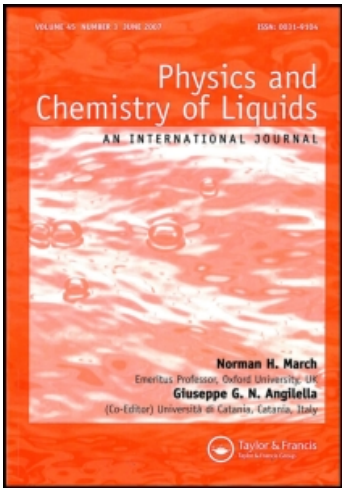

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Influence of Al on the structure of liquid $Cu_{0.70}Si_{0.30}$ eutectic alloy

S. Mudry[a]; I. Shtablavyi[a]
[a] Ivan Franko Lviv National University, Physics of Metals Department, Lviv, Ukraine

To cite this Article Mudry, S. and Shtablavyi, I.(2005) 'Influence of Al on the structure of liquid $Cu_{0.70}Si_{0.30}$ eutectic alloy', Physics and Chemistry of Liquids, 43: 1, 5 — 12
To link to this Article: DOI: 10.1080/00319100420003035O9
URL: http://dx.doi.org/10.1080/00319100420003035O9

Physics and Chemistry of Liquids
Vol. 43, No. 1, February 2005, 5–12

Taylor & Francis
Taylor & Francis Group

Influence of Al on the structure of liquid $Cu_{0.70}Si_{0.30}$ eutectic alloy

S. MUDRY* and I. SHTABLAVYI

Ivan Franko Lviv National University, Physics of Metals Department,
Kyrylo i Mefodiy str. 8, Lviv, 79005, Ukraine

(Received 15 July 2004)

Short-range order of liquid $Cu_{0.7}Si_{0.3}$ eutectic alloy doped with 5, 10, 15 and 20 at.% of Al has been studied by means of X-ray diffraction method. Total structure factors and pair correlation functions are analyzed. It is shown that aluminum atoms form the self-associated structural units which are stable within some temperature range.

Keywords: Liquid alloys; Structure factor; Short-range order

1. Introduction

Eutectic melts are known as liquids whose structure deviates from random atomic distribution and reveals an inhomogeneous short-range order. Most of the liquid eutectic alloys which have been studied by X-ray diffraction method and the measurements of physical properties are characterized by a tendency to form groups of like kinds of atoms [1–5]. Temperature dependencies of structure parameters indicate a breakage of such self-associated units during heating and the existence of a trend to random atomic distribution at heating.

After the production of metallic amorphous solids, the interest in liquid eutectic alloys has grown significantly. As is well-known, some metallic alloys can be easily amorphized by quenching from the liquid state; especially those whose compositions are close to the composition of "deep" eutectic points in equilibrium phase diagrams [6]. In order to improve the properties of amorphous solids obtained in this way, the doping with other elements is commonly used. Dopants are also needed to obtain nanocrystals by annealing of an amorphous phase, which makes it possible to influence the structure formation process. The aim of this influence is to promote the cluster formation and to limit their growth because they are required to be of nanoscale size [7].

*Corresponding author. E-mail: shtihor@rambler.ru

Physics and Chemistry of Liquids
ISSN 0031-9104 print: ISSN 1029-0451 online © 2005 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0031910042000303509

Therefore, it is of considerable importance to study how various dopants influence the structure of an alloy in the liquid state. Hence, the study of structured stability in liquid eutectics on addition of other elements is an interesting problem. Such systems can be considered as ternary materials but many of them are not yet completely established. For the same reason, for many systems there is not much information, from phase diagrams, about the interatomic interactions and their influence on phase formation upon solidification.

In this work, the structure of liquid $Cu_{0.70}Si_{0.30}$ eutectic alloy doped with 5, 10, 15, and 20 at.% of Al has been studied. Each alloy was investigated at three temperatures: $T = 1005$ K, 1055 K and 1155 K, respectively.

We have established earlier [8] that liquid $Cu_{0.70}Si_{0.30}$ eutectic alloy possesses a heterocoordinated structure whose topology is close to that of liquid Cu. It has also been shown that the main maximum position of the liquid eutectic is in agreement with peaks for crystalline η phase (Cu_3Si). Perhaps some part of the Cu-atoms are self-associated, but the fraction in the melt is supposed to be small. The question arises whether the Al-atoms are diluted in the structure of molten $Cu_{0.70}Si_{0.30}$ eutectic alloy.

Equilibrium phase diagrams of Al–Cu and Al–Si systems and the enthalpy of mixing (negative for Al–Cu and positive for Al–Si) [9] allowed us to propose that the Al-atoms attempt to interact with the Cu ones, whereas they try to form self-associated units with Si-atoms. We have no confirmation of the existence of ternary compound in the Al–Cu–Si system. In order to make a clear understanding of the atomic distribution in a mixture of $Cu_{0.70}Si_{0.30}$ and Al, X-ray diffraction studies were carried out.

2. Experimental

$(Cu_{0.70}Si_{0.30})_{1-x} + Al_x$ alloys of different Al content (5, 10, 15 and 20 at.%) were prepared by arc melting in a furnace filled with argon. Samples were placed in the chamber of an X-ray diffractometer filled with pure helium in order to avoid the oxidation during the experiment. Cu K_α radiation, monochromatized by using a LiF crystal, installed in initial beam and Breg–Brentano focusing geometry were employed. The scattered intensities were recorded with different angular steps, which were less within the region of principal peak and larger at the rest of the values of the scattering angles. Experimental results of intensities were corrected for polarization, absorption and incoherent scattering according to [10]. Upon the procedure described in [10], they were normalized and then used for calculation of the structure factors (SF), and the pair correlation function (CF). The main structure parameters obtained from these functions were analyzed.

3. Results and discussion

The experimental SF for alloys of different concentration of Al are shown in figure 1. The main features of the SF observed for a liquid $Cu_{0.70}Si_{0.30}$ eutectic alloy are also revealed for melts with aluminum added. Nevertheless, some changes in their profile can be seen. The concentration dependence of the first peak position ($k_1(x)$) in SF and its height ($S(k_1)$) are shown in figure 2. The addition of Al atoms causes a decrease

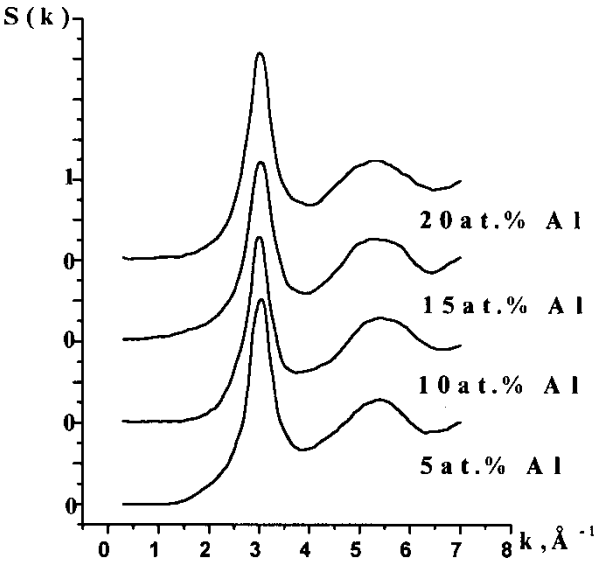

Figure 1. Experimental SF for alloys of different concentration of Al.

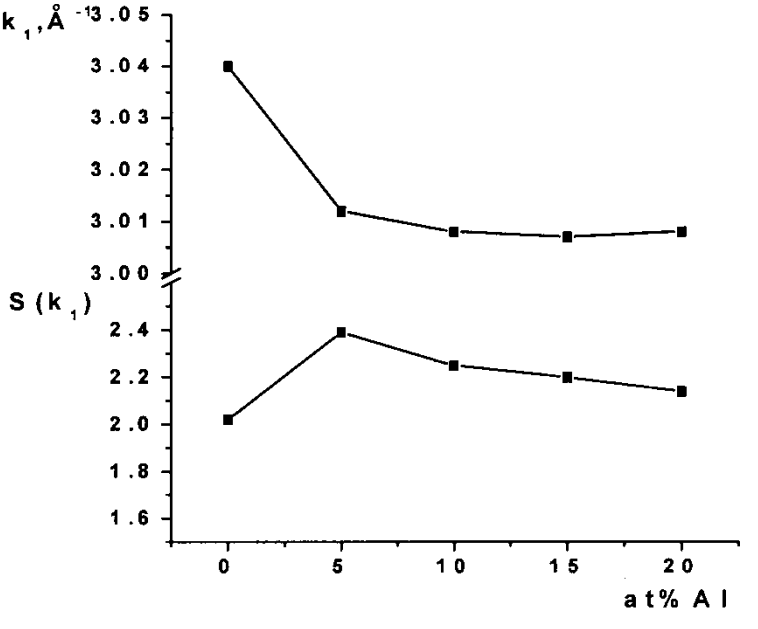

Figure 2. Concentration dependence of first peak position ($k_1(x)$) in SF and its height ($S(k_1)$).

in $k_1(x)$, if the content of Al is not higher than 5 at.% and such a feature occurs at three temperatures. At higher concentration of Al this parameter is almost unchangeable. The second parameter of SF – the principal peak height $S(k_1)$ which depends on the packing density of atomic distribution, shows small changes in its concentration

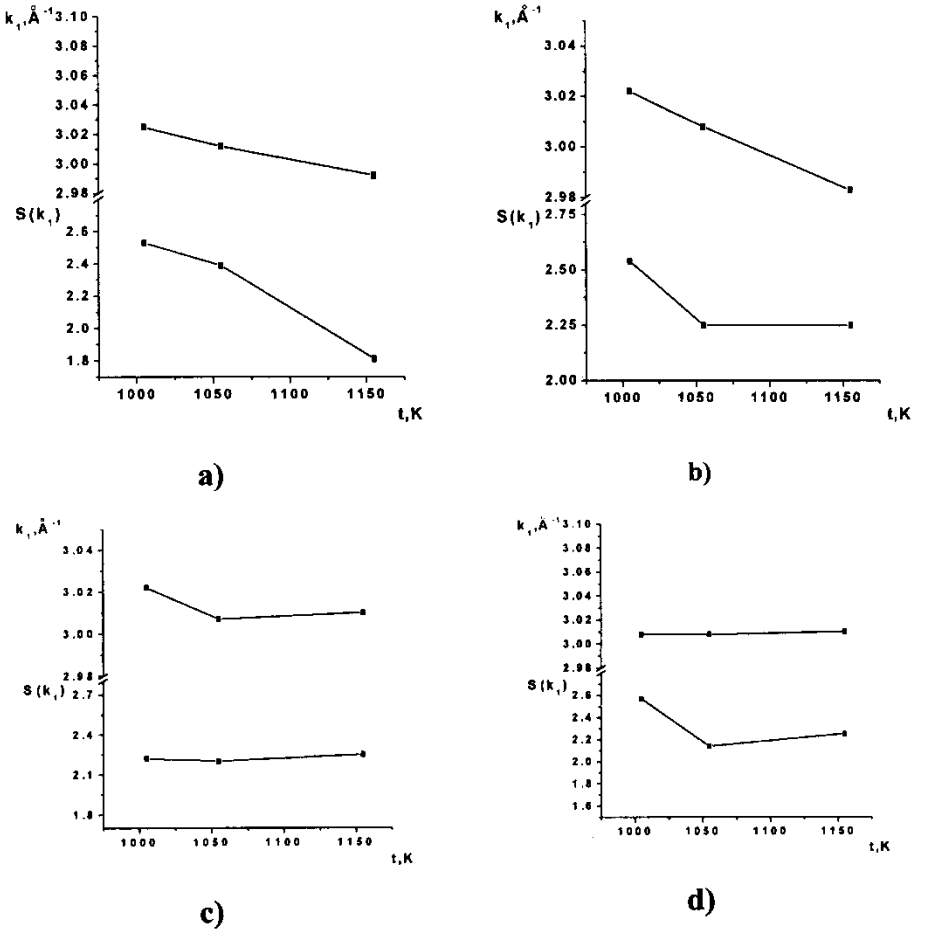

Figure 3. Temperature dependencies of main structure parameters for melts, containing (a) 5 at.% Al, (b) 10 at.% Al, (c) 15 at.% Al, (d) 20 at.% Al.

dependence. These facts allowed us to propose that Al additions do not significantly change the packing density of this eutectic melt. Temperature dependencies of main structure parameters, obtained from SF for melts, containing 5 and 10 at.% Al (figure 3) show a decrease in the first peak position and its height with temperature. Obviously, such a behavior is caused by topological disordering at higher temperatures. A different behavior of these parameters is observed for molten alloys of higher Al content (15 and 20 at.%). The first peak position and its height are almost the same at three different temperatures. We assume that such a behavior can be presented as a sum of two tendencies: the first of them being characterized by a shift of k_1 to low k-values and the second one, its increase with temperature. The former is typical for metallic liquids while the latter can be attributed to the breaking of some structural units and forming of a less "defective" atomic arrangement where the atomic groups are smaller. Therefore the temperature dependence of the main structure parameters for these melts predicts the existence of chemically ordered atomic distributions.

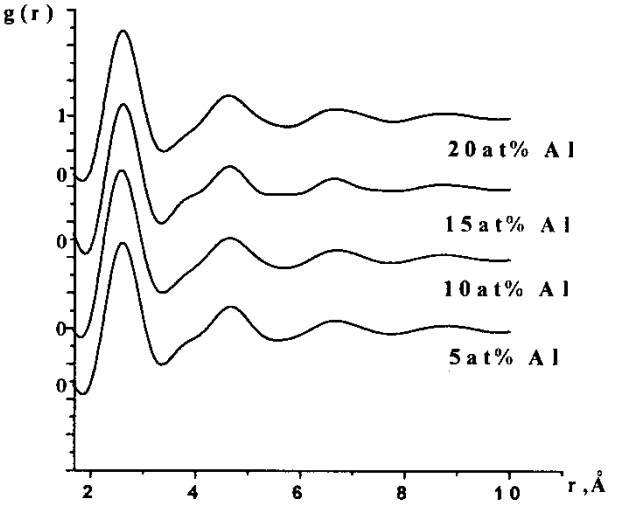

Figure 4. Pair correlation functions for $(Cu_{0.70}Si_{0.30})_{1-x} + Al_x$ alloys of different concentration.

Table 1. Structure parameters obtained from structure factors and pair correlation functions.

at.% Al	K_1, Å^{-1}	$S(K_1)$	r_1, Å	r_2, Å	r_2/r_1	Z
0	3.04	2.02	2.61	4.72	1.81	8.50
5	3.01	2.39	2.66	4.78	1.80	9.70
10	3.01	2.25	2.66	4.84	1.82	9.74
15	3.01	2.20	2.66	4.78	1.80	9.68
20	3.01	2.14	2.66	4.76	1.79	9.32

In order to confirm whether or not this assumption is correct, pair correlation functions have also been analyzed (figure 4). The main features of SF for the eutectic melt are also observed in liquid alloys with Al added. The values of the structure parameters obtained from these functions are listed in table 1, and their concentration dependencies are shown in figure 5. The most important of them, namely the distance to the nearest neighbors r_1 increases upon the first addition of Al atoms (5 at.% Al) and then shows no changes from the content of Al. There are no changes also in the concentration dependence of r_2 values. The square under the first coordination peak Z of atomic density distribution function, determined as $G(r) = 4\pi r^2 \rho_0 g(r)$ (ρ_0 – mean atomic density) shows the increase upon the first addition of Al atoms (5 at.%) and then it decreases to about the initial value. Such a behavior indicates that a small part of the Al atoms, however, is diluted in the molten eutectic alloy. Most of them are aggregated and form an arrangement similar to the structure of liquid Al.

Similar concentration dependence is also observed at a higher temperature (50 K above previous temperature). The first peak position somewhat shifts to small k-values, upon an addition of 5 at.% Al and then it is almost the same at different concentrations. The most probable interatomic distances r_1 and r_2 show a slow increase with concentration of Al. The square under the first peak of $G(r)$ function increases upon the addition of 5 at.% Al and then it shows a slight decrease at higher Al content only. A further increase of temperature up to 1255 K leads to additional

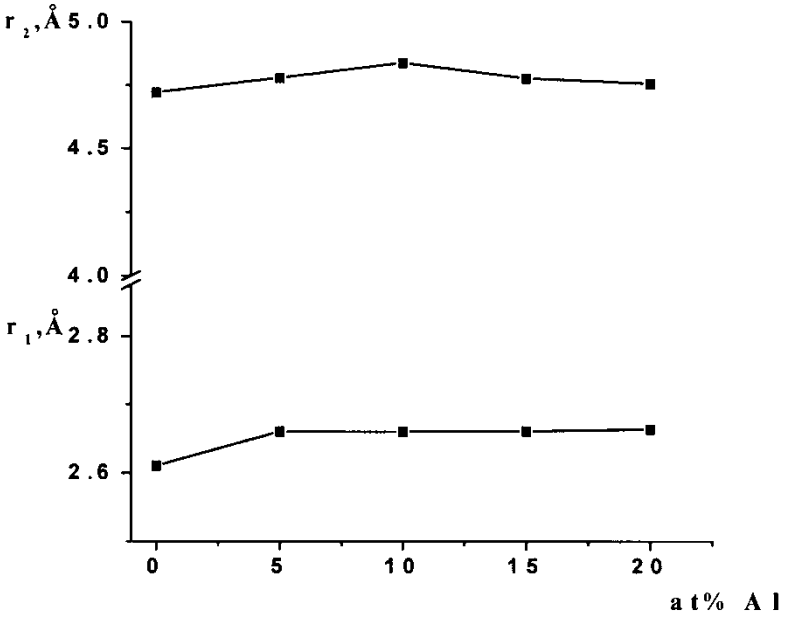

Figure 5. Concentration dependencies of main structure parameters.

structural disordering and increase of interatomic distances for the eutectic melt. At this temperature, on addition of Al atoms, there are no significant changes in the main structure parameters. Only the area under the first peak of $G(r)$ function is not governed by such a rule. This parameter increases with a concentration of added atoms, indicating the formation of atomic distribution of higher atomic density.

Analyzing the temperature change of these structure parameters for different Al content in eutectic $Cu_{0.70}Si_{0.30}$ melt, it is possible to conclude that there are significant changes in concentration dependence as well. Most sensitive to temperature is the area under the first peak of $G(r)$ function, contrary to dependence of s_1, $a(s_1)$, r_1 and r_2 parameters. But it should be noted that Z parameter is commonly estimated with less accuracy than the other ones. For alloys of higher Al content, the changes in structure parameters with temperature are less significant. From the obtained data it follows that square under the first peak of $G(r)$ function (Z) shows the same behavior in its decrease with temperature for the studied melts of various Al content. An exception to this rule is a melt containing 20 at.% Al. At $T = 1150$ K temperature Z is lower than for neighboring concentration points.

Analyzing these data, the suggestion about the existence of inhomogeneous short-range order upon the addition of Al atoms can be drawn.

In order to confirm the possibility of Al atoms to form the like-kind atomic groups, we have calculated the structure factor in the assumption of additive scattering both from the Al–Al regions and the eutectic matrix. The formula for this procedure can be easily obtained, using SF, both for aluminum and eutectic melt.

$$a(s) = C_{\mathrm{Al}} K^2_{\mathrm{Al}} a_{\mathrm{Al}}(s) + C_{\mathrm{Cu_{0.70}Si_{0.30}}} K^2_{\mathrm{Cu_{0.70}Si_{0.30}}} a_{\mathrm{Cu_{0.70}Si_{0.30}}}(s)$$

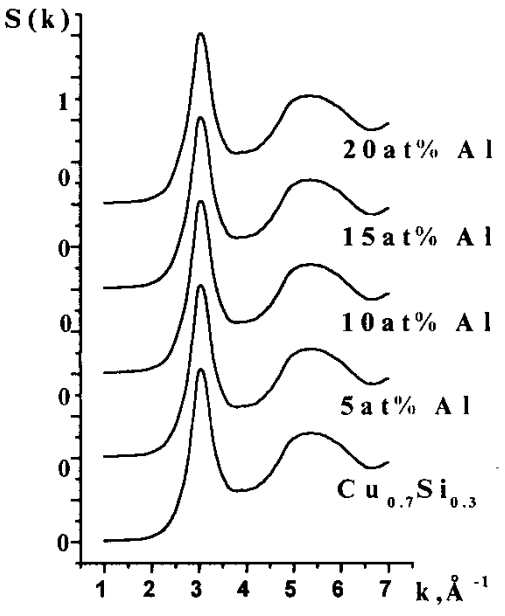

Figure 6. Structure factors, calculated according to additive assumption.

where

C_{Al}, $C_{Cu_{0.70}Si_{0.30}}$ – fractions of aluminum and eutectic structural units;
K_{Al}, $K_{Cu_{0.70}Si_{0.30}}$ – their scattering abilities.

The result of such a calculation in the region of principal peak is shown in figure 6. As it can be seen, there exists some contribution of the Al–Al self-associated atomic groups to the total structure factor.

Taking into account the data on the structure of the liquid $Cu_{0.7}Si_{0.3}$ eutectic molten alloy, where heterocoordinated arrangement of Cu and Si atoms is responsible for total atomic distribution, we can suppose that the Al atoms rather attempt to form self-associated structural groups. While the content of Al is small, it can be diluted by occupation of ''vacancies'' in the structure of eutectic $Cu_{0.7}Si_{0.3}$ melt. Such a route to alloy formation is marked by an increase of atomic density, which is displayed in some increase of principal peak height of the structure factors. With a further Al content increase the solubility of this element in structural units of eutectic melt decreases because the interaction between the Cu and Si atoms is stronger than that between the Cu or Si atoms with Al. This is in agreement with the fact that solubility of Si in Cu in solid state is significant, as follows from the equilibrium phase diagram [11]. These facts allowed us to propose that aluminum forms self-associated atomic groups, but formation of ternary heterocoordinated structure is not confirmed. The existence of such a kind of structure leads to some changes of interatomic distances and number of neighbor atoms. On the other hand, a small part of Al-based atomic groups, but attempt to be diluted in Cu–Si eutectic matrix with heating. Therefore, it is feasible to propose that clusters of aluminum are randomly distributed in a hetero-coordinated matrix of Cu and Si atoms. When the temperature increases, the size

of Al clusters becomes less, but significant changes of structure in the Cu–Si matrix and the Al-based units are not observed.

4. Conclusions

The addition of Al atoms to eutectic $Cu_{0.7}Si_{0.3}$ melt promotes the formation of an inhomogeneous structure. The Al atoms are aggregated in like-kind of atomic groups, which are randomly distributed in matrix, consisting of a heterocoordinated distribution of Cu and Si atoms.

References

[1] D. Wilson. *Structure of Liquid Metal Alloys*, p. 247, Moscow (1972) (in Russian).
[2] H. Neuman, W. Hoyer, M. Wobst. Wissenschaftliche Zeitschrift. *Techn Univ. Chemnitz*, **33**(4), 381–390 (1991).
[3] P.A. Egelstaff. *An Introduction to the Liquid State*, p. 390, Oxford (1992).
[4] M. Ivanov. *Z. Metallkunde*, **82**(1), 53–58 (1991).
[5] M.J. Regan, P.S. Pershan, O.M. Magnussen, B.M. Ocko, M. Deutsch, L.E. Berman. *Physical Review B*, **55**(23), 15874–15884 (1997).
[6] M. Naka, A. Inoue, T. Masumoto. *Sci Rep. RITU A*, **29** (184) 1981.
[7] T. Kulik. *Journal of Non-Crystalline Solids*, **287**, 145–161 (2001).
[8] S. Mudry, A. Korolyshyn, I. Shtablavyi. *Melts* (in Russian) (to be published).
[9] R. Hulgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley. *Selected Values of the Thermodynamic Data of Binary Alloys*, p. 1435, American Society for Metals, Ohio (1973).
[10] D.T. Cromer, J.T. Waber. *Acta Cryst.*, **18**(5), 104 (1965).
[11] T. Massalsky. *Binary Alloy Phase Diagrams*, Vol. 1, 2, 2233, American Society for Metals, Metalls Park, Ohio (1998).