

## ATOMIC STRUCTURE, DIFFUSIVITY AND VISCOSITY OF $Al_{1-x}Mg_x$ MELTS FROM *ab initio* MOLECULAR DYNAMICS SIMULATIONS

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### Abstract

Atomic structure, diffusivity and viscosity of  $Al_{1-x}Mg_x$  ( $x=0, 0.0039, 0.1172, 0.9180, 0.9961, 1$ ) melts at 875, 1000, 1125, and 1250K were investigated by the *ab initio* molecular dynamics (AIMD) simulations. The simulated results are compared with available experimental and calculated data in the literature with reasonable agreements. Considering the results of pair correlation function  $g(r)$ , it can be observed that Mg atoms in  $Al_{0.8828}Mg_{0.1172}$  melt aggregate more obviously at 1000 and 1250K. For  $Al_{0.0820}Mg_{0.9180}$  Al atom segregation is more obvious at 875 and 1000K. The tracer diffusion coefficients of Al or Mg in  $Al_{1-x}Mg_x$  ( $x=0.1172, 0.9180$ ) melts, and interdiffusion coefficients of  $Al_{0.8828}Mg_{0.1172}$  and  $Al_{0.0820}Mg_{0.9180}$  melts are all close to the self-diffusion coefficients of Al or Mg. With the increasing temperature, the diffusivity increases linearly. In dilute melts, the tracer diffusion coefficients of solute atom and the interdiffusion coefficients increase nonlinearly with the increasing temperature. For  $Al_{0.8828}Mg_{0.1172}$  and  $Al_{0.0820}Mg_{0.9180}$  melts, the viscosities  $\eta$  are comparatively higher than pure melts. The viscosities of all melts decrease with the increasing temperature, then increase at 1250K. The results obtained in the present work provide an insight into the design of Al and Mg alloys.

**Keywords:**  $Al_{1-x}Mg_x$  melt; AIMD; Diffusivity; Viscosity

### 1. Introduction

Al and Mg based alloys have been widely used as structural materials in automobile, aerospace, and construction fields owing to their light weight, high strength, excellent thermal conductivity, corrosion resistance, and oxidation resistance [1]. With the development of low carbon economy and light weight technique, enhancing the microstructure and mechanical properties has become the common issue of researchers.

ZL301 as casting Al-based alloy, containing 10.68 wt. % Mg, is the one with the best mechanical properties among the commonly used casting Al-based alloys. The mechanical properties include tensile strength, ductility, and hardness, which are all higher than the national standard. The corrosion resistance and machinability properties of ZL301 are excellent as well, and it has lower density [2]. However, the castability of ZL301 is not good enough, the technology of production is complex, and the solidification range is wide. Therefore, improving the overall performance of alloys during solidification is of key importance. Mg-9Al is a typical casting Mg-

based alloy containing 9 wt. % Al, which is the prime component of the most widely used industrial Mg based alloy AZ91. AZ91 alloy is mainly used to produce thin-wall and complex component in shape, owing to the excellent physical properties of liquid [3]. With the present technology, the performance of mechanical component is excellent. However, the productivity of mechanical component is unsatisfied. According to the relations between liquids and solids, one of the most critical reasons is that the structural and physical properties of Mg based alloy melts are scarce, attributing to the difficulty in measurements.

To our knowledge, the understanding of the behavior and more particularly the knowledge of the thermophysical properties of molten alloys prior to solidification are essential for the development of materials with predetermined characteristics. Among the physical properties, diffusivity and viscosity in metallic liquids are vital, especially with respect to the formation of bulk metallic glasses (BMGs) [4, 5]. Quite surprisingly, experimental values for liquid aluminum, magnesium, and their alloys are scarce. That is because the measurements of diffusivity and viscosity in metallic melts are both costly and

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difficult, which is due to the effects of buoyancy-driven convective flow, chemical reactions between melts and containers, and high temperatures encountered [6-8]. Therefore, reliable theoretical data of viscosity and diffusivity in metallic melts [9-11] will be extremely valuable.

In recent years, the *ab initio* molecular dynamics (AIMD) approach has demonstrated its capability in predicting accurately the atomic structures [12-15] and physical properties [16-19]. For Al, there are predicted values from AIMD approach for the self-diffusion coefficient  $D$  and viscosity  $\eta$  by Jakse et al. [20] at temperature 875, 1000, 1125, and 1250K, and by Hui et al. [21] at 1000, 1200, 1500, and 1800K. They reported similar results at the same temperature, but underestimated the experimental data  $D$ , and overestimated the experimental data  $\eta$ . For casting Al-based alloy ZL301, there are no dynamic properties investigated from experiments and simulations, and for Mg and Mg-9Al, there are only a few dynamic properties reported from experiments, which mostly motivates the present investigations. Considering the melting points of Al and Mg, and in order to compare with the available experimental and theoretical data, 875, 1000, 1125, and 1250K are selected in the present work.

In this paper, we address the important issue of the determination of the dynamic properties of liquid Al, casting Al-based alloy ZL301, Mg-9Al, and Mg at 875, 1000, 1125, and 1250K by utilizing AIMD simulations. For these melts, the self-diffusion coefficients of Al and Mg, and the interdiffusion coefficients of these two commercial alloys are investigated, together with the microscopic shear viscosity. With the aim of carrying out a systematic study, a dilute Al-based alloy and a Mg-based alloy are also investigated for the impurity diffusion coefficients of Al and Mg. The remainder is organized as follows. In section two, the simulation methodology is shown. The results are discussed in section three in the terms of an analysis of the atomic structure, an evaluation of the diffusivity  $D$  and viscosity  $\eta$ . Finally, a summary is presented in section four.

## 2. Simulation methodology

The present AIMD simulations were carried out by utilizing the Vienna *ab initio* package (VASP) [22, 23], based on the DFT with the ion-electron interaction described by the projector augmented wave (PAW) [24] method and electronic exchange correlation interaction by the generalized gradient approximation (GGA) [25]. The simulations in this paper are performed in a canonical ensemble (NVT), with constant atomic number, constant volume and temperature. The atomic configuration is fully relaxed and the temperature is controlled by a Nose

thermostat [26]. The Newton's equation of motion is solved via the Verlet algorithm with a time step of 1 fs, and the simulations were performed at the  $\Gamma$  point only with a low precision as commonly used in AIMD simulations [12, 25, 27, 28]. The  $1 \times 1 \times 1$   $k$ -point sampling the Brillouin zone is generated according to Monkhorst-Pack scheme [29], while the cutoff energy is set 400eV with the energy convergence criterion of electronic self-consistency chosen as  $1 \times 10^{-4}$  meV/atom for all the simulations.

The simulated supercell is cubic, containing 256 atoms distributed in fcc lattice due to the initial supercell is constructed through expanding the fcc unit cell  $4 \times 4 \times 4$ . For the simulation of liquid Al, the atoms in the supercell are all Al, dilute Al-based alloy, there is one Mg atom in the supercell, for ZL301, there are 226 Al and 30 Mg in the supercell, which contains 10.68 wt. % Mg, for Mg-9Al, there are 21 Al and 235 Mg, containing 9 wt. % Al, and for dilute Mg-based alloy and Mg, there are 255 Mg and 1 Al, respectively. All simulations in the present work are carried out at four different temperatures: 875, 1000, 1125, and 1250 K. At each temperature, the supercell volume is varied systematically, and the equilibrium volume is obtained according to the condition of zero external pressure [12, 14-16, 30], and the detailed procedures are as follows: firstly, the initial configuration is relaxed for 4 ps under 10000 K generating a random distributed configuration; secondly, several small isotropic volume strains are applied to the configuration obtained above, then run 4000 steps for each supercell at the target temperature with a volume strain to derive the exact external pressure; thirdly, the pressure-volume data are fitted by a quadratic polynomial, and the volume corresponding to zero pressure is taken as the equilibrium volume at that temperature. Then, the simulation under equilibrium condition is finally carried out for 20 ps. Hence, 20000 configurations are collected at each temperature and the last 10000 configurations are used to evaluating the mean square displacement of individual atoms.

## 3. Results and discussions

### 3.1 Local structure analysis

The pair correlation function  $g(r)$  is usually used to characterize structural evolution of the liquid states [31, 32], which is defined as the probability of finding one atom apart from another atom for a homogeneous distribution. The distance is between the centers of the two atoms. The expression for the generalized pair correlation function in terms of the partial pair correlation functions is given by the Faber-Ziman formalism [33],

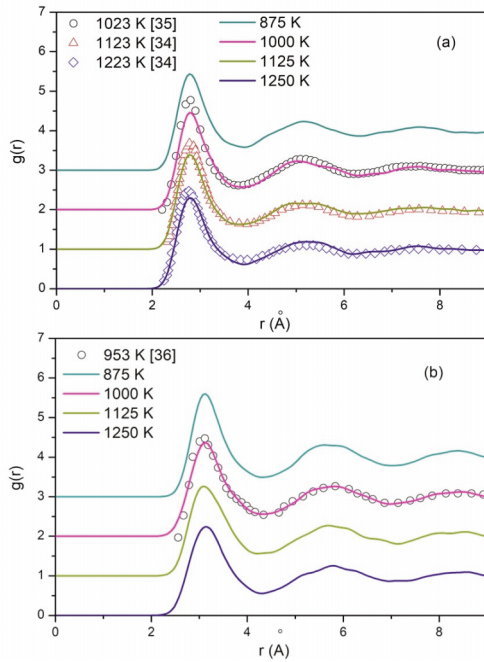
$$g(r) = \frac{1}{b^2} (x_i^2 b_i^2 g_{ii}(r) + 2x_i x_j b_i b_j g_{ij}(r) + x_j^2 b_j^2 g_{jj}(r)) \quad (1)$$



Where  $b = x_i b_i + x_j b_j$ ,  $x_i, x_j$  are the mole fractions of atom  $i, j$  and  $b_i, b_j$  are atomic scattering factor.  $g_{ij}(r)$  is the partial pair correlation function expressed as follows:

$$g_{ij}(r) = \frac{V}{N_A N_B} \left\langle \sum_{i=1}^{N_A} n_{iB}(r, \Delta r) \right\rangle / 4\pi r^2 \Delta r \quad (2)$$

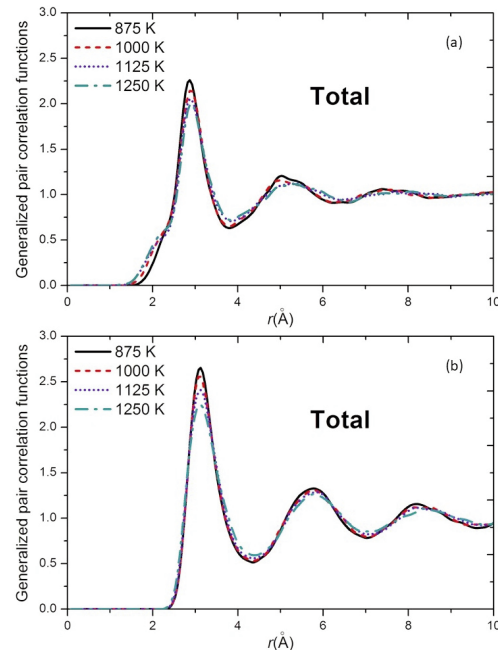
The calculated results  $g(r)$  of Al and Mg melts at 875, 1000, 1125, and 1250K are demonstrated in Fig. 1; these results are compared with the reported data of Al [34, 35] and Mg [36] in the literature. As seen in Fig. 1(a), the present simulated results at 1000, 1125 and 1250K are in excellent agreement with the measured  $g(r)$  at 1023 [35], 1223 [34] and 1323K [34]. Even for the second and the third peaks, our calculated  $g(r)$  can satisfactorily reproduce the experimental curve. The evaluated  $g(r)$  of Mg at 1000K is in good agreement with the experimental  $g(r)$  at 953 K [36] as well, seen in Fig.1(b). These validate the reliability of the present AIMD simulations. In addition, compared with the  $g(r)$  of Mg, the peak positions of the  $g(r)$  of Al shift left, meanwhile, the peak intensity is lower, as shown in Fig. 1. This is due to the size and the scattering factor of Al atom being smaller than those of Mg atom.



**Figure 1.** (a) Pair-correlation functions of Al. The open circles, triangles, and diamonds correspond to experimental values at 1023 [35], 1123 [34], and 1223K [34], respectively. The curves for 875, 1000, and 1125 K are shifted upwards by an amount of 3, 2, and 1, respectively. (b) Pair-correlation functions of Mg. The open circles correspond to experimental values at 953K [36]. The curves for 875, 1000, and 1125K are shifted upwards by an amount of 3, 2, and 1, respectively

Fig. 2(a) and Fig. 2(b) display the  $g(r)$  of  $\text{Al}_{0.9961}\text{Mg}_{0.0039}$  and  $\text{Al}_{0.0039}\text{Mg}_{0.9961}$ , respectively. Considering these dilute melts just containing one Al atom or one Mg atom, the total  $g(r)$  will be discussed. In Fig. 2(a) and Fig. 2(b), it is seen that the first peak strength of  $g(r)$  decreases with the increase of temperature. This phenomenon shows that the order degree of melts decreases with the increasing temperature. Nevertheless, the position of the first peak is nearly 2.8Å of  $\text{Al}_{0.9961}\text{Mg}_{0.0039}$  and 3.1Å of  $\text{Al}_{0.0039}\text{Mg}_{0.9961}$ , unchanged with the increasing temperature. The position of the first peak 2.8Å is similar with the corresponding result 2.79Å of pure Al calculated in the present work and 2.74Å in the literature [37], while the first peak position 3.1Å of  $\text{Al}_{0.0039}\text{Mg}_{0.9961}$  is close to the present predicted first peak position 3.1Å of Mg. The second peak strength of  $g(r)$  decreases with the increasing temperature and the position is nearly invariable. In Fig. 2(a), there is a small bump ahead of the first peak compared with Fig. 2(b), demonstrating that another short-range order exists in the first coordination shell of the glass structure [14].

The  $g(r)$  and partial  $g_{ij}(r)$  of  $\text{Al}_{0.8828}\text{Mg}_{0.1172}$  and  $\text{Al}_{0.0820}\text{Mg}_{0.9180}$  are shown in Fig. 3 and Fig. 4, respectively. The first peak strength of  $g(r)$  decreases with the increasing temperature for  $\text{Al}_{0.8828}\text{Mg}_{0.1172}$  and  $\text{Al}_{0.0820}\text{Mg}_{0.9180}$  melts, which indicates that the order degree of these melts decreases with the increasing temperature. Meanwhile, the first peak position is 2.9Å, unchanged with the increasing temperature. In Fig. 3, at 1000, 1125, and 1250K, it is seen that the



**Figure 2.** Evolution of the total pair-correlation functions of temperature of  $\text{Al}_{0.9961}\text{Mg}_{0.0039}$  melt (a) and  $\text{Al}_{0.0039}\text{Mg}_{0.9961}$  melt (b)



strength of the second peak of  $g(r)$  decreases with the increasing temperature, while the position is permanent. However, the second peak shifts left at 875K, indicating that the atoms are more tightly packed under supercooled state than high-temperature condition. In addition, the trend of the  $g_{Al-Al}(r)$  and  $g_{Al-Mg}(r)$  is similar with the trend of  $g(r)$ . The first peak of  $g_{Al-Al}(r)$  and  $g_{Al-Mg}(r)$  locates at 2.9Å and 3.1Å, adjacent to the present predicted value 2.8Å of pure Al and 3.1Å of pure Mg, respectively. This demonstrates that the interaction between Al-Al and Al-Mg in  $Al_{0.8828}Mg_{0.1172}$  melt is similar to pure metal. The curve of  $g_{Mg-Mg}(r)$  changes rapidly due to the low content of Mg in melt. Ignore the noise, the changing trend of the first peak with temperature can be seen clearly. The stronger the strength, the more concentrated the Mg

atoms. Therefore, Mg atoms aggregate obviously at 1000K and 1250K. In Fig. 4, the second peak strength decreases with the increasing temperature, while the position is fixed. The trend of the  $g_{Al-Mg}(r)$  and  $g_{Mg-Mg}(r)$  is similar with the  $g(r)$  curve. The first peaks of  $g_{Al-Mg}(r)$  and  $g_{Mg-Mg}(r)$  locate at 2.8Å and 3.1Å, adjacent to the present predicted pure Al 2.8Å and pure Mg 3.1Å, respectively, which displays that the interaction between Al-Al and Al-Mg in  $Al_{0.0820}Mg_{0.9180}$  melt is in analogous to pure metal. For  $g_{Al-Al}(r)$ , the second peak shifts left at 875 and 1000K, which exhibits obvious Al-atom aggregation. The content of Al is low in  $Al_{0.0820}Mg_{0.9180}$  melt leading to the rapid change of the  $g_{Al-Al}(r)$  curve. Ignore the noise, the changing trend of the first peak with temperature can be seen clearly. The stronger the

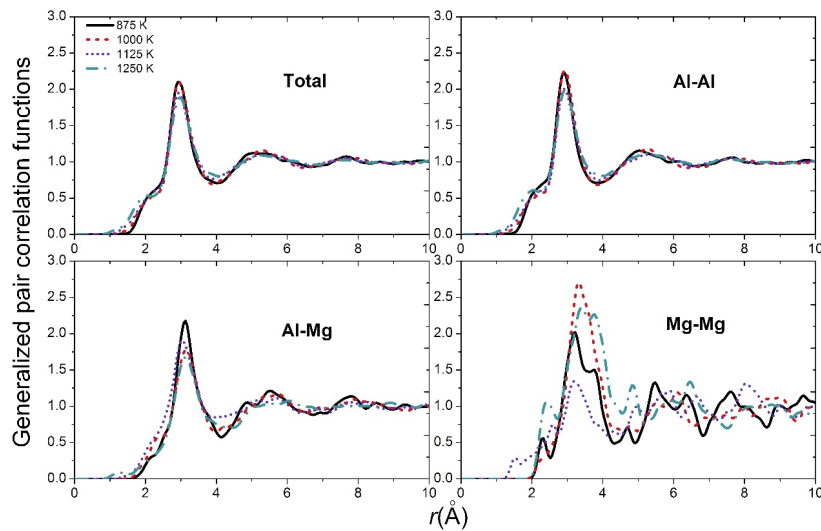


Figure 3. Evolution of the total pair-correlation functions and partial pair correlation function of temperature of  $Al_{0.8820}Mg_{0.1172}$  melt

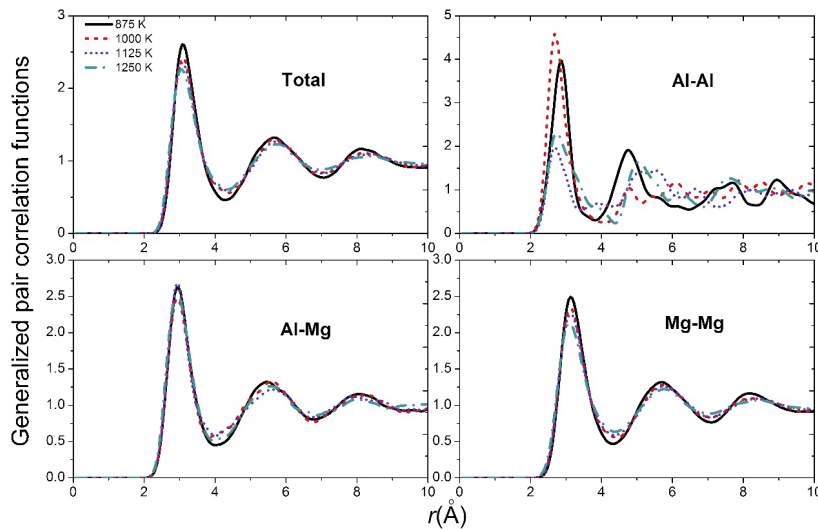


Figure 4. Evolution of the total pair-correlation functions and partial pair correlation function of temperature of  $Al_{0.0820}Mg_{0.9180}$  melt

strength, the more obvious the aggregation of Al atoms. Hence, at 1125K and 1250K, Al-Mg neighboring atomic pair is easier to form.

Fig. 5 illustrates the distribution of coordination numbers as a function of temperature, together with the available data by AIMD simulations [20] and experiment[38]. It is observed that the average coordination numbers of atoms in  $Al_{1-x}Mg_x$  ( $x=0, 0.0039, 0.1172, 0.9180, 0.9961, 1$ ) are between 11.5 and 14.5. Compared with the previous simulated coordination numbers of liquid Al 12.5 at 875K to 11.5 at 1250K via GGA approximation by Jakse et al. [20], the present calculated ones are 12.8 at 875K to 12.5 at 1250K. There are two measured coordination numbers of Al 12.3 at 1125K and 11.9 at 1273K [38], which is lying between the present data and the previous simulated ones. Furthermore, with a decrease of the temperature, the average coordination numbers increase except for the data of Mg at 1000 K and  $Al_{0.8828}Mg_{0.1172}$  at 1250 K, indicating formation of more close-packed local ordering in  $Al_{1-x}Mg_x$  ( $x=0, 0.0039, 0.1172, 0.9180, 0.9961, 1$ ) melts.

### 3.2 Diffusion and viscosity coefficients

The atomic tracer diffusion coefficient can be determined from the Einstein relation based on its mean square displacement (MSD) [9, 13, 16, 19]:

$$D_i = \lim_{t \rightarrow \infty} \frac{\langle R_i^2(t) \rangle}{6t} = \lim_{t \rightarrow \infty} \frac{\langle \sum_{j=1}^{N_i} |R_j(t+t_0) - R_j(t_0)|^2 \rangle}{6N_i t} \quad (3)$$

where  $\langle \dots \rangle$  denotes here averaging over all the atoms.  $\langle R_i^2(t) \rangle$  is the mean square displacement of atom  $i$ ,  $N_i$  is the number of atom  $i$ ,  $R_j(t_0)$  denotes the

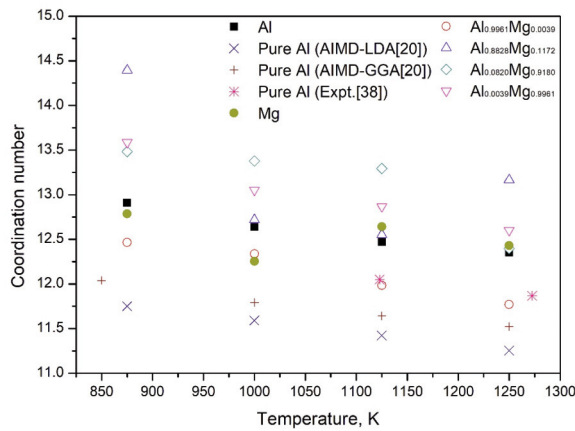


Figure 5. The average coordination numbers of atoms in  $Al_{1-x}Mg_x$  ( $x=0, 0.0039, 0.1172, 0.9180, 0.9961, 1$ ) melts with respect to temperature, together with the simulated data via LDA and GGA approximation by Jakse et al. [20], and the measured data by Gonzalez et al. [38]

position of the  $j$ th  $i$  atom at the moment  $t_0$  and  $R_j(t+t_0)$  denotes the position of the  $j$ th  $i$  atom at the moment  $t+t_0$ .  $\langle \sum_{j=1}^{N_i} |R_j(t+t_0) - R_j(t_0)|^2 \rangle$  is the mean square displacement of all  $i$  atoms during a period of  $t$ .

In the present work, the interdiffusion coefficient in Al-Mg melts is predicted by Darken equation [39], as follows:

$$\tilde{D} = (x_{Mg}D_{Al} + x_{Al}D_{Mg})f_i \quad (4)$$

where  $f_i$  is the thermodynamic factor related to the Gibbs energy [40, 41].

Fig. 6 and Fig. 7 show the MSD of Al or Mg in pure melt and Al or Mg in  $Al_{1-x}Mg_x$  ( $x=0.0039, 0.1172, 0.9180, 0.9961$ ) melts as a function of time, respectively. It is seen that the MSD of most Al and Mg atoms in pure melt or in  $Al_{1-x}Mg_x$  ( $x=0.0039, 0.1172, 0.9180, 0.9961$ ) melts are proportional to  $t^2$  before 0.1 ps, as expected for ballistic motion. For longer times, they increase linearly with time, illustrating that long-range diffusion also takes places. However, the MSD of Mg in  $Al_{0.9961}Mg_{0.0039}$  melt and Al in  $Al_{0.0039}Mg_{0.9961}$  melt shows nonlinear nature, seen in Fig. 7(a) and (d). This is due to only one Mg atom in  $Al_{0.9961}Mg_{0.0039}$  melt and one Al atom in  $Al_{0.0039}Mg_{0.9961}$  melt. Unlike the MSD of Al in Mg melt, the MSD of Mg in Al melt at 875K is lower than that at other temperatures.

According to the Equation (4), the self-diffusion coefficients of liquid Al and liquid Mg are evaluated,

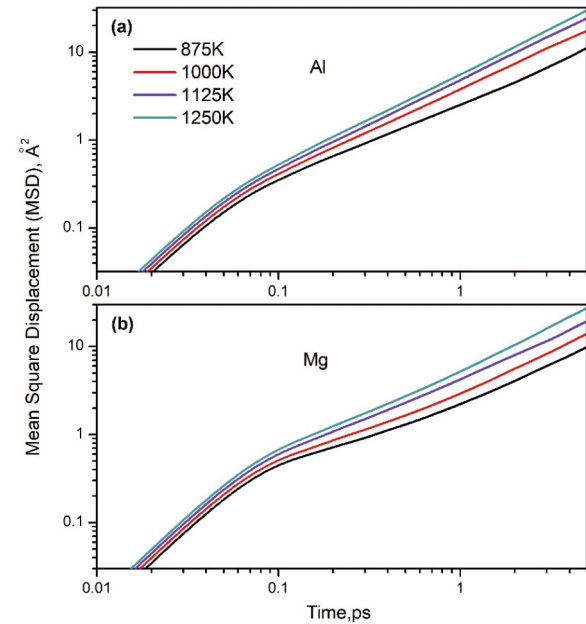
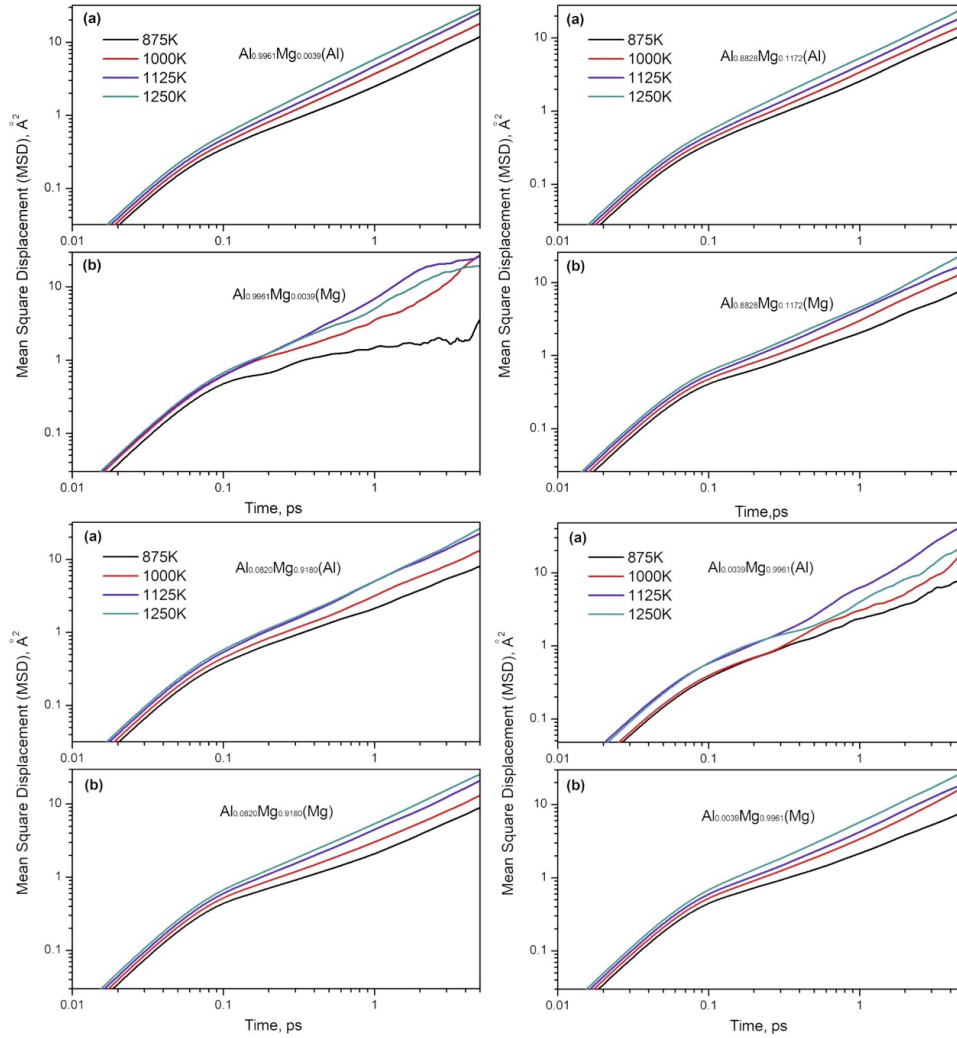


Figure 6. The mean square displacement (MSD) of pure Al (a) and Mg (b)





**Figure 7.** The mean square displacement (MSD) of Al (upper) and Mg (lower) in liquid  
 (a)  $Al_{0.9961}Mg_{0.0039}$  (b)  $Al_{0.8828}Mg_{0.1172}$  (c)  $Al_{0.0820}Mg_{0.9180}$  (d)  $Al_{0.0039}Mg_{0.9961}$

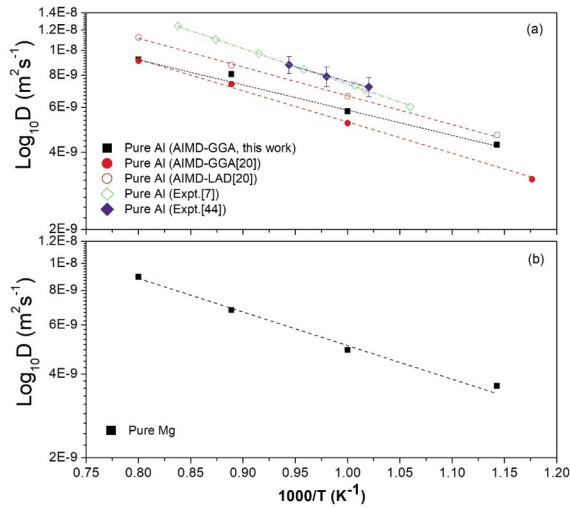
with lines fitted by Arrhenius relation [42, 43],  $D = D_0 e^{-Q/k_B T}$  displayed in Fig. 8(a) and Fig. 8(b), respectively. Meanwhile the available theoretical data predicted by Jakse et al. [20] and experimental data measured by Kargl et al. [7] and Hansen et al. [44] of Al, which are also fitted by an Arrhenius relation [42, 43], are plotted in Fig. 8(a). In the above equation,  $D_0$  is the prefactor, and  $Q$  is the activation energy of melts. In Fig. 8(a), it is seen that the present results lie between the predicted data with GGA approximation and LDA approximation by Jakse et al. [20]. Compared with the measured self-diffusion coefficients of Al, all calculated results lie a little lower. In Fig. 9, the tracer diffusion coefficients of Al and Mg in  $Al_{1-x}Mg_x$  ( $x=0.0039, 0.1172, 0.9180, 0.9961$ ) melts with lines fitted by an Arrhenius relation [42, 43]. The prefactor and activation energy for diffusion coefficient are predicted, shown in Table 1. As seen in Fig. 9, the tracer diffusion coefficients of

Al and Mg in  $Al_{1-x}Mg_x$  ( $x=0.0039, 0.1172, 0.9180, 0.9961$ ) melts is close to the self-diffusion coefficients of Al and Mg, increasing with the increasing temperature, in addition to the diffusion coefficient of Al in  $Al_{0.0039}Mg_{0.9961}$  melt or Mg in  $Al_{0.9961}Mg_{0.0039}$  melt. In dilute melts, the mean square displacement of the solute atom Al or Mg is nonlinear. This leads to the nonlinear change of the diffusion coefficients of solute atom.

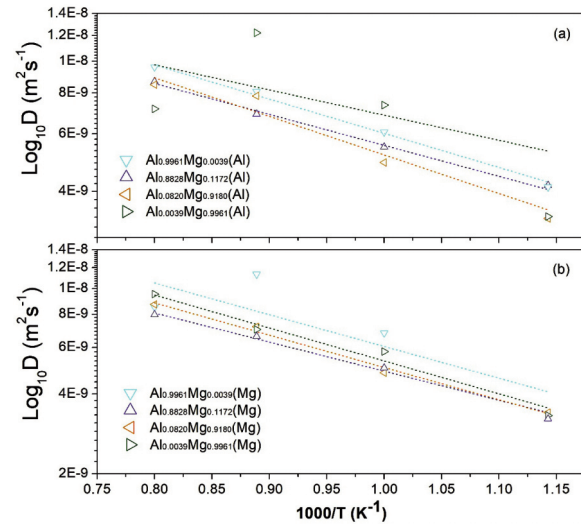
The thermodynamic factor used to evaluate the interdiffusion coefficient is calculated by ThermoCalc and thermodynamic database, as shown in Fig. 10. The needed equation is shown as below:

$$f_i = \frac{d \ln a_i}{d \ln x_i} = 1 - x_i \frac{d \ln y_i}{dx_i} \quad (5)$$

in which,  $f_i$  is the thermodynamic factor,  $a_i$  and  $y_i$  are the activity and activity coefficient of element  $i$ , and  $x_i$  is the mole fraction of  $i$ . As seen in Fig. 10, the



**Figure 8.** Self-diffusion coefficients of liquid Al (a) and liquid Mg (b) with lines fitted by an Arrhenius relation,  $D = D_0 e^{-Q/k_a}$ , together with the available theoretical ( $\circ$ : Jakes et al. [20]) and experimental ( $\diamond$ : Kargl et al. [7],  $\blacklozenge$ : Hansen et al.[44]) data of Al fitted by an Arrhenius relation

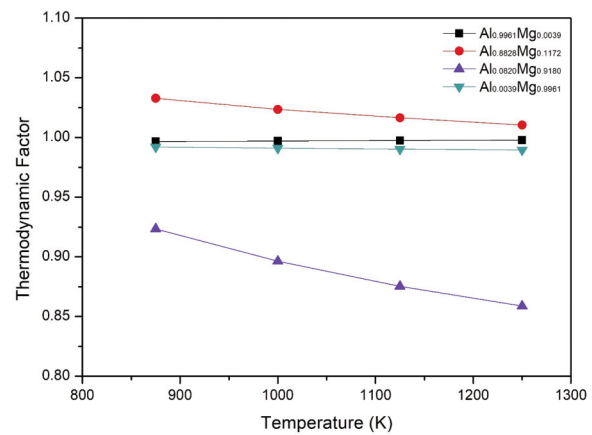


**Figure 9.** Tracer diffusion coefficients of Al (a) and Mg (b) in  $Al_{1-x}Mg_x$  ( $x=0.0039, 0.1172, 0.9180, \text{ and } 0.9961$ ) melts with lines fitted by an Arrhenius relation

**Table 1.** Prefactor and activation energy for diffusion coefficient and viscosity of Al-Mg melts

	$D_0(\text{Al}) (\text{m}^2\text{s}^{-1})$	$Q(\text{Al}) (\text{kJ/mol})$	$D_0(\text{Mg}) (\text{m}^2\text{s}^{-1})$	$Q(\text{Mg}) (\text{kJ/mol})$	$\eta_0 (\text{mPas})$	$Q (\text{kJ/mol})$	T (K)
Al	$5.6 \times 10^{-8}$	18.8			0.256	13.8	
$Al_{0.9961}Mg_{0.0039}$	$6.7 \times 10^{-8}$	20	$9.5 \times 10^{-8}$	22.9	0.00336	48.8	875
$Al_{0.8828}Mg_{0.1172}$	$4.9 \times 10^{-8}$	18.1	$6.1 \times 10^{-8}$	21	0.311	13	
$Al_{0.0820}Mg_{0.9180}$	$7.8 \times 10^{-8}$	22.6	$8.3 \times 10^{-8}$	23.3	0.368	13	1250
$Al_{0.0039}Mg_{0.9961}$	$4.0 \times 10^{-8}$	14.8	$9.3 \times 10^{-8}$	23.8	0.129	18.8	
Mg			$8.2 \times 10^{-8}$	23.1	0.298	12.8	

present predicted thermodynamic factor is small, indicating the interaction is weak. For the two dilute melts, the thermodynamic factor nearly fixes with the increasing temperature. For  $Al_{0.8828}Mg_{0.1172}$  melt and  $Al_{0.0820}Mg_{0.9180}$  melt, the thermodynamic factor decreases gradually with the increasing temperature, the interaction between atoms decreases as well. In Fig.11, the interdiffusion coefficients of  $Al_{1-x}Mg_x$  ( $x=0.0039, 0.1172, 0.9180, 0.9961$ ) calculated by Equation (4), together with self-diffusion coefficients of pure Al and Mg are displayed. At 875K, the interdiffusion coefficient of  $Al_{0.9961}Mg_{0.0039}$  melt is the minimum, apart from others a little far. However, the datum of  $Al_{0.0039}Mg_{0.9961}$  melt is similar to the results of other melts. At 1000 and 1125K, it is seen that the interdiffusion coefficients of the two dilute melts are similar, both higher than the self-diffusion of pure melts. At 1250K, the interdiffusion coefficients of



**Figure 10.** Thermodynamic factors as a function of temperature calculated from the thermodynamic database

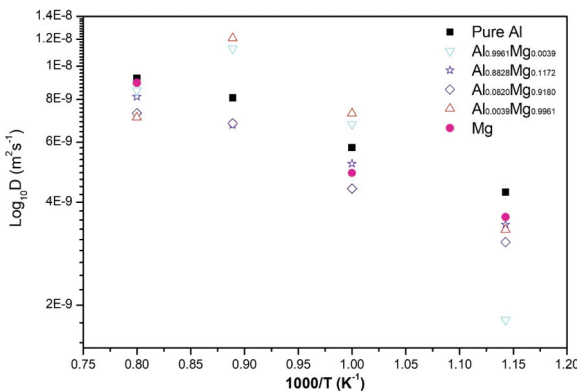


dilute melt are adjacent to the results of other melts. At the considered temperatures, the interdiffusion coefficients of  $Al_{1-x}Mg_x$  ( $x=0.1172, 0.9180$ ) melts are close to the self-diffusion coefficients, increasing as the temperature increases. This is due to the similarity of self-diffusion coefficients for Al and Mg. Meanwhile, the thermodynamic factor is adjacent to 1, which impacts the interdiffusion coefficient weakly.

The macroscopic shear viscosity  $\eta$  is evaluated using the Stokes-Einstein equation derived for the motion of a macroscopic particle in a viscous medium as follows:

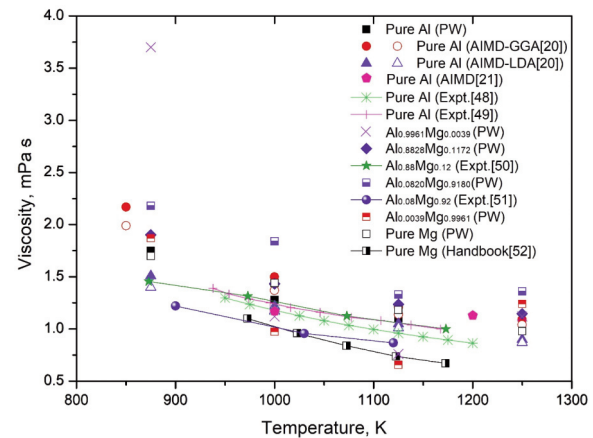
$$\eta = \eta_0 \exp\left(\frac{Q}{k_B T}\right) \quad (6)$$

where  $k_B$  is the Boltzmann's constant, T Kelvin temperature, c is a constant determined by boundary condition (Under slip boundary condition  $c=4$  and nonslip boundary condition  $c=6$ ) [45], and  $r_{SE}$  the hydrodynamic particle radius which is equal to the first peak position of the generalized pair correlation function. In the present work, because of the particles moving freely, there is no shear stress [46, 47], the slip boundary condition is adopted. According to the Equation (6), we obtained the viscosities of liquid  $Al_{1-x}Mg_x$  ( $x=0, 0.0039, 0.1172, 0.9180, 0.9961, 1$ ) melts, seen in Fig. 12. For pure Al melt, there are predicted viscosities  $\eta$  via AIMD approach by Jakse et al. [20] at temperatures 875K, 1000K, 1125K, 1250K, and by Hui et al. [21] at 1000 K, 1200K. Assael et al. [48] and Sato et al. [49] reported the experimental viscosities of Al during 950-1200K and 937-1167K, respectively. As seen in Fig. 12, the present data at 875K and 1000K lie nearly between the data simulated by Jakse et al. [20] via the transverse current correlation function or the Stokes Einstein relation, no matter with GGA or LDA approximation [20]. At 1000K, the present 1.28mPa.s is adjacent to 1.21mPa.s evaluated by Jakse et al. [20] through the Stokes Einstein



**Figure 11.** Interdiffusion coefficient of  $Al_{1-x}Mg_x$  ( $x=0.0039, 0.1172, 0.9180, \text{ and } 0.9961$ ) calculated by Darken equation with self-diffusion coefficients of pure Al and Mg

relation with LAD approximation. At the same temperature, 1.17mPa.s was given by Hui et al. [21] via AIMD simulations, which is in good agreement with 1.17mPa.s at 1000K evaluated via the transverse current correlation functions with LDA approximation by Jakse et al. [20]. Compared with the experimental data, it is seen that the present results 1.28mPa.s and 1.10mPa.s at 1000K and 1125K agree well with the data 1.25mPa.s at 995K and 1.03mPa.s at 1137K measured by Sato et al. [49]. The present calculated results and the measured data by Sato et al. [49] are both a little higher than the data measured by Assael et al. [48]. For  $Al_{0.9961}Mg_{0.0039}$ , at 875K, the viscosity  $\eta$  is much more than that of pure Al, which resulted from the smaller MSD of Mg in  $Al_{0.9961}Mg_{0.0039}$  melt. However, at 1000K and 1125K, the data decrease fast, showing the similar results of pure Al. At 1250K, the datum increases a little higher than the result of pure Al again, the change comes from the larger tracer diffusion coefficients and interdiffusion coefficients. For  $Al_{0.8828}Mg_{0.1172}$ , the viscosities  $\eta$  at the considered temperatures are all a little higher than those of pure Al, seen in Fig. 12. Compared with the experimental data by Lihl et al. [50], the present calculated ones are a little higher.



**Figure 12.** Viscosity calculated from the Stokes-Einstein equation with data of  $Al_{1-x}Mg_x$  ( $x=0, 0.0039, 0.1172, 0.9180, 0.9961, \text{ and } 1$ ) from present AIMD simulations (pure Al: ●,  $Al_{0.9961}Mg_{0.0039}$ : ×,  $Al_{0.8828}Mg_{0.1172}$ : ◆,  $Al_{0.0820}Mg_{0.9180}$ : ▣,  $Al_{0.0039}Mg_{0.9961}$ : ▢), pure Mg: □ and the available data in reference. The calculated viscosity of pure Al by Jakes et al. [20] (AIMD-GGA: ○ - evaluated by the Stokes Einstein relation, ● - evaluated by the transverse current correlation functions, AIMD-LDA: △ - evaluated by the Stokes Einstein relation, ▲ - evaluated by the transverse current correlation functions), the simulated results of Al by Hui et al. [21] (◆), the experimental data of pure Al by Assael et al. [48] (\*) and Sato et al. [49] (+). The measured viscosity of  $Al_{0.8828}Mg_{0.1172}$  by Lihl et al. [50] (★). The measured viscosity of  $Al_{0.0820}Mg_{0.9180}$  by Mi et al. [51] (—■). The viscosity of Mg from Handbook [52] (—●).





However, Lihl et al. [50] measured the viscosities of  $\text{Al}_{0.8828}\text{Mg}_{0.1172}$  are similar with the present evaluated results of pure Al. For  $\text{Al}_{0.0820}\text{Mg}_{0.9180}$  melts, the trend of the present predicted data is similar to the measured data by Mi et al. [51]. However, the differences are large, from 0.5mPa.s to 0.95mPa.s, which is due to the kinematic viscosity measured by Mi et al. [51]. For the dilute  $\text{Al}_{0.0039}\text{Mg}_{0.9961}$  melt, at 875K and 1250K, the viscosities  $\eta$  are a little larger than those of pure Mg evaluated in the present work. At 1000K and 1125K, the results decrease lower than that of pure Mg. The changes come from the larger tracer diffusion coefficients and interdiffusion coefficients. For pure Mg melts, the present predicted viscosities are a little larger than the data from Handbook [52]. The viscosities of all melts show the same tendency, which decreases with the increasing temperature, then increases at 1250K. At the same time, it can be seen that the viscosities  $\eta$  of  $\text{Al}_{0.8828}\text{Mg}_{0.1172}$  and  $\text{Al}_{0.0820}\text{Mg}_{0.9180}$  melts are comparatively higher than pure melts at the present considered temperatures. The present predicted viscosity is fitted by an Arrhenius relation, as well. In the equation,  $\eta_0$  is the prefactor,  $Q$  is the activation energy of melts, which are both shown in Table 1 as reference.

#### 4. Conclusions

In the present work AIMD simulations are used in the present work to investigate the  $\text{Al}_{1-x}\text{Mg}_x$  ( $x=0, 0.0039, 0.1172, 0.9180, 0.9961$ , and 1) melts, including the pair correlation function, the coordination number, diffusion coefficient and viscosity as a function of temperature. The present predicted pair correlation functions of Al and Mg melts, diffusion coefficients and viscosity of Al melt agree very well with the available experimental and theoretical data in literature.

According to the results  $g(r)$  and  $g_{ij}(r)$  of  $\text{Al}_{0.8828}\text{Mg}_{0.1172}$  and  $\text{Al}_{0.0820}\text{Mg}_{0.9180}$ , it can be concluded that Mg atoms aggregate more obviously at 1000K and 1250K for  $\text{Al}_{0.8828}\text{Mg}_{0.1172}$ . For  $\text{Al}_{0.0820}\text{Mg}_{0.9180}$  melt, Al atom segregation is more obvious at 875K and 1000K, Al-Mg neighboring atomic pair is easier to form at 1125K and 1250K.

The tracer diffusion coefficients of Al or Mg in  $\text{Al}_{1-x}\text{Mg}_x$  ( $x=0.1172, 0.9180$ ) melts, and interdiffusion coefficients of  $\text{Al}_{0.8828}\text{Mg}_{0.1172}$  and  $\text{Al}_{0.0820}\text{Mg}_{0.9180}$  melts are close to the self-diffusion coefficients of Al and Mg, increasing linearly as the temperature increases. In dilute melts, the tracer diffusion coefficients of solute atom and the interdiffusion coefficients increase nonlinearly with the increasing temperature.

The viscosities  $\eta$  of the two considered dilute melts are larger than the data of pure melt at 875K, due to the lower MSD and interdiffusion coefficients. Then the data decrease fast to the same level of pure

melt at 1000K and 1125K, and increase over the values of pure melt at 1250K. For  $\text{Al}_{0.8828}\text{Mg}_{0.1172}$  and  $\text{Al}_{0.0820}\text{Mg}_{0.9180}$ , the viscosities  $\eta$  are comparatively larger than those of pure melts at the present considered temperature. The viscosities of all melts show the same tendency, which decreases with the increasing temperature, then increases at 1250K.

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## ATOMSKA STRUKTURA, DIFUZIVNOST I VISKOZITET $Al_{1-x}Mg_x$ RASTOPA DOBIJENE *ab initio* SIMULACIJOM MOLEKULARNE DYNAMIKE

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### Apstrakt

*Ab initio simulacijom molekularne dinamike (AIMD) ispitivani su atomska struktura, difuzivnost i viskoznost  $Al_{1-x}Mg_x$  ( $x=0, 0.0039, 0.1172, 0.9180, 0.9961, 1$ ) rastopa pri temperaturama od 875, 1000, 1125, i 1250K. Rezultati dobijeni simulacijom upoređeni su sa dostupnim eksperimentalnim i izračunatim podacima u literaturi, i slaganje je bilo prihvatljivo. Uzimajući u obzir rezultate parne korelacijske funkcije  $g(r)$ , može se uočiti da se Mg atomi u  $Al_{0.8828}Mg_{0.1172}$  rastopu očitije spajaju pri temperaturama od 1000 i 1250K. Za  $Al_{0.0820}Mg_{0.9180}$  segregacija atoma Al je očitija pri temperaturama od 875 i 1000K. Difuzioni koeficijenti Al ili Mg u rastopima  $Al_{1-x}Mg_x$  ( $x=0.1172, 0.9180$ ), i interdifuzioni koeficijenti  $Al_{0.8828}Mg_{0.1172}$  i  $Al_{0.0820}Mg_{0.9180}$  rastopa su blizu koeficijentima samodifuzije Al ili Mg. Sa povećanjem temperature, difuzivnost raste linearno. U razblaženim rastopima, koeficijent difuzije rastvorenog atoma i interdifuzioni koeficijenti rastu nelinearno sa porastom temperature. Za  $Al_{0.8828}Mg_{0.1172}$  i  $Al_{0.0820}Mg_{0.9180}$  rastope, viskoziteti  $\eta$  su komparativno veći nego za čiste rastope. Viskoziteti svih rastopa se smanjuju sa porastom temperature, a onda rastu pri temperaturi od 1250K. Rezultati dobijeni u ovom radu daju uvid u strukturu Al i Mg legura.*

**Ključne reči:**  $Al_{1-x}Mg_x$  Rastop; AIMD; Difuzivnost; Viskozitet

