Because the potential minimum of liquid Sn or Pb is deeper than that of liquid Na [18,23], the short-range order in liquid Na–polyvalent metal alloys consists in ionic bonding due to the unlike ion-pair interaction. On the contrary, the potential minimum of liquid noble metals is deeper than almost all liquid polyvalent metals [18]. Therefore, the direction of the electron transfer in liquid Na–polyvalent metals is different from that in noble metal–polyvalent metals alloys.

4. Concluding remarks

The rigid electronic density of state of Ag in liquid Ag–polyvalent metal alloys has a large contribution to the stability or the occurrence of some ordering on the Ag-rich side. This point corresponds to the Hume-Rothery rule in the solid state which expresses the restriction in the solubility of polyvalent metals. The short-range order in polyvalent metal-rich region consists of the local structure of the unlike ion pair neighbors in contrast to the case in Ag-rich region.

In the case of liquid Ag–Bi and Ag–Pb, the electronic state of Ag changes under the influence of addition of polyvalent impurities. The strength of the ordering in Cu–, Ag– and Au–Zn(Sn, In) is very different. Each noble metal has a different interaction with the polyvalent metals because of the different *s–d* hybridization.

In Na–polyvalent metal alloys, the interaction of the unlike ion pair gives rise to the short-range order. In this case, the charge is transferred from Na to polyvalent metal atoms. This point is opposite to the case of liquid Ag–polyvalent metal alloys.

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