Molecular dynamic investigation of atomic distribution in molten Al-Al$_2$Cu eutectic alloy

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Abstract. Structure of Al$_{0.83}$Cu$_{0.17}$ eutectic alloy has been studied in liquid state by means of X-ray diffraction and molecular dynamic methods. The total and partial structure factors are analyzed. These functions were used in order to calculate pair correlation functions and partial correlation functions, whose analysis allowed us to conclude that Al$_2$Cu-like atomic groups are distributed in Al-matrix.

1. Introduction

Growth of interest to Al-Cu binary alloys is motivated by opening of new spheres of their practical application although these materials are used during long time. Besides, Al-Cu binary is the base for synthesizing of such comparatively new (1984) materials as quasi crystals. In order to understand the mechanism of processes aimed the improvement of properties the complex studies of structure features including the liquid state are needed.

The structure of liquid Al-Cu has been investigated by diffraction methods and results are published in [1]. Analysis of these data allowed us to conclude that the structure of this alloy is far from random atomic distribution. Tendency to preferred interaction of unlike atoms is confirmed by structure sensitive physical properties measurements. Particularly, enthalpy of mixing shows the negative value with minimum corresponding to Al$_2$Cu stoichiometry. It was noted that chemical ordering in Al$_2$Cu persists upon melting but it is unclear whether this ordering influences the structure of another melts in this system.

In this work we represent the results on diffraction and molecular dynamic studies of Al$_{0.83}$Cu$_{0.17}$ eutectic melt.

2. Experimental

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$_\alpha$ 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$^{-1}$ < s < 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 than 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.

Scattered intensities as functions of scattering angels were recorded and corrected on absorption, anomalous dispersion and incoherent scattering [2].

The structure factors (SF) were obtained from angular dependences of scattered intensities. Pair correlation functions (PCF) were calculated from SF by means of Fourier-transformation. From this functions the main structure parameters – first and second peak positions \( k_1, k_2, r_1, r_2, \) number of neighbors – \( Z \) and first peak height \( a(k_1) \) were determined.

In our work for MD simulations we have used nanoMD program, developed at the Gdansk University of Technology by M. Bialoskorski. This C++ program was created with typical non-equilibrium molecular-dynamic (NEMD) applications and has previously been used with success in various studies [3 - 5]. Our MD simulations were performed at constant volume regime. A usual time step is in order of 1 fs, and in our case it was equil 2.5 fs. We have decided to choose a fourth-order Gear predictor-corrector algorithm as the numerical integrator. Nose, Nose-Hoover and Gaussian thermostats have also been implemented.

In this work we chose to use the Sutton-Chen (SC) potential [6, 7] which has a simple power law form and relatively long-range character.

The SC many-body potential has the form

\[
U_{tot} = \sum_i U_i = \sum_i \epsilon \left[ \sum_{j \neq i} \frac{1}{2} V(r_{ij}) - c \rho_{ij}^{1/2} \right],
\]

\[
V(r_{ij}) = \left( \frac{\alpha_{ij}}{r_{ij}} \right)^n,
\]

\[
\rho_i = \sum_{j \neq i} \phi(r_{ij}) = \sum_{j \neq i} \left( \frac{\alpha_{ij}}{r_{ij}} \right)^m.
\]

where \( r_{ij} \) is the distance between atom \( i \) and \( j \). \( V(r_{ij}) \) is a repulsive pair potential between atoms \( i \) and \( j \), accounting for the Pauli repulsion between the core electrons. The cohesion associated with atom \( i \) is captured in a local energy density \( \rho_i \). \( \epsilon \) sets the overall energy scale and \( c_i \) is a dimensionless parameter scaling the attractive term. \( a \) is a length parameter leading to a dimensionless form for \( V \) and \( r \).

In calculating the structure, we included quantum corrections, leading to the quantum Sutton–Chen, or Q-SC force field.

For alloys we use the following combination rules to describe the interaction between different types of atoms:

\[
e_{ij} = \sqrt{e_{ii} e_{jj}},
\]

\[
n_{ij} = \frac{1}{2} (n_i + n_j),
\]

\[
m_{ij} = \frac{1}{2} (m_i + m_j),
\]
3. Results and discussion
Experimental structure factor for liquid Al$_{0.83}$Cu$_{0.17}$ eutectic alloy is interpreted comparing it with structure factors for liquid Al and Cu. As can bee seen (Fig.1) the significant disagreement between three SFs is observed. But it should be noted here that position of principal peak is significantly shifted in respect to corresponding peak of liquid aluminum. As can be seen from figure 1 and table 1 this parameter has a value 2.86 Å$^{-1}$ lying between corresponding values for liquid Al and Cu ($\alpha_{\text{Al}}^{\text{ref}} = 2.70$ Å$^{-1}$; $\alpha_{\text{Cu}}^{\text{ref}} = 3.00$ Å$^{-1}$). If suppose the formation of random atomic distribution in melt, this value should be significantly less and can be estimated using the additive law ($\alpha_{\text{Al}}^{\text{ref}} = 2.75$ Å$^{-1}$). The same behavior is also observed in pair correlation function. Most probable interatomic distances change in similar way. These feature allowed us to conclude that atomic distribution in eutectic melt differs from one for atomic solution that was suggested.

![Figure 1](image1.png)

**Figure 1.** Structure factors for liquid Al$_{0.83}$Cu$_{0.17}$ eutectic alloy comparing with structure factors for liquid Al and Cu.

![Figure 2](image2.png)

**Figure 2.** Experimental and model structure factors of liquid Al$_{0.83}$Cu$_{0.17}$ eutectic alloy.

Early we have analyzed the diffraction data for Al-Cu molten alloys with using of simple two models: random atomic distribution and quasi-eutectic structure [8]. It was shown that SF, calculated according to this model roughly agrees with experimental structure factor. At the same time it should be noted that some discrepancy is observed in values of principal peaks and lager disagreement reveals in main peaks region where the maximum existence display the presence of medium range order [9].

In order to avoid the discrepancies mentioned above in this work we use another model, which suppose an existence of Al$_2$Cu- clusters and Al-based structural units (Fig. 2). In case of this model the discrepancy between calculated and experimental values becomes less. Therefore one can suppose that Al$_2$Cu- nanogroups are arranged in matrix of Al.

In order to confirm this suggestion the structure of Al$_{0.83}$Cu$_{0.17}$ eutectic melt have been studied by means of molecular dynamic (MD) method. In our calculations the cubic cell containing 10000 atoms was chosen as initial structural unit. Volume of this cell was determined assuming that model density equals to experiment one. The calculated SF and experimental one show a good agreement (Fig. 3). Using a model atomic configuration a Faber-Ziman partial structure factors (PSF) and partial pair correlation function (PPCF) were calculated (Fig. 4).
PSFs and PPCFs related to Al-Cu and Cu-Cu distribution show the features in the wave vector interval 1-2 Å⁻¹. Such features were investigated in [7] and it was established that they are caused by substructure formation due to preferred interaction of unlike kind atoms. Partial structure factor related to Al-al atoms distribution is close to structure factor of pure liquid aluminum that is obvious because these atoms forms a matrix containing Al₂Cu-nanogroups. On the other hand the PSF describing partial Cu-Cu atomic distribution is in disagreement with SF for liquid copper indicating the lack of cu-like structure upon alloying.

At least the PSF related to Al-Cu interaction shows the averaged profile in respect to structure factors of Al and Cu, indicating the heterocoordinated atomic distribution.

**Table 1.** The main structure parameters of liquid Al₀.₈₃Cu₀.₁₇ eutectic alloy.

| T,K  | s₁,Å⁻¹ | s₂,Å⁻¹ | a(s₁) | Δs  | r₁,Å | r₂,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  |
|      | Al     | 2.70   | 4.94  | 2.46| 0.68 | 2.82 | 5.30  | 11.5  |
|      | Cu     | 3.00   | 5.44  | 2.57| 0.66 | 2.57 | 4.80  | 11.3  |

**Figure 3.** Experimental structure factor of liquid Al₀.₈₃Cu₀.₁₇ comparing with structure factor calculated by means of MD method.

**Figure 4.** Faber-Ziman partial structure factors (a) and partial pair correlation function (b).
4. Conclusions
The diffraction studying of Al$_{0.83}$Cu$_{0.17}$ eutectic alloy shows the inhomogeneous atomic distribution in liquid state at temperatures close to crystallization point. Molecular dynamic calculations confirm this kind structure.
Analysis of partial structure factors obtained by means of molecular dynamic shows the significant influence of Al$_2$Cu-like chemical ordering on atomic distribution in eutectic melt. It is shown that Al$_2$Cu-nanogroups are distributed in al-matrix.

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