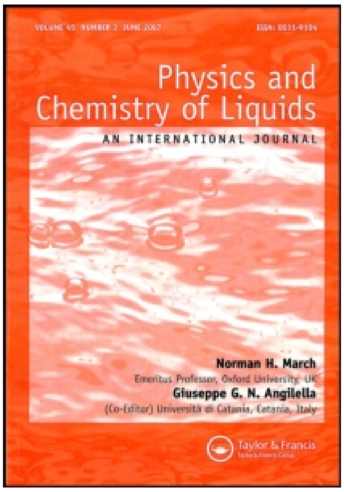

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Effects of compound formation on liquid structure in Cu-Sn melts as a function of temperature

Fang-Qiu Zu[a]; Yun Xi[a]; Rong-Rong Shen[a]; Xian-Fen Li[a]; Yan Zhang[a]; Zhi-Hao Chen[a]
[a] College of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, People's Republic of China

To cite this Article Zu, Fang-Qiu , Xi, Yun , Shen, Rong-Rong , Li, Xian-Fen , Zhang, Yan and Chen, Zhi-Hao(2006) 'Effects of compound formation on liquid structure in Cu-Sn melts as a function of temperature', Physics and Chemistry of Liquids, 44: 5, 543 — 550

To link to this Article: DOI: 10.1080/00319100600757458

URL: http://dx.doi.org/10.1080/00319100600757458

Physics and Chemistry of Liquids
Vol. 44, No. 5, October 2006, 543–550

Effects of compound formation on liquid structure in Cu–Sn melts as a function of temperature

FANG-QIU ZU*, YUN XI, RONG-RONG SHEN, XIAN-FEN LI, YAN ZHANG and ZHI-HAO CHEN

College of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, People's Republic of China

(*Received 5 April 2006; in final form 15 April 2006*)

Through the theoretical study of concentration-dependent thermodynamic and microscopic functions in some reports, chemical short-range orders (CSROs) have been proved to persist in Cu–Sn melts. However, it is not clear insofar in which concentration and temperature ranges do these CSROs exist in melts, and how they change with temperature. This study investigates the liquid structure with temperature of Cu–Sn alloys by electrical resistivity and DSC. The results show that some CSROs inheriting solid structures bring abnormal transition of resistivity at a temperature hundreds of degrees above the liquidus for all the studied Cu–Sn melt. Especially for the melts with 50 to 70% Cu, there also exist 'associates' of unlike atoms, which reduce continuously with increasing temperature after melting and result in negative temperature coefficients of resistivities (TCRs). In the figures of DSC-temperature, some endothermic peaks consistent with the temperatures of resistivity transitions verify these abnormal transitions of liquid structure.

Keywords: Copper–tin melts; Electrical resistivity; Chemical short-range orders

PACS: 61.20.Gy; 61.25.Mv; 61.46.+w; 66.30.Qa

1. Introduction

From recent studies [1–20], topological and chemical short-range orders (TSROs and CSROs, respectively) corresponding to the crystal structures have been proved to persist in some single- and multi-component liquids as a function of composition. Meanwhile, it is well known that noble metals could form various compounds on alloying with polyvalent metals in solid state, and there also exist strong correlations between the atomic and electronic structures in liquid melts as in the case of crystalline solids [17,21]. Copper–tin (Cu–Sn) is such a compound-forming alloy, the various compounds being labeled as η (Cu_6Sn_5), β (Cu_5Sn), γ (Cu_3Sn), δ ($Cu_{31}Sn_8$) etc. over the whole composition range in solid state. Through the study of concentration-dependent thermodynamic and microscopic functions, [20] shows that the CSROs exist in Cu–Sn melts.

---

*Corresponding author. Tel.: +86-551-2905057. Email: fangqiuzu@hotmail.com

Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online
DOI: 10.1080/00319100600757458

However, thermodynamic methods are less quantitative in investigating liquid structures and the studies of CSROs with temperature have not been reported earlier, to our knowledge.

It is known that some peculiar variations of the physical properties of liquid alloys with composition are basically caused by changes in their electronic and/or atomic structures like that in the solids [17]. Electrical resistivity is such a structure-sensitive property, and it is of interest to study the electronic transport properties that provide additional information about liquid structures, which cannot be provided by ordinary thermodynamic methods [22]. This article deals with the experimental investigation of the temperature dependence of electrical resistivity for Cu–Sn alloys with composition of Cu ranging from 20 to 70 wt%. Some abnormal resistivity turning points appear on the resistivity–temperature curves. Two kinds of CSROs are suggested to exist in Cu–Sn melts around the concentration of Cu from 60 to 80 wt% while only one kind of CSRO exists in melts with Cu concentration C_{Cu} less than 60 wt%. One CSRO with crystal structure results in the significant transition of resistivity at a temperature hundreds of degrees above the liquidus for all studied Cu–Sn melts, while another, which exists only in the melts with 50–70% Cu as associates of unlike atoms, reduces continuously with increasing temperature after melting and results in negative temperature coefficients of resistivities (TCRs) for 50–70 wt% Cu–Sn melts. In Differential Scanning Calorimeters (DSC) experiments, the endothermic peaks confirm these abnormal transitions of Cu–Sn melts.

2. Experimental

In this article, six compositions of Cu–Sn liquid alloys (for 10, 20, 40, 50, and 60 wt% of Cu) were subjected to experiment. All the Cu–Sn samples were prepared with pure tin (99.9%) and pure Cu (99.9%). After melting for 40 min at the temperature 100°C above liquidus, the melts were poured into quartz cells and then cooled to the temperature below liquidus for the following experiments. The electrical resistivities were measured by the DC four-probe method. The details of the measuring method have been described elsewhere [23]. For each liquid sample, we measured the temperature dependence of resistivities (TDRs) by heating and by cooling both at the rate of $5^{\circ}\mathrm{C\,min^{-1}}$. All the experiments have been repeated and the results are consistent well with each other. The DSC studies are performed for 40 and 70 wt% Cu–Sn with NETZSCH DSC-404.

3. Results and discussion

In recent research, the unlike atoms clustering with the crystal structures have been found in compound-forming melts. Moreover, for the eutectic $Cu_{37}Sb_{63}$ alloy, segregation into clusters corresponding to an association of Sb-atoms and association of unlike atoms was found [24]. However, most of these studies focused on the concentration dependence of the structure of melts, and it is not clear at what temperature ranges they exist and how the structure of the clusters are related to that of the solid intermetallic compounds.

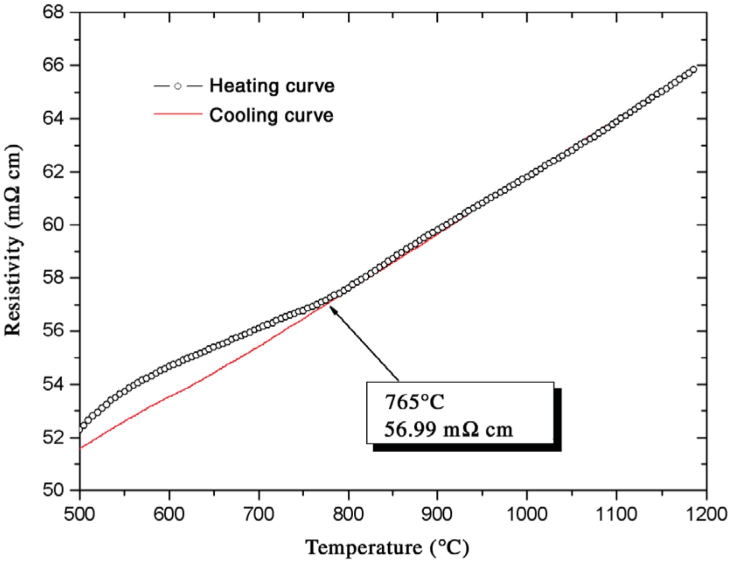

Figure 1. Temperature dependence of the electrical resistivity of 10 wt% Cu–Sn.

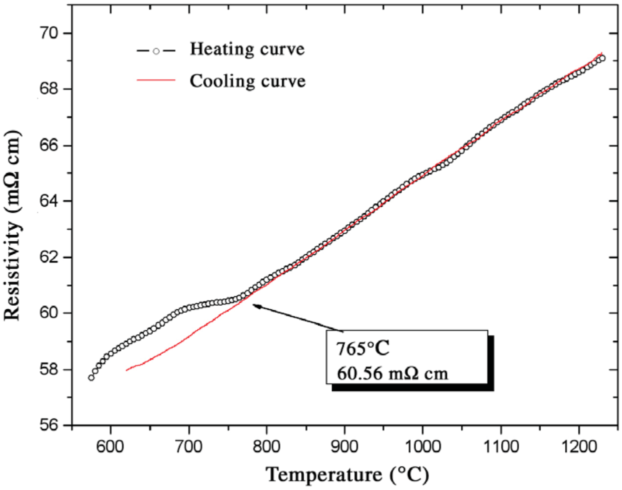

Figure 2. Temperature dependence of the electrical resistivity of 20 wt% Cu–Sn.

In this study for Cu–Sn melts, both the temperature and concentration dependence of resistivity show some interesting phenomena. Figures 1–5 give the TDRs by heating and cooling of 10, 20, 40, 50, and 60 wt% Cu–Sn, respectively. Figure 6 shows the DSC of 40 wt% Cu–Sn. In the TDRs and DSCs, some abnormal turning temperatures have been found. For convenient description, we can mark anomalous turning points on the heating curves, which are shown in the corresponding figures. On the heating curves of 10 and 20 wt% Cu–Sn, the resistivities increase linearly within the measuring error

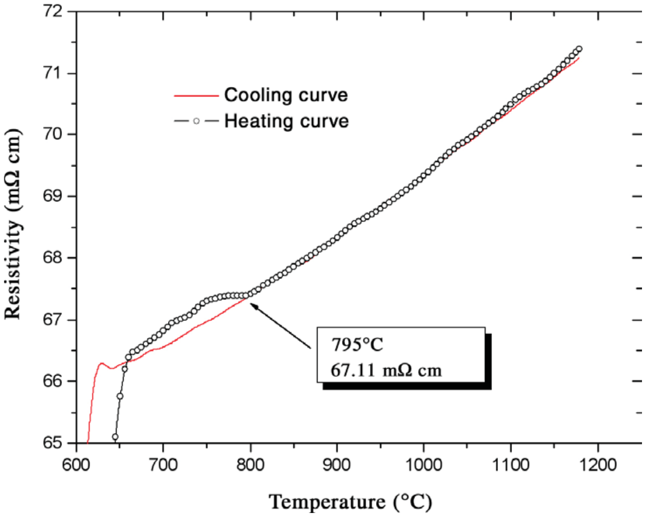

Figure 3. Temperature dependence of the electrical resistivity of 40 wt% Cu–Sn.

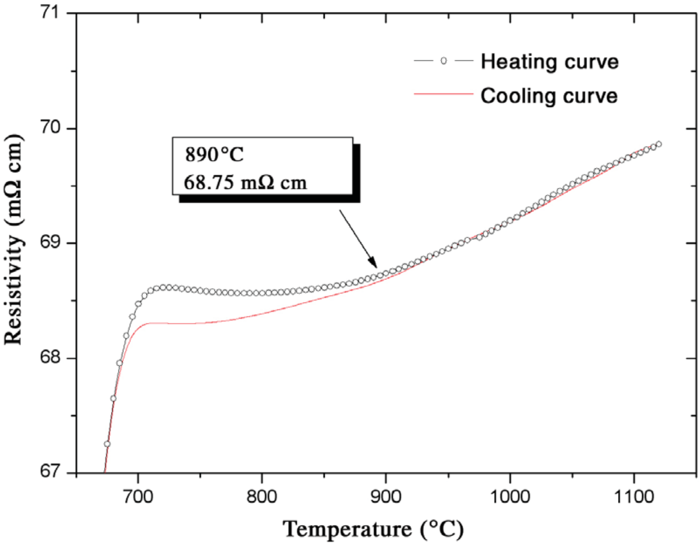

Figure 4. Temperature dependence of the electrical resistivity of 50 wt% Cu–Sn.

at first and then begin to drop rapidly. After the turning temperature, the resistivities of the melts increase linearly again with temperature in the following measurement. However, on the cooling curves of 10 and 20 wt% Cu–Sn, the resistivities decrease linearly with decreasing temperature and no turning point is found any more above liquidus. For 40 wt% Cu–Sn, the pattern of resistivity is similar to that of 10 wt% Cu–Sn while the curves become slightly bended. However, for the resistivities of 50 and 60 wt% Cu–Sn samples, the resistivity–temperature curves are not linear anymore

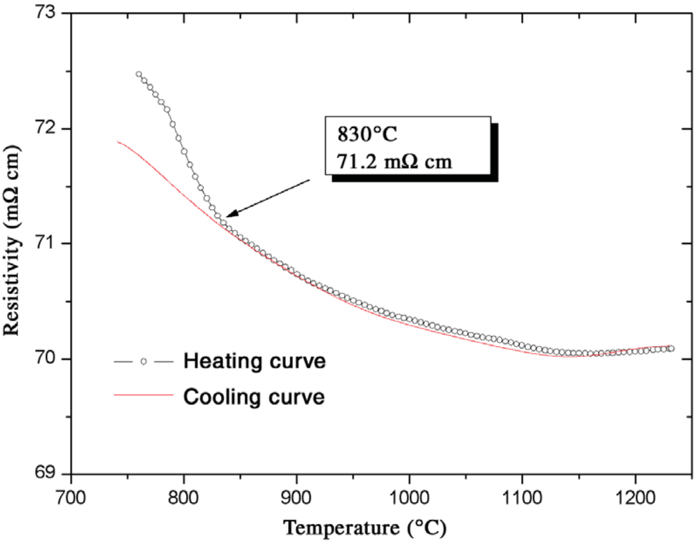

Figure 5. Temperature dependence of the electrical resistivity of 60 wt% Cu–Sn.

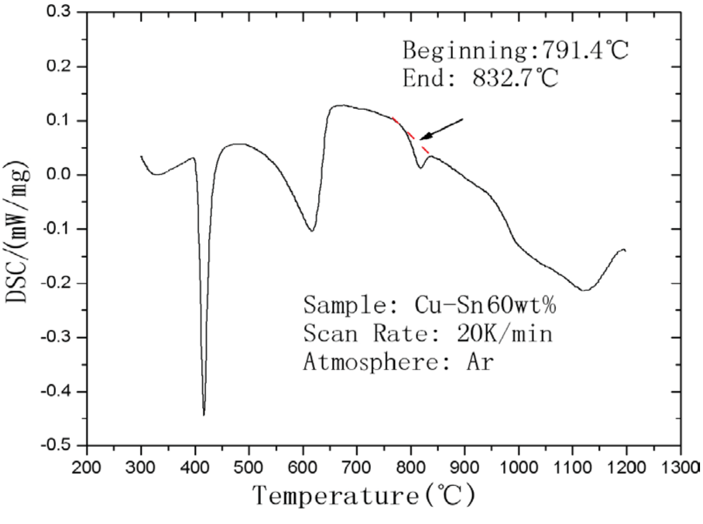

Figure 6. DSC curve of 40 wt% Cu–Sn.

and the TCR of each liquid increases from a negative value to a positive one gradually (table 1) and the temperature at which the TCR equals to zero increases with the increasing Cu concentration. Above the turning point, the heating and cooling curves tend to be consistent for all studied melts. In [25], the resistivity of 90 wt% Cu–Sn by cooling is measured and it is also a constant, but the TDR by heating is not mentioned.

Cu–Sn system is a typical binary alloy between an IB group metal with a polyvalent metal, which may form various compounds in solid state. And the corresponding liquid alloys are characterized by specific physical properties around the composition where

Table 1. Anomalous turning temperatures by heating and TCRs by cooling of Cu–Sn alloys.

Composition (wt% Cu–Sn)	Anomalous turning temperature (°C)	$d\rho/dT$ ($\times10^{-3}$ mΩ cm °C^{-1})
10	765	21.3
20	765	19.2
40	795	10.1
50	890	A variable from 0 to 9.9
60	830	A variable from −19.5 to 4.6
90	–	A small positive constant [24]

electron compounds are found in the solid state [26–28]. For compound-forming alloys, there are some CSROs remaining in the melts above the liquidus, and the compound-forming liquid alloys are known to influence the resistivity and TCR markedly [23]. According to the calculation results of quantum mechanics, Cu and Sn atoms have strong interaction between each other. Then it can be concluded that the distribution of Cu and Sn atoms in molten metals is not microscopically random and that the compound structure in solid metals remains in the liquids at low degrees of superheating [18]. Furthermore, through the study of concentration-dependent thermodynamic and microscopic functions in [20], Prasad *et al.* indicate that the CSROs exist in Cu–Sn melt and the maximum order occurs at the concentration of $C_{\mathrm{Cu}} = 0.75$. By thermodynamics calculation, [29] suggests that different kinds of compound structures could coexist in Cu–Sn melts.

From the resistivity–temperature curves and the studies mentioned above, it is reasonable to consider that the CSROs maintained in melts after the melting process and they will have effects on the resistivity and TCR in the liquid alloys. For Cu–Sn melts, in this study, it is assumed that there are two kinds of CSROs with strong bonds exiting in Cu–Sn melts, which are called C′ and C″.

After melting, there are some CSROs (called C′) with compound structure of solid remaining in Cu–Sn melts, which makes the resistivities in heating procedure greater than that in the cooling procedure. With increasing temperature, these bonds of C′ are broken at hundreds of degrees above the liquidus. The breaking of such CSROs releases free electrons and the resistivities of these melts begin to drop. In figure 6, the endothermic peak above the liquidus has been shown on the DSC curves. Considering the heating rate, the peak temperatures are consistent with the abnormal turning temperatures on the resistivity curve. Such CSROs do not come into being anymore in the cooling procedures.

Moreover, in the compound-forming composition region of Cu–Sn melt (C_{Cu} of 50–70 wt%), besides C′ with crystal structure, there is another kind of 'associations' (C″) $\mathrm{Cu}_m\mathrm{Sn}_n$, which comes into being from the strong interaction between Cu and Sn atoms by dynamical equilibrium as $m\mathrm{Cu} + n\mathrm{Sn} \leftrightarrow \mathrm{Cu}_m\mathrm{Sn}_n$. $\mathrm{Cu}_m\mathrm{Sn}_n$ are often called complexes or associates. These CSROs (C″) have no effects on above abnormal turning points, but they reduce continuously over a wide temperature range after melting. As shown in figures 4, 5 and table 1, the TCRs of 50 and 60 wt% Cu–Sn change from negative values to positive ones with temperature while those of 10, 20, 40 and 90 wt% Cu–Sn [25] are constants above the liquidus. The negative values of TCRs have been reported in numerous papers for compound-forming liquid alloys such as references [16,22,19,30].

In the cooling procedure for Cu–Sn alloys of different concentration, such CSROs of C′ do not come into being anymore and there are no abnormal turning points in the cooling curves. However, the concentration of CSROs of C″ is a function of temperature and it affects TCRs according to following equations [16]:

$$\frac{\mathrm{d}\rho}{\mathrm{d}T} = \frac{\mathrm{d}\rho^0}{\mathrm{d}T} + \rho_\mathrm{a}\frac{\mathrm{d}s}{\mathrm{d}T} \tag{1}$$

and,

$$\mathrm{d}s/\mathrm{d}T = -T_\mathrm{m}T^{-2}s(T) < 0 \tag{2}$$

where ρ^0 is the total resistivity of the liquid alloy; ρ_a is the resistivity of the 'associate', and s is its concentration. Therefore, the TCRs of the melts can be positive, zero, or negative depending on the concentration of associates and the temperature during both the heating and cooling procedures.

4. Conclusions

The present work has studied the TDR and DSC for Cu–Sn alloys and the experimental and theoretical results show that:

(1) Through the investigations of the temperature dependence of electrical resistivity for Cu–Sn alloys with composition of Cu ranging from 10 to 60 wt%, some abnormal resistivity turning points appear on resistivity–temperature curves. And the endothermic peak on DSC-temperature curve, which is consistent with the temperature of resistivity transition, verifies the abnormal transition with temperature of liquid structure.

(2) The resistivities show evident variations at a temperature of hundreds of degrees above liquidus for all Cu–Sn melts by heating, which implies that, the CSROs (C′) with crystal structures are broken abruptly with increasing temperature. These CSROs (C′) do not come into being anymore during the cooling procedure.

(3) Besides the CSROs (C′), some associates (C″) persist in the melts by dynamical equilibrium with 50–60 wt% Cu and they reduce or increase continuously with increasing or decreasing temperature in the melts, which results in negative, zero, or positive TCRs of 50–60 wt% Cu–Sn melts. For 10–40 wt% Cu–Sn and 90 wt% Cu–Sn, very little C″ exist in the melts and the TCRs are positive constants except for that at the abnormal turning points.

Acknowledgments

This work has been supported by the National Natural Science Foundation of China Grant No. 50371024, by the key project of Chinese Ministry of Education No. 104106, and by Natural Science Foundation of Anhui Province No. 03046202.

References

[1] Q. Wang, K.Q. Lu, Y.X. Li. *Acta Phys. Sin.*, **50**, 1355 (2001).
[2] Q. Wang, K.Q. Lu, Y.X. Li. *Chin. Sci. Bull.*, **46**, 990 (2001).
[3] Y.R. Wang, K.Q. Lu, C.X. Li. *Phys. Rev. Lett.*, **79**, 3664 (1997).
[4] Y. Kawakita, S. Takeda, M. Inui, S. Hosokawa, K. Maruyama. *J. Non-Cryst. Solids*, **312–314**, 366 (2002).
[5] H. Richter, G. Breitling. *Z. Metallkd.*, **61**, 628 (1970).
[6] A.H. Narten. *J. Chem. Phys.*, **56**, 1185 (1972).
[7] Y. Kita, *et al. J. Phys.: Condens. Matter*, **6**, 811 (1994).
[8] D.R. Nelson. *Phys. Rev. B*, **28**, 5515 (1983).
[9] O.M. Magnussen, *et al. Phys. Rev. Lett.*, **74**, 4444–4447 (1995).
[10] F. Spaepen. *Nature*, **408**, 781 (2000).
[11] E.J. Enderby. *J. Non-Cryst. Solids*, **31**, 1 (1978).
[12] E. Buhler, P. Lanparter, S. Steeb. *Z. Naturforsch. A*, **42**, 507 (1987).
[13] X.F. Bian. *Chin. Sci. Bull.*, **41**, 1239 (1996).
[14] Jin Zhunzhi, *et al.*, J. Wuhan Univ. (Natural Science Edition), Vol. 41, pp. 337–340 (1995).
[15] I. Kaban, Th. Halm, W. Hoyer. *J. Non-Cryst. Solids*, **288**, 96 (2001).
[16] M.I. Ivanov, V.V. Berezutski. *J. Alloys Comp.*, **375**, 58 (2004).
[17] I. Kaban, W. Hoyer. *J. Non-Cryst. Solids*, **312–314**, 41 (2002).
[18] B.C. Anusionwu. *Physica B*, **311**, 272 (2002).
[19] L.C. Prasad, A. Mikula. *J. Alloys Comp.*, **299**, 175 (2000).
[20] L.C. Prasad, R.N. Singh, V.N. Singh, S.K. Chatterjee. *Physica B*, **215**, 225 (1995).
[21] R. Gampp, F. Baumann, H.-G. Boyen, *et al. J. Non-Cryst. Solids*, **236**, 156 (1993).
[22] V.V. Berezutski, M.I. Ivanov. *J. Alloys Comp.*, **282**, 1 (1999).
[23] Y. Xi, F.Q. Zu, X.F. Li, *et al. Phys. Lett. A*, **329**, 221 (2004).
[24] Th. Halm, H. Neumann, W. Hoyer. *Z. Naturforsch.*, **49A**, 530 (1994).
[25] B.J. Monaghan. *Inter. J. Thermophys.*, **20**(2), 677–690 (1999).
[26] S. Takeuchi, O. Uemura, S. Ikeda. *Sci. Rep. Res. Inst. Tohoku Univ. A*, **25**, 41 (1974).
[27] O. Kubaschewski, J.A. Catterall. *Thermochemical Data of Alloys*, Pergamon, London (1956).
[28] O. Uemura, T. Satow, T. Yagihashi. *Phys. Chem. Liq.*, **8**, 107 (1978).
[29] Zhang Jian. *Special Steel*, **15**(6), 43 (1994) (In Chinese).
[30] G. Busch, H.-J. Güntherodt. *Solid State Phys.*, **29**, 255 (1974).