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RMC simulations of the liquid Al—Ge alloys

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ABSTRACT

The structure of Al—Ge melts has been studied in a wide temperature-concentration range by Reverse Monte Carlo simulations and Voronoi-Delaunay diagrams. The experimental structure factors of the Al—Ge melts with ≥20 at.% Ge have a shoulder on high-Q side of the first peak that coincides with the one on the S(Q) of liquid Ge. There is the same shoulder on partial $S_{GeGe}(Q)$ that indicates the primary role of Ge in formation of the structure of binary melts near liquidus temperatures. The obtained data point out the quasi-eutectic structure of Al—Ge melts, which consist of atomic clusters with structure of homogeneous solution of Ge atoms in aluminium matrix and clusters with local structure like liquid Ge. The latter exist due to incomplete metallization of covalent Ge bonds during melting. An increase in temperature causes a metallization of Ge bonds resulting in disappearance of signs of pure liquid germanium's structure on experimental S(Q) and g(r) curves. Formation of the homogeneous solution with the increase in temperature promotes the process of metallization of residual covalent bonds in Al—Ge melts till complete conversion at ≈1800 K.

1. Introduction

The Al—Ge alloys belong to simple eutectic system with limited solid solubility of components and eutectic point at 28.6 at.% Ge and 690 K [1]. The formation of metastable Al—Ge phases during rapid quenching from liquid state with different cooling rates was reported [2–7]. The similar results of the existence of rhombohedral and monoclinic phases had been obtained in [5–7] and later were confirmed in [8]. An extension of the solid solubility of germanium in aluminium up to ≈7.2 at.% has also been shown. The obtained results indicate certain changes in the nature of atomic interactions in Al—Ge melts as compared with solid state. Metastable Al—Ge phases are also formed under high pressure [9–11]. The γ-phase with composition $Al_{30}Ge_{70}$ and simple hexagonal structure ($a = 2.83$ Å, $c = 2.622$ Å) was found [9] after thermobaric treatment of solid alloys (9 GPa, 593 K). The solid solution region extents to ≈18 at.% Ge at 10 GPa pressure [10]. The formation of the metastable γ-phase with hexagonal crystal lattice and subsequent transformation to amorphous state in the range 2.5–8 GPa were also reported in [11]. Besides an extension of the solid solution regions, increase of the pressure causes a significant shift of the eutectic point to the region with higher Ge content and slight increase of the eutectic temperature [12–13].

Changes in the phase composition of Al—Ge alloys under high pressure are caused by gradual metallization of Ge—Ge covalent bonds with simultaneous formation of more close-packed and high-coordinated structures that are typical for metals [14]. The value of metallic radius for Ge atom (1.37 Å) with coordination number of 12 appears to be close to the atomic radius of Al (1.43 Å) [15] that corresponds to the conditions of formation of a wide range of solid solutions.

A metallization of sp^3-covalent bonds [16] occurs also during melting of germanium, thereby leading to the distinct increase in electrical conductivity, density (≈5%), coordination number and nearest interatomic distance ($R_1 = 2.66$ Å). The last one significantly exceeds the length of the covalent bond in solid germanium (2.45 Å). These changes result in slightly stronger interaction between unlike atoms in Al—Ge melts that leads to low negative values of enthalpy of mixing [17]. Simulations of thermodynamic properties of Al—Ge melts interpret this effect due to the presence of weak associates with composition Al_2Ge_3 [18] and necessity to take into account attractive forces in the model of binary mixture of hard spheres [19]. It can be assumed that the existence of a solid alumunium-based solution [1] is caused by metallization of germanium during melting. Therefore, melting and high pressure cause metallization of the covalent bonds of the solid germanium that explains the appearance of metastable phases in Al—Ge alloys during both quenching of the melts and applying of the high pressure on solid alloys. The degree of metallization of the covalent bonds in solid germanium depends on the applied pressure and the coordination number of 12 (hexagonal close packing) is reached at $P \geq 125$ GPa [14].

Liquid aluminium is typical metallic melt with coordination number of 11.5 ± 0.5 [20–22]. On the other hand liquid Ge has more complex local atomic structure. A characteristic feature of the structure of liquid germanium is a shoulder on the high-Q side of the first peak of the structure factor (SF). Other features are weekly defined first peak and rapid damping of subsequent oscillations of atomic pair distribution

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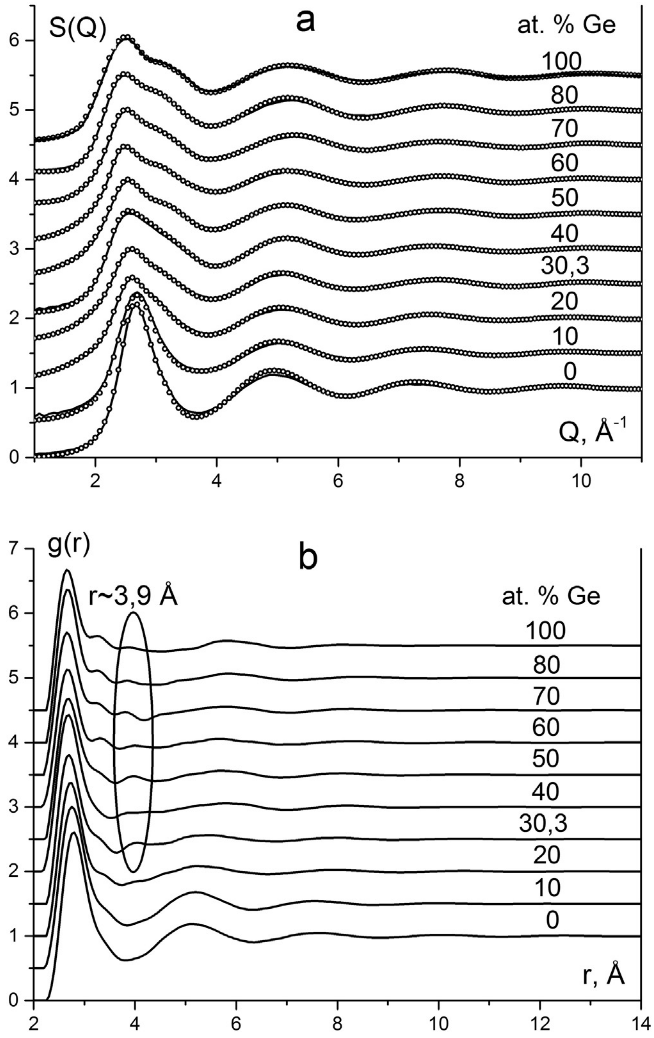

Fig. 1. The experimental (open circles) and model (line) structure factors (a) and experimental pair distribution functions (b) of Al—Ge melts near the liquidus temperatures [31].

function (PDF). The presence of covalent bonds of fluctuation type in liquid germanium has been suggested on the base of results of diffraction studies [23–26]. The residual covalent bonds in liquid Ge have been confirmed by the results of molecular dynamics simulations [27–28] and features of electronic structure [29].

Neutron diffraction study of the structure of liquid Al—Ge alloys with 20, 40, 60 and 80 at.% Ge at 1250 K was reported in [30]. It was shown that the experimental SF curves can be satisfactorily described by a binary mixture of hard spheres using Silbert-Yang repulsive potential. In our previous work [31] X-ray diffraction study of Al—Ge melts in a wide temperature and concentration range has been reported. The obtained results indicate a presence of microheterogeneous structure in the binary melts: regions with Ge-like local structure and aluminium-based solution.

The aim of this study is to obtain structure models of the liquid Al—Ge alloys by means of Reverse Monte Carlo (RMC) method and to perform their analysis by Voronoi-Delaunay diagrams. The analysis of RMC models was conducted in order to determine the possible physical causes that affect on formation of the structure and properties of the Al—Ge melts, as well their relationships with the character of the interatomic interactions in solid state. The degree of preservation of the Ge-like local atomic structure in the binary melts and its transformations with increasing temperature were also investigated.

2. Experimental procedure

The structure models of Al—Ge binary melts with 10, 20, 30.3, 40, 50, 60, 70, 80 at.% Ge at various temperatures were reconstructed by means of RMC method from experimental SF curves [31]. In all cases the basic cubic cell contained 10^4 particles with stoichiometric composition, and its size was consistent with the atomic number density of the liquid binary alloy at the temperature of the X-ray study [32]. Distances of the closest approach of two atoms (cut-off distances) were set as $d(\text{Al—Al}) = 2.25$ Å, $d(\text{Ge—Ge}) = 2.25$ Å, $d(\text{Al—Ge}) = 2.30$ Å. Values for $d(\text{Al—Al})$ and $d(\text{Ge—Ge})$ were calculated from the experimental PDF for pure liquid aluminium and germanium, respectively, as intersection point of the left side of first peak and abscissa. Models were optimized by minimizing the convergence factor:

$$\chi^2 = \sum_i \frac{\left[S_m(Q_i) - S_{\exp}(Q_i)\right]^2}{\sigma_e}, \tag{1}$$

where $S_m(Q)$ and $S_{exp}(Q)$ are model and experimental structure factors respectively, σ_e is the experimental error.

The partial structure factors $S_{ij}(Q)$, partial atomic pair distribution functions $g_{ij}(r)$, interatomic distances $\mathrm{R}_1(i\text{–}j)$ were calculated from obtained RMC models. The analysis of the triplet correlation has been performed by the bond-angle distribution function $g_3(\theta)$, where θ is the angle formed by two vectors joining a central atom with any other two neighbors. The analysis of local atomic structure of RMC models by Voronoi-Delaunay method [33] has been also performed. All model cells were divided into Voronoi polyhedrons (VPs), which metric and topological characteristics were calculated. In disordered systems such as metallic melts the VPs have different shapes and, as consequence, different characteristics. However, a set of the VPs can be described by the distributions of their structure characteristics. As the quantitative parameters of local structure of Al and Ge atoms, the values of mathematical expectations $(\overline{K_{sph}})$ and standard deviations (σ) of distribution coefficient of sphericity were used. K_{sph} was calculated by equation:

$$K_{\text{sph}} = \frac{36\pi V^2}{S^3} \tag{2}$$

where V is volume and S is surface area of Voronoi polyhedron, and distribution curves were calculated. It was shown earlier [34] that the high values of the $\overline{K_{sph}}$ and low values of the σ correspond to a dense atom packing and high level of structural organization of local atomic structure in liquid alloys.

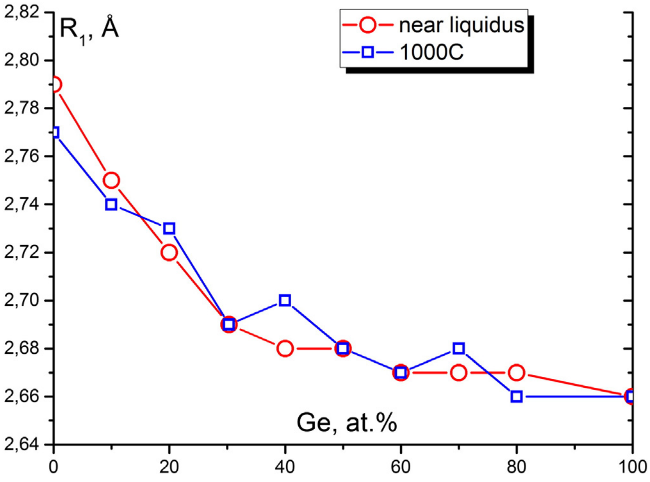

Fig. 2. Concentration dependence of nearest interatomic distance (R_1) in Al—Ge melts.