Archives of Materials Science and Engineering

Volume 34
Issue 1
November 2008
Pages 14-18

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

Liquid eutectic alloys as a cluster solutions

S. Mudry [a,*], I. Shtablavyi [a], I. Shcherba [b]

[a] Physics of Metals Department, Ivan Franko Lviv National University,
Kyrylo and Mephodii str. 8, 79005 Lviv, Ukraine
[b] Institute of Technique, Academy of Pedagogy,
ul. Podchorążych 2, 30-084 Kraków, Poland
* Corresponding author: E-mail address: mudry@physics.wups.lviv.ua

Received 15.08.2008; published in revised form 01.11.2008

ABSTRACT

Purpose: In this research work the results of structure studies for $Al_{0.88}Si_{0.12}$, $Bi_{0.995}Cu_{0.005}$, $Al_{0.83}Cu_{0.17}$ eutectic and $Co_{0.05}Cu_{0.95}$ peritectic melts have been presented. The structure parameters of molten alloys are compared with ones for liquid pure components and with model values.

Design/methodology/approach: The structure in liquid state has been studied with use of X-ray diffractometer containing special attachment for investigation of liquid metallic alloys. The system was equipped with special camera for sample, filled with pure helium in order to avoid the oxidation. Experimental data were interpreted with using of random atomic distribution model and self-associated one.

Findings: The research has shown that structure of liquid alloys $Al_{0.88}Si_{0.12}$, $Bi_{0.995}Cu_{0.005}$, $Al_{0.83}Cu_{0.17}$ and $Co_{0.05}Cu_{0.95}$ shows the deviation from random atomic distribution model and these alloys in liquid state at temperatures not far from melting point can be considered as cluster solutions.

Practical implications: Existence of clusters in eutectic and peritectic melts influence the structure and properties of corresponding solid alloys, that is important for casting, soldering, welding and at producing of composite materials on the base of eutectic matrix.

Originality/value: Cluster structure of eutectic melts is responsible for behaviour of structure and physical-chemical properties. The change of this structure allows to improve the properties of solidificated alloys, both crystalline and amorphous.

Keywords: Liquid metallic alloys; Structure factor; Pair correlation function; Cluster

MATERIALS

1. Introduction

Interest to eutectic alloys is motivated by their many physical-chemical properties but low melting temperature is the most important of them. Due to this feature the eutectic alloys during a long time have been used as a solders and a casting materials. Eutectic reactions between components are also used for alloying at significantly less temperatures in comparison with classic alloying at temperatures higher than lowest melting temperature of any component of eutectics. Such process is known as a contact melting and it has a practical application too [1-4].

Some eutectic alloys, especially ones with deep eutectic point in phase diagrams, reveal a large glass forming ability [5]. It is also known that eutectic alloys, particularly aluminum-based ones have been widely used as a matrix for composite materials [6-11] On that reason it is of great importance to study the interrelation between the structure of eutectic melt and corresponding amorphous alloy. Such interaction is also important for producing of composite materials by controlled crystallization.

Besides, the interest to practical use, eutectic alloys attract the attention of researcher from fundamental point of view. Particularly, liquid eutectic alloys reveal the significant deviation from random atomic distribution resulting the untypical behaviour of physical properties concentration dependences (viscosity, density, electrical conductivity, etc). In other words the atomic distribution in such alloys shows both topologic and chemical short range order. The tendency to have a like kind atoms as a

neighbours results the formation of clusters with various composition structure and size.

Parameters of cluster structure are very sensitive to temperature and other thermodynamic factors especially before transition from liquid state to solid one. Unfortunately, the available information on changes of cluster structure parameters with temperature for eutectic melts is rather poor to drawn some general conclusions about interrelation between liquid and solid state near phase transition point.

In order to decrease the incompleteness of such studies we focus the attention on analysis of structure data for eutectic melts at temperatures near melting points in this paper. Peritectic alloys are close to eutectic ones in respect to structure in liquid state. At nonequilibrium crystallization the structure of peritectic alloys is similar to one of eutectic alloys. On that reason the structure of $Co_{0.05}Cu_{0.95}$ peritectic melt. The obtained data are interpreted according to existing models and by comparison with literature thermodynamic data.

2. Experimental

Samples were prepared in arc melting furnace filled with pure argon. The purity of the initial metals was 99.999%. The diffraction studies were carried out using a high-temperature diffractometer with a special attachment that allows to investigate the solid and liquid samples at different temperatures up to 1800 K. Cu-K_α radiation monochromatized by means of LiF single crystal as a monochromator and Breg-Brentano focusing geometry were used. The scattered intensities as a function of the scattering angle were recorded within the range $1Å^{-1} < k < 7Å^{-1}$, with different angular step, which was equal to 0.05° within the region of principal peak and 0.5° at rest values of wave vectors. The measuring of scattered intensity was done with accuracy, better then 2%. In order to obtain the more accurate scattered intensities, the scan time was equal to 100 s. The diffracted intensity was recorded using a NaI(Tl) scintillator detector in conjunction with an amplification system. The sample was placed in a rounded cup of 20 mm diameter. Intensity curves were corrected on polarization, absorption and incoherent scattering [12]. After this procedure they were normalized to electron units by Krogh-Moe method [13]. Obtained intensity curves were used to calculate the SF and than the pair correlation function PCF. Main structure parameters, obtained from SF and PCF were analyzed.

3. Results and discussion

The structure factors for liquid $Co_{0.05}Cu_{0.95}$ peritectic alloy (Figure 1) is compared with ones for liquid component. It can be seen that main structure parameters – principal peak's positions show the difference which can not interpreted with using of existing simple models: random atomic distribution and self-associated atomic arrangement. Certainly, that all the thermodynamic factors (positive enthalpy of mixing, large size factor, small electronegativity difference) suggest the deviation from an ideal atomic solution model. On the other hand, both elements belong to same raw in Periodic Table of Elements and their structure parameters in liquid state are close. Most probable interatomic distance r_1 equals to 2.57 Å for liquid copper and 2.56 Å for liquid cobalt. Numbers of nearest neighbours are in fact also the same (Z_{Cu}=11.3; Z_{Co}=11.4). Therefore it is possible to suppose that such similarity of structure parameters predict the some solubility in liquid state.

Analyzing the structure factors obtained at different temperatures (Figure 1) one can see that addition of Co to Cu is accompanied by anomalous change of principal peak position. Namely, this peak should be shifted slightly to large q-values if suppose the formation of atomic solution. Really the shift is observed in opposite direction (2.97 $Å^{-1}$ at T=1365 K). This is smaller than those for liquid pure Cu (3.00 $Å^{-1}$). Similar tendency is also observed for second maxima.

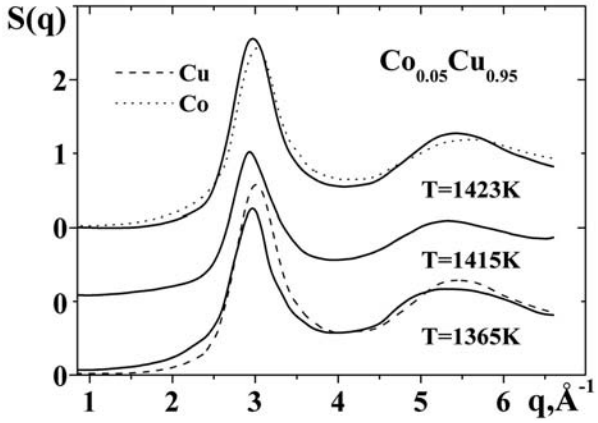

Fig. 1. Structure factors for liquid $Co_{0.05}Cu_{0.95}$ alloy

Besides, the second maximum for molten eutectic alloy reveals the flatness in its right-hand side branch. Therefore one can suppose that atoms of Cu and Co are self associated forming in such way the units with Cu and Co-like atomic arrangement. Using of model interpretation method we have calculated the model value of most probable interatomic distance r_1^{mod}

$$r_1^{\text{mod}} = c_{Cu}K_{Cu}^2 r_{Cu}^2 + c_{Co}K_{Co}^2 r_{Co}^2 \quad (1)$$

where c_{Cu}, c_{Cu} – atomic fraction of components; K_{Cu}, K_{Co} – scattering abilities, which were estimated from atomic factors:

$$K_{Cu}^2 = \frac{\left\langle f_{Cu}^2(q)\right\rangle}{\left\langle \left(c_{Cu} f_{Cu}^2(q) + c_{Co} f_{Co}^2(q)\right)^2\right\rangle}; \quad (2)$$

$$K_{Cu}^2 = \frac{\left\langle f_{Co}^2(q)\right\rangle}{\left\langle \left(c_{Cu} f_{Cu}^2(q) + c_{Co} f_{Co}^2(q)\right)^2\right\rangle}$$

The model value r_1^{mod} was compared with experimental one and in result the deviation from this model notes that real structure of eutectic melt is more complicated.

Taking into account the data of [14] we suggest that $CoCu_n$ clusters exists in liquid state. Co-atoms diluted in Cu-matrix disturb its atomic distribution resulting the formation of cluster structure.

Similar results were obtained for molten eutectic alloy with simple kind of phase diagram (Cd-Tl, Ag-Tl) [15]. Both components in these systems are metals, whose atomic distribution in liquid state is characterized by close packing of atoms. Nevertheless, due to significant value of size factor determined as

$$P = \frac{2(r_A - r_B)}{r_A + r_B}, \quad (3)$$

and small value of electronegativity difference the formation of random atomic distribution in liquid state is damped.

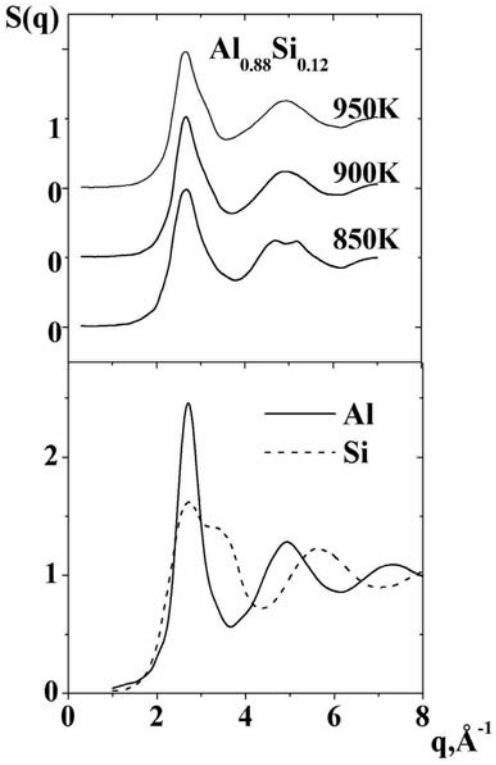

Fig. 2. Structure factors for liquid eutectic $Al_{0.88}Si_{0.12}$ in comparison with ones for Al and Si

To other kind of eutectic systems belong the alloys where the structure and physical-chemical properties of components are significantly different.

For instance, in case of $Al_{0.88}Si_{0.12}$ eutectic alloy investigated in this work, the structure of Si in liquid state is of less atomic packing density with some part of covalent bonds. Most probable interatomic distances for Al and Si ($r_1^{Al} = 2.82$ Å; $r_1^{Si} = 2.50$ Å) and number of neighbours (Z_{Al}=11.5; Z_{Si}=6.4) indicate that there are unfavourable conditions for atomic solution formation.

The structure factors and calculated from them pair correlation functions are shown in Figures 2 and 3.

There is a group of eutectic alloys whose phase diagram reveals the eutectic point at small content of one component (degenerated eutectic). One of such eutectic, namely $Cu_{0.995}Bi_{0.005}$ have been studied in this work. The structure factor for eutectic melt at temperature 550 K is compared with one for liquid Bi (Figure 4).

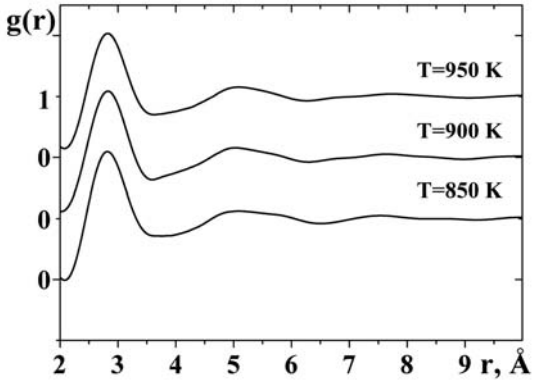

Fig. 3. Pair correlation function for liquid eutectic $Al_{0.88}Si_{0.12}$

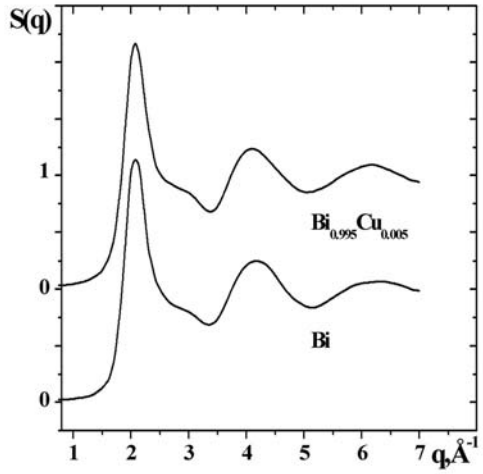

Fig. 4. Structure factors for liquid eutectic $Bi_{0.995}Cu_{0.005}$ and for liquid Bi

Table 1.
The main structure parameters of $Bi_{0.995}Cu_{0.005}$ eutectic melt

	q_1, Å^{-1}	q_2, Å^{-1}	$S(q_1)$	r_1, Å	r_2, Å	Z
Bi	2.14	4.18	2.08	3.34	6.78	8.09
Cu	3.00	5.46	2.59	2.57	4.80	11.3
$Bi_{0.995}Cu_{0.005}$	2.07	4.10	2.16	3.36	6.78	7.92

The main structure parameters obtained from structure factors and pair correlation functions are listed in Table 1. As it can be seen there is anomalous shift of structure factor's principal peak position. In case of ideal solution or self-associated atomic distribution the use of model interpretation method gives the shift to large q-values, that is opposite to shift estimated from experimental data.

Similar behaviour is also observed in structure parameter obtained from pair correlation functions. Particularly, r_1 parameter for eutectic melt is somewhat larger in comparison with one for liquid Bi. The behaviour of number of neighbours is also anomalous and with addition of Cu this parameter slightly decreases. It is known that for cooper it is higher than for Bi and in assumption that liquid eutectic alloy is an atomic solution this parameter should not be reduced.

Therefore in this eutectic melt enriched by one component (Bi) the existence of untypical atomic arrangement is observed. Some increase of mean interatomic distance with addition of smaller diameter atom (Cu) was suggested to be caused by cluster formation. We suppose that Cu-atoms, diluted in Bi-matrix disturb the distribution of nearest atoms and in such way they become a centres of clusters.

Al-Cu binary system as well as Al-Si one show the negative enthalpy of mixing over entire concentration range [16], indicating the tendency to preferred interaction of unlike kind atoms. But contrary to Al-Si system the Al-Cu one is characterized by formation of Al_2Cu chemical compound which is one component of eutectic.

Total structure factors for $Al_{0.83}Cu_{0.17}$ eutectic melt at different temperatures, compared with SF for liquid Al and Cu are shown in Figure 5. Main parameter – the principal peak position q_1 for eutectic melt is located between respective peak positions for Al and Cu. The same is also observed for second maxima. It can be seen that height of principal peak in S(q) for liquid eutectic is significantly less that for liquid components. This permits to note that degree of structural ordering in liquid melt is less than in liquid copper and aluminium. Therefore the structure of molten $Al_{0.83}Cu_{0.17}$ eutectic alloy is transformed in respect to molten Al, although its content prevails in total composition. The small fraction of Cu-atoms influence the atomic distribution of Al more then it is expected for simple solution of copper in aluminium. We suppose also that real structure of molten eutectic is somewhat different from mixture of Cu_n and Al_m structural units.

In order to confirm this supposition we have calculated the structure factor in assumption of additive scattering both from Al and Cu microregions (Figure 6). The formula for this procedure can be easy obtained, using SF of liquid aluminium and copper.

$$S(q) = c_{Al} K^2_{Al} S_{Al}(q) + c_{Cu} K^2_{Cu} S_{Cu}(q) \qquad (4)$$

where c_{Al}, c_{Cu} – fractions of aluminium and eutectic structural units

K_{Al}, K_{Cu} – their scattering abilities.

As it can be seen from Figure 6, the model structure factor differs from experimental one. At first, the principal peak height of calculated SF is significantly higher than in $S_{exp}(q)$. The characteristic feature of experimental SF is the shoulder in the small k-values region q≈1.5 $Å^{-1}$. This shoulder is commonly interpreted as pronounce of medium-range order [17]. In case of Al-Cu molten alloy the resolution of this shoulder is maximum for concentration corresponding to Al_2Cu stoichiometric compound [18]. Our results also indicate this shoulder for $Al_{0.83}Cu_{0.17}$ eutectic confirming the assumption about existence of chemically ordered microgroups in this melt.

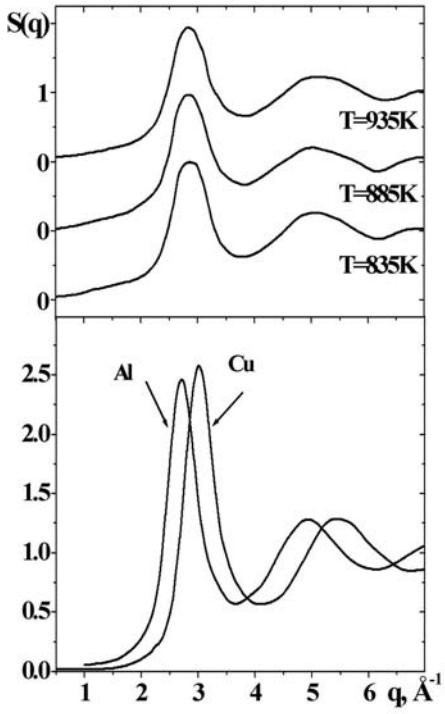

Fig. 5. Total structure factors for $Al_{0.83}Cu_{0.17}$ eutectic melt at different temperatures

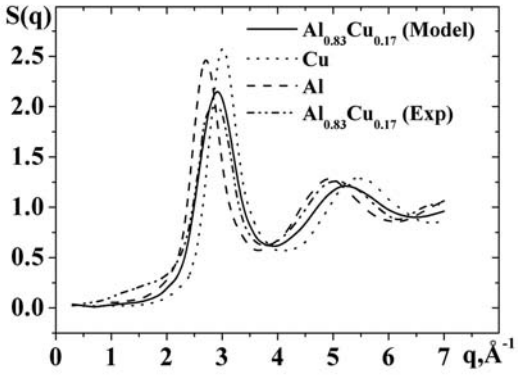

Fig. 6. Structure factors for liquid eutectic $Al_{0.83}Cu_{0.17}$ (— · · — · · – experimental, ———— – model) and liquid Al and Cu

The similar features are also observed in pair correlation functions. As follows from Table 2, interatomic distances r_1 and r_2 are different than respective values in Al and Cu. Parameter r_1 is closer to corresponding value for liquid Al, whereas r_2 is closer to one for copper. Number of neighbours Z is less then in Cu and Al. Such nonregular behaviour of these parameters also allows assuming that molten eutectic alloy has a structure which deviates from one for simple eutectic melt.

Table 2.
The main structure parameters of $Al_{0.83}Cu_{0.17}$ eutectic melt

T, K	q_1,Å^{-1}	q_2,Å^{-1}	$S(q_1)$	Δq	r_1,Å	r_2,Å	Z
835	2.86	5.06	1.99	0.84	2.74	4.87	10.4
885	2.84	5.02	1.96	0.88	2.76	4.85	10.5
935	2.81	5.07	1.93	0.88	2.78	4.82	10.0

The temperature dependences of S(q) and g(q) reveal the thermal disordering, accompanied by increase of r_1 parameter and decrease of r_2. Number of neighbours slightly reduces. Half height width of principal peak Δq somewhat increases indicating the decrease of structural units size L

$$\left(L = \frac{2\pi^3}{2.5^2 \Delta q} \right) \tag{5}$$

Consequently, the results on temperature dependence of main structure parameters show the some stability of atomic arrangement within 835-935 K temperature range.

Therefore, the different kind of eutectic alloys, whose components show the small electronegativity difference, can be considered as cluster solutions.

4. Conclusions

The structure of different kind of eutectic alloys has been studied in liquid state: ($Al_{0.88}So_{0.12}$, $Cd_{0.73}Tl_{0.27}$) with small solubility in solid state; degenerated eutectic melt ($Bi_{0.995}Cu_{0.005}$, $Ag_{0.974}Tl_{0.006}$) with small solubility in solid state; $Co_{0.05}Cu_{0.95}$ peritectic melt and eutectic molten alloy ($Al_{0.83}Cu_{0.17}$) whose one component is a chemical compound (Al_2Cu).

From analysis of structure data follows that all kind of eutectic melts can be considered as cluster solutions. These clusters are the self-associated atomic groups in the case of simple eutectic, whereas they are chemically ordered structural units in the case of degenerated eutectics ($Bi_{0.995}Cu_{0.005}$, $Ag_{0.974}Tl_{0.006}$), peritectic ($Co_{0.05}Cu_{0.95}$) and eutectic where one component is a chemical compound ($Al_{0.83}Cu_{0.17}$). Some deviation from this behaviour is $Al_{0.88}So_{0.12}$ eutectic alloy where beside Al-Al and Si-Si clusters the chemically ordered Al_nSi_m ones also exist.

References

[1] A.K. Shurin, N.A. Razumova, Thermograph study of the contact melting of metals, I. Simple systems, Powder Metallurgy and Metal Ceramics 33 (1995) 304-306.

[2] M. Lacroix, Contact melting of a phase change material inside a heated parallelepedic capsule, Energy Conversion and Management 42 (2001) 35-47.

[3] O. Enaldieva, T. Orkvasov, M. Ponezhev, V. Sozaev, Contact melting of lead-based solid solutions and metals, Technical Physics Letters 31/9 (2005) 765-766.

[4] P Korotkov, T. Orkvasov, V. Sozaev, The size effect in contact melting of metals, Technical Physics Letters 32 (2006) 61-63.

[5] H. Ishii, M. Naka, T. Masumoto, Preparation of amorphous metallic powder, Science Report, RITU 29 (1981) 343-350.

[6] S. Mudry, V. Prokhorenko, S. Prokhorenko, I. Shtablavyj, A. Panas, Influence of Ni-atoms addition on the structure of In-Ga-Sn liquid ternary eutectic alloy, Proceedings of the 13th International Scientific Conference "Achievements in Mechanical and Materials Engineering" AMME'2005, Gliwice−Wisła, 2005, 451-454.

[7] G. Mrowka-Nowotnik, J. Sieniawski, M. Wierzbinska, Intermetallic phase particles in 6082 aluminium alloy, Archives of Materials Science and Engineering 28/2 (2007) 69-76.

[8] A. Dolata-Grosz, M. Dyzia, J. Śleziona, Solidification analysis of AMMCs with ceramic particles, Archives of Materials Science and Engineering 28/7 (2007) 401-404.

[9] B.P. Pisarek, The crystallization of the aluminium bronze with additions of Si, Cr, Mo and/or W, Archives of Materials Science and Engineering 28/8 (2007) 461-466.

[10] L.A. Dobrzański, M. Kremzer, A. Nagel, Aluminium EN AC-AlSi12 alloy matrix composite materials reinforced by Al_2O_3 porous performs, Archives of Materials Science and Engineering 28/10 (2007) 593-596.

[11] M. Dyzia, J. Śleziona, Aluminium matrix composites reinforced with AlN particles formed by in situ reaction, Archives of Materials Science and Engineering 31/1 (2008) 17-20.

[12] D.T. Cromer, J.T. Waber, Scattering factors computed from relativistic dirac-slater wave functions, Acta Crystallographica 18 (1965) 104-109.

[13] J. Krogh-Moe, A method for converting experimental X-ray intensities to an absolute scale, Acta Crystallographica 9 (1956) 951-953.

[14] B. Baum, G. Hasin, G. Tiagunov, Zhidkaja stal, Moskwa, Metallurgiya, 1984 (in Russian).

[15] Ya. Dutchak, N. Klym, V. Galchak, S. Mudry, Korrelacija difrakcionnyh I termodinamicheskih dannyh dvojnych rasplavov na osnove tallija, Zhurnal fizicheskoj himii 54 (1980) 875-879 (in Russian).

[16] D.S. Kanibolotsky, O.A. Bieloborodova, N.V. Kotova, V.V. Lisnyak, Thermodynamic properties of liquid Al–Si and Al–Cu alloys, Journal of Thermal Analysis and Calorimetry 70 (2002) 975-983.

[17] S.R. Elliot, Medium-range structural order in covalent amorphous solids, Nature 354 (1991) 445-452.

[18] J. Brillo, A. Bytchkov, I. Egry, L. Hennet, G. Mathiak, I. Pozdnyakova, D.L. Price, D. Thiaudiere, D. Zanghi, Local structure in liquid binary Al-Cu and Al-Ni alloys, Journal of Non-Crystalline Solids 352 (2006) 4008-4012.