For personal use only. This is the accepted manuscript prior to copy editing and page composition. It may differ from the final official version of record: Journal of Molecular Liquids 249 (2018) 470–476 https://doi.org/10.1016/j.molliq.2017.11.061 ©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license

Physicochemical properties of Al, Al-Mg and Al-Mg-Zn alloys

T. Gancarz¹, J. Jourdan², W. Gasior¹, H. Henein²

¹ Institute of Metallurgy and Materials Science, Polish Academy of Science, Krakow, Poland

² Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB, Canada

Corresponding author: tomasz.gancarz@imim.pl

Abstract

The effect of the addition of Mg and Zn to Al on its physicochemical properties was investigated. Using the discharge crucible method, three thermophysical properties (density, surface tension and viscosity) were determined for the Al, Al-Mg and Al-Mg-Zn alloys. The measurements were performed for Al and Al-Mg alloys in Krakow, in the temperature range from 723 to 1053 K, and for the Al-Mg-Zn alloys in Edmonton in the temperature range of 773 to 973K. The obtained viscosity values of pure Al show good agreement with the literature data. The viscosity data of Al-Mg alloys are lower those for pure metal Al and Mg. The addition of Zn to an Al-Mg alloy caused a slight increase in viscosity. For Al-Mg alloys, the surface tension results were compared with the Butler model, and the viscosity with several models.

Keywords: density, surface tension, viscosity, liquid, Al-Mg alloys, Al-Mg-Zn alloys

1. Introduction

The demands of the automotive industry and higher environmental standards (EU Directive) initiated the trend for the use of Al and Mg. Al alloys are characterised by superplasticity [1], their quick plastic forming process (QPF) [2], and a high temperature deformation process [3]. Mg alloys, which are characterised by low density, can be used for applications in the aeronautics

©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license industry [4]. Indeed, most magnesium components are produced using melting and casting processes wherein as-cast products are finished through thermo-mechanical processing or through small machining of the surface [5]. Therefore, good physicochemical properties of the liquid magnesium alloys are essential. A one per cent addition of Zn is almost standard in Mg alloys, and Zn can be dissolved in both the α and β phases with the expectation that this process will strengthen the alloys [6]. The addition of aluminum to Mg or Mg alloys causes increased strength and corrosion resistance [7]. However, investigations of Al-Mg alloys opened new perspectives, as the most commonly used aluminum alloys are the 6000 series containing Mg and Si, and the 5000 series alloys (with high amounts of Mg). The 7000 series, with high Zn content, was recently studied due to their high mechanical properties [8]. Al-Mg-Si alloys show the mechanisms of cluster hardening at room temperature, and can therefore have several applications, such as for automotive body panels [9]. The possibility of using Al-Mg alloys in industry is high, and therefore studies are greatly encouraged. In this work, the physicochemical properties (density, surface tension and viscosity) of Al, Al-Mg and Al-Mg-Zn alloys were studied using the discharge crucible (DC) method, and experimental results were compared with values calculated by different models.

2. Experimental

In this study, alloys were prepared from pure metals: 99.999% Al and Zn, and 99.99% Mg. Measurements in Krakow were obtained using a glove-box with a high purity Ar (6N) atmosphere provided with a purification system (high temperature cleaner with shavings of Ti working at a temperature of 1123 K) [10, 11]. The levels of O₂ and H₂O were below 1ppm as measured by solid-state analysers for oxygen and moisture. The protective gas circulated continuously between the purification system and the glove-box at the rate of 35 m³/h, removing oxygen, water and nitrogen. At the University of Alberta, the experiments were conducted in a protective atmosphere of Ar 99.999% and the chamber was pumped and filled a few times with Ar gas. Samples were heated using a 20kW induction furnace. The details of the apparatus are described in [12]. In both cases, a graphite crucible with a 5 mm drilled orifice at the bottom was used. The DC method was used to determine the density, surface tension and viscosity of pure Al,

©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license Al-Mg and Al-Mg-Zn alloys. The measurements were performed for Al and Al-Mg alloys in Krakow in the temperature range from 723 to 1053K, and for Al-Mg-Zn in Edmonton in the temperature interval from 773 to 973K. The results were compared with literature and modelled data. The measurements obtained from Al served as the calibration data for determining the C_D versus Re for the crucible design used. The calibration tests were conducted in Krakow.

Measurement method

The DC method, proposed by Roach and Henein [13, 14], simultaneously measures surface tension, viscosity and density. The equations are derived from the well-known Bernoulli flow equation for inviscid liquids. The maximal volumetric capacity of the liquid outflow Q (the volume V of the liquid flowing out for time t) through the orifice of radius r, from the container in which the liquid's meniscus is at height h, is proportional to the cross-sectional area of the orifice r_0 and the rate of the flowing liquid $\sqrt{(2gh)}$:

$$Q = \pi r^2 \sqrt{2gh} \tag{1}$$

In the case of viscid liquids, equation (1) is modified by the introduction of the discharge coefficient C_d , which is defined as the ratio of the actual (experimental) rate u_e of the liquid in the orifice of radius r to the theoretical one:

$$C_d = \frac{u_e}{\sqrt{2gh}} \tag{2}$$

Under the conditions of volumetric flow, the coefficient expressed by equation (2) assumes the following form:

$$C_d = \frac{Q_e}{\pi r^2 \sqrt{2gh}} \tag{3}$$

Taking into consideration the effect of the pressure originating from surface tension, the authors [13, 14] proposed the relation below:

$$Q_e = \pi r^2 C_d \sqrt{2 \left(h - \frac{\sigma}{\rho g r_0}\right)} \tag{4}$$

The parameter C_d is related to the Reynolds number Re by the equation which, beside viscosity and density of the liquid flowing through the orifice of radius r, also includes Q_e :

For personal use only. This is the accepted manuscript prior to copy editing and page composition. It may differ from the final official version of record: Journal of Molecular Liquids 249 (2018) 470–476 https://doi.org/10.1016/j.molliq.2017.11.061 ©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license $Re = \frac{2\rho u_e}{\eta} = \frac{2\rho Q_e}{\pi r_0 \eta}$ (5)

The comparison of equations (5) and (6) shows that the parameter C_d is related to the Reynolds number and to Q_e , which is seen after the rearrangement of formula (6) into the following form:

$$Q_e = \frac{\pi r_0 \eta \operatorname{Re}}{2\rho} \tag{6}$$

 C_d is a function of the height of the liquid inside the crucible h by relation (5). Determining Q_e experimentally for a well-known liquid (viscosity, density and surface tension) yields coefficient parameters for the set-up of a crucible/hole (2r) by plotting C_d vs R_e with a linear, parabolic or polynomial regression curve. Coefficient parameters, described by equations (7 and 8), are used to find the last three thermophysical parameters for an unknown alloy.

 C_d is the function of the height of the liquid in crucible *h*. By experimentally determining Q_e for a liquid of known viscosity, one can establish, for the particular diameter of the orifice 2r, the relation between C_d and Re in the form of a linear, parabolic or polynomial relation, and next apply it to calculate the surface tension, density and viscosity. To that end, we determine the height of the column of liquid equation (7):

$$h_e = \frac{1}{2g} \left(\frac{Q_e}{C_d \pi r_0^2} \right)^2 + \frac{\sigma}{\rho g r_0}$$
(7)

next, after we insert into equation (7) a description of the dependences of C_d on Re, which is determined on the basis of the results of the reservoir calibration, e.g. in the form of a second degree polynomial:

$$C_{d} = a_{3}(Re)^{2} + a_{2}(Re) + a_{1}$$
(8)

here: a_i are the coefficient calculated from the calibration results, and we obtain a relation describing *h* as the function of Re:

For personal use only. This is the accepted manuscript prior to copy editing and page
composition. It may differ from the final official version of record:
Journal of Molecular Liquids 249 (2018) 470–476
https://doi.org/10.1016/j.molliq.2017.11.061
©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license

$$h_{e} = \frac{1}{2g} \left(\frac{Q_{e}}{(a_{4} \left(\frac{2\rho Q_{e}}{\pi r_{0}\eta}\right)^{3} + a_{3} \left(\frac{2\rho Q_{e}}{\pi r_{0}\eta}\right)^{2} + a_{2} \left(\frac{2\rho Q_{e}}{\pi r_{0}\eta}\right) + a_{1} \pi r_{0}^{2}} \right)^{2} + \frac{\sigma}{\rho g r_{0}}$$
(9)

By measuring cumulative liquid mass C_m which has flowed out after the given time *t* (load cell measurement), a curve in the form of $C_m = sum(C_i t_i)$ may be obtained, and the relation describing Q_e as a function of C_i may be derived.

$$Q_{e} = \frac{\frac{dC_{m}}{dt}}{\rho}$$
(10)

Equation (9) was used to calculate the parameters of surface tension and viscosity of the studied liquid Al-Mg and Al-Mg-Zn alloys. The numerical scheme used was based on the Hooke–Jeeves method [10].

In this study to obtain density, surface tension and viscosity values of Al-Mg and Al-Mg-Zn alloys, the first step was to determine the appropriate calibration of the crucible for C_d vs Re. Calibration was performed with runs of Al at 973, 993 and 1013 K for collected data mass vs time, and using the programme with literature data for viscosity [15], density [15] and surface tension to obtain coefficient C_d (located in equation (9) $a_1...a_4$). Afterwards, the "averaged" C_d coefficients were used to calculate, using equation (9) density, surface tension and viscosity for Al (T>1073K), Al-Mg and Al-Mg-Zn alloys.

The measurement results of the density and surface tension versus temperature were elaborated by a linear and viscosity using an Arrhenius equation (see Table 1), along with the equation parameters, estimated errors and values calculated at the temperature of 973 K.

3. Results and discussion

3.1 Physicochemical properties

3.1.1 Pure Al

At the beginning were carried out the measurements for pure Al as stated above. The results of density for liquid Al in are shown Fig. 1, and compared with literature data [14-17]. The values

©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license of density compared to earlier data [14] obtained by the same method are almost identical, with an observed difference of less than 1%. The equation for density Al proposed by Assael et al. [17], which is based on the value of density given in the literature, shows the same slope, and the obtained value is in very good agreement (differences below 0.3%) with data obtained in this study. The surface tension (Fig. 2) was shown, and compared with literature data [14, 18-25]. The values of surface tension obtained in this study are very similar to those in the literature, and the differences observed are less than 1%. Observed differences between the surface tension, obtained in this study using the DC method, and those from [14] are lower than 10 mN/m at 973 K. However, with increasing temperature the difference increases to 15 mN/m at 1100 K, which is less than 2%. Mills and Su [18] report surface tension results for pure Al and for Al with an oxygen saturated surface, the latter having lower surface tension values than the former. Work by Garcia-Cordovilla [25] shows that oxygen dissolution in Al decreased its surface tension. The results reported here are consistent with Al having an oxygen saturated surface.

Viscosity results for Al are presented in Fig. 3. These results are in good agreement with the literature data, falling between the data obtained by Gebhardt [15], Assael [17] and Rothwellt [26], Kisunko [27]. The differences in the results obtained for pure Al could be caused by differences in the purity of the protective atmosphere and of the Al. There is a marked difference between the results obtained in this work and those reported by Roach and Henein [14]. This is clearly due to the lower oxygen content in the atmosphere in the experiments that were the foundation for this paper. This result confirms the hypothesis presented by Gancarz et al. [12] that the higher values of viscosity of Al reported by Roach and Henein are due to the oxygen content in the atmosphere. The purity of the metal used, the atmosphere and the method of conducting viscosity measurements for Al occurring in literature were collected by Assael et al. [17], and the viscosity value for Al with the proposed equation shows very good agreement with data obtained in this study.

3.1.2 Al-Mg and Al-Mg-Zn alloys

The measurements for the Al-Mg alloys (compositions: Al38.6Mg, Al52.8Mg and eutectic Al69.2Mg (at. %)) will now be reported. For the Al-Mg-Zn alloys, low content of ~ 2 % Zn (at. %) was selected. Fig. 4 presents the density of Al-Mg and Al-Mg-Zn alloys, which decrease as Mg content increases. The addition of Zn to the Al-Mg alloy resulted in an increase in the

©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license density. The same trends were observed for surface tension, and are shown in Fig. 5. Increased Mg content decreases the surface tension of the Al-Mg alloys. The addition of Zn slightly increases the surface tension of Al-Mg-Zn alloys in comparison to Al-Mg alloys. The reduction of these properties for Al-Mg alloys seems to be the result of the addition of Mg addition. The surface tension and density of Mg are lower than Al, 1.577 (g·cm⁻³) and 2.371 (g·cm⁻³), 541.85 (N·m⁻¹) and 900 (N·m⁻¹) [16], respectively at a temperature of 973 K. The increase of physicochemical properties of Al-Mg-Zn alloys in comparison to Al-Mg alloys is related to the addition of Zn, because at the same temperature it has the highest density and surface tension 6.719 (g·cm⁻³) and 740.8 (N·m⁻¹) [11] (973 K).

The viscosity of Al-Mg and Al-Mg-Zn alloys is shown in Fig. 6. The obtained experimental results-were compared with literature data for Al-Mg alloys [15]. Increased Mg content in Al-Mg alloys involves a decrease in viscosity, and the addition of Zn content to Al-Mg-Zn alloys results in a slight increase, in contrast with the highest viscosity of Zn, which is 2.090 (mPas⁻¹) [11] at 973 K. According to a previous study of the Al-Zn system [29], it was found that increased addition of Zn resulted in an increase in viscosity of Al-Zn alloys. Moreover, the viscosity study of Al-Mg-Zn system by Yakymovych et al. [28] confirms this, showing that, at 973 K, the 10.0Al-55.0Mg-35.0Zn (wt %) has a higher value of viscosity (1.840 (mPas⁻¹)) compared to that for 22.0Al-60.0Mg-18.0Zn (wt %), which is 1.439 mPas⁻¹. However, in the original paper [28], the presented values of viscosity for Al-Mg-Zn alloys shift between the 10.0Al-55.0Mg-35.0Zn and 22.0Al-60.0Mg-18.0Zn alloys, demonstrating the further calculations presented in that study [28]. Viscosity values found for Al-Mg alloys at 973 K (1.21 (mPa's⁻¹)) are lower than those for pure Al and Mg, at 1.06 (mPa's⁻¹) [16] at the same temperature. This may be due to the occurrence of eutectic in the Al-Mg system, similarly to the Sn-Sb system [11, 30] where, for eutectic alloy, the lowest viscosity value was reported.

3.2 Modelling

Density

The ideal solution for density ρ_{Ideal} for the Al-Mg system was calculated using equation (11) [31, 32].

For personal use only. This is the accepted manuscript prior to copy editing and page
composition. It may differ from the final official version of record:
Journal of Molecular Liquids 249 (2018) 470–476
https://doi.org/10.1016/j.molliq.2017.11.061
©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license

$$\rho_{Ideal} = \frac{1}{\frac{y_{Al}}{\rho_{Al}} + \frac{y_{Mg}}{\rho_{Mg}}}$$
(11)

where y_{Al} and y_{Mg} are the concentrations of Al and Mg (in wt %/100), and ρ_{Al} , ρ_{Mg} are the densities of the pure components Al and Mg as taken from [16].

One of the model for calculating density was proposed by Brillo and Egry [33]:

$$\rho = \frac{X_{Al} M_{Al} + X_{Mg} M_{g}}{X_{Al} \frac{m_{Al}}{\rho_{Al}} + X_{Mg} \frac{m_{Mg}}{\rho_{Mg}} + V_E}$$
(12)

where: X_{Al} , X_{Mg} are the atomic concentrations of Al and Mg, $m_{Al}=26.981$ (g·mol⁻¹) and $m_{Mg}=24.305$ (g·mol⁻¹) are the corresponding molar masses, and ρ_{Al} , ρ_{Mg} are the densities of the pure components Al and Mg as taken from [16]. V_E is the excess volume, which is the difference between the real volume V and the ideal volume V_{Ideal} [33]. The authors [33] assume that the excess volume V_E depends on the concentration according to

$$V_E = X_{Al} X_{Mg} V_X \tag{13}$$

with V_X being a type of interaction parameter. In our case, the value of V_X obtained from such fit is approximately 0.00247 (m³·mol⁻¹).

Fig. 7 presents the isothermal at 973K of density vs. X_{Mg} for Al-Mg alloys. The obtained data for Al38.6Mg are the same as the value obtained from the ideal solution, and slightly higher compared to the Brillo model. A different character is observed for Al52.8Mg and Al69.2Mg, with the obtained values of density being lower compared to the ideal solution and the Brillo model. The lower density could correspond to the phase diagram of the Al-Mg system [34], where the chemical composition of the Al52.8Mg alloy corresponds to the formation of the Al₁₂Mg₁₇ phase and the Al69.2Mg alloy eutectic point.

Surface tension

©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license The Butler model [35], described in our previous work [12], was used to estimate the surface tension of Al-Mg alloys. This model [35] was used to analyse the surface tension, with the molar surface area, using the following equation:

$$\sigma = \sigma_{Al} + \frac{RT}{A_{Al}} ln \frac{(1 - x_{Mg}^{S})}{(1 - x_{Mg}^{B})} + \frac{1}{A_{Al}} [G_{Al}^{E,S}(T, X_{Mg}^{S}) - (G_{Mg}^{E,B}(T, X_{Mg}^{B})] =$$

$$= \sigma_{Mg} + \frac{RT}{A_{Mg}} ln \left(\frac{X_{Mg}^{S}}{X_{Mg}^{B}}\right) + \frac{1}{A_{Mg}} [G_{Mg}^{E,S}(T, X_{Mg}^{S}) - G_{Mg}^{E,B}(T, X_{Mg}^{B})]$$
(14)

Where R is the gas constant in (J/mol K), T is the temperature in (K), σ_{A1} and σ_{Mg} are the surface tensions of pure Al and Mg in (mN/m), A_i is the molar surface area of a monoatomic layer of pure liquid (i=Al or Mg) in (m²), and X_{Mg}^S and X_{Mg}^B are the mole fractions of Mg in the surface and the bulk phase, respectively, $G_i^{E,S}$ (T, X_i) and $G_i^{E,B}$ (T, X_i) are the partial excess Gibbs energies of component *i* in the surface and bulk phases as functions of T and X_i, with X_i being the mole fraction of component *i* in (J/mol). The Al surface tension data from this work, and Mg surface tension values from [18], used for the calculation and the thermodynamics data, were taken from [34, 36].

Fig. 8 shows the isotherm at 973 K of surface tension, and demonstrates that the experimental data is in very good agreement with data from the Butler model. A slightly deviation in experimental data of surface tension from those calculated using the Butler model (14) for Al-Mg alloys is observed, therefore the differences amount less than ~1%. As presented in Fig. 8, the Butler model ideal solution, was calculated for G_i^{E} set to zero. The surface tension from [37] for low Mg content in Al-Mg alloys up to 8.9 (at. %) shows very good agreement with Butler models. The data of surface tension of Al-Mg alloys was taken for alloys with stable O₂ content. The value of surface tension for unoxidised Al-Mg alloys is higher (~250 (N·m⁻¹)) compare to the alloys with dissolved O₂. Therefore, using the maximum bubble pressure method [37], it can be shown that surface tension values for different O₂ content from 62 up to 220 (ppm) are similar, after time of 10 (s), as for O₂ content from 300 (ppm). Taking into account the measurements using the DC method, the obtained value for Al-Mg alloys (with dissolved O₂) show very good agreement with the Butler model.

©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license *Viscosity*

The viscosity of Al-Mg alloys at 1073K was compared to the literature data [15] and calculated using several models, as presented in Fig 9. The following models were used to calculate viscosity: Kozlov, Romanov and Petrov (KRP) [38], Du Sichen, Boygen and Seetharaman (SBS) [39], Seetharaman and Du Sichen (SS) [40], Kaptay (K) [41], Morita-Iida-Ueda (MIU) [42], Moelwyn-Hughes (MH) [43], Gasior and Moser (G1) [44], and Gasior (G2) [45] (they are described in our previous work [12]), which are given by the following equations:

KRP:
$$\eta = \exp\left[\sum_{i=1}^{2} X_i \ln(\eta_i) - \frac{\Delta H_m}{3RT}\right]$$
 (15)

SBS:
$$\eta = Aexp\left(\frac{G^*}{RT}\right)$$
 $A = \frac{hN\rho}{M}$ $G^* = \sum_{i=1}^2 X_i G_i^* + RT \sum_{i=1}^1 \sum_{k=i+1}^2 X_i X_k + \Delta G'$ (16)

SS:
$$\eta = \operatorname{Aexp}\left(\frac{G^*}{RT}\right)$$
 $A = \frac{hN\rho}{M}$ $G^* = \sum_{i=1}^2 X_i G_i^* + 3RT \sum_{i=1}^1 \sum_{k=i+1}^2 X_i X_k + \Delta G'$ (17)

K:
$$\eta = \frac{hN}{\sum_{i=1}^{2} X_{i}V_{i} + \Delta V^{E}} \exp\left(\frac{\sum_{i=1}^{2} X_{i}\Delta G_{i}^{*} - \alpha\Delta H_{m}}{RT}\right)$$
(18)

MIU:
$$\eta = (\eta_1 X_1 + \eta_2 X_2) \left\{ 2 \left[1 + \frac{X_1 X_2 (\sqrt{M_1} - \sqrt{M_1})^2}{(X_1 \sqrt{M_1} + X_2 \sqrt{M_1})^2} \right]^{\frac{1}{2}} - 1 - \frac{5 X_1 X_2 (d_1 - d_2)^2}{X_1 d_1^2 + X_2 d_2^2} - \Delta \right\}$$
(19)

MH:
$$\eta = (\eta_1 X_1 + \eta_2 X_2) \left(1 - 2 \frac{\Delta H_m}{RT} \right)$$
 (20)

G1:
$$\eta = (\eta_1 X_1 + \eta_2 X_2) \left(1 - k \frac{S^{ex}}{R} \right) \quad k = 1 + 2 \sqrt{\frac{(\eta_1 - \eta_2)^2}{(\eta_1 + \eta_2)^2}}$$
 (21)

G2:
$$\eta = (\eta_1 X_1 + \eta_2 X_2) \left(1 - 2 \frac{S^{ex}}{R} \right)$$
(22)

In Equations 15-22, the symbols mean: $\eta_{I(2)}$ and $X_{I(2)}$ - the viscosity and mole fraction of component 1 and 2, G^* - Gibbs activation energy, $\Delta G'$ - change of Gibbs activation energy, T -

©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license the temperature, $G^*{}_1$ and $G^*{}_2$ - the activation energy of components, R - gas constant, ρ - alloy density, N - Avogadro number, h - Planck constant, M - atomic mass of alloy, α -coefficient, which, according to the author, amounts to 0.155±0.015, V_i and ΔV^E refer to the molar volume of alloy components and the excess molar volume of the alloy, and S^{ex} to the excess entropy of the liquid solution. The data of density and viscosity for Al come from this work, and for Mg from [15], for the calculation of viscosity values for Al-Mg alloys. The thermodynamics data were taken from [34].

The viscosity results obtained in this work for Al-Mg alloys are in good agreement with those presented in [15] and [46]. The model of Sichen et al. [39] and Seetharaman and Du Sichen [40], which has negative deviations from the ideal solution, shows the best fit with the experimental data for viscosity. The viscosity obtained by Lihl et al. [47] for the Al-Mg system is much higher than in this study and [15, 46], and has a positive deviation from the ideal solution. However, the method for measuring viscosity in [15] and [47] used the same oscillating viscometer. The same method was used by Sato et al. [48], but only one alloy of Al5.5Mg (at. %) was measured. The obtained value of viscosity is similar to [47], and shows negative deviation from linear viscosity for the Al-Mg system. The highest value of viscosity of the Al-Mg system was obtained in [49], using the same equipment (torsional oscillation viscometer) as in [47, 48]. The authors of [49] explain such value of viscosity by the glass-forming ability for metallic melt. The changes of viscosity are correlated with fluid clusters in the melts with increasing Mg content, as the Mg atoms start to be dissolved in pure Al clusters [49]. When the Mg content is higher, the dispersed fluid clusters in the melt and obstructs the formation of a periodic structure, while favouring the formation of an amorphous structure [49]. Such increase of viscosity (2.345 (mPa's⁻¹)) for All1Mg compared to 1.766 (mPa⁻s⁻¹) for Al9Mg alloy (at. %), could be interpreted as short-range ordering in liquid, but the chemical composition of the measured alloy is so far from that of the intermetallic compounds β - Al36.2Mg [34] it makes the value obtained improbable. The lowest viscosity of the Al-Mg system, given in Jones et al. [50], was obtained using a viscometer based on the principle of an outer rotating cylinder. The obtained value for pure Al is two times lower, which caused the viscosity for Al-Mg alloys to have such low value.

@2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license **Conclusions**

The experimental data of the density, surface tension and viscosity of Al, Al-Mg and Al-Mg-Zn alloys obtained in this study using the DC method show good agreement with the literature data [15, 46]. The values of density, surface tension and viscosity decrease with the addition of Mg to Al-Mg alloys. The addition of Zn to Al-Mg alloys causes an increase of density and viscosity, with an apparently slight effect on surface tension. The surface tension calculated using the Butler model is in good agreement with experimental data. The best matching of viscosity calculated for Al-Mg alloys was obtained using the Sichen et al. [39] and Seetharaman and Du Sichen [40] models.

For the viscosity of Al-Mg alloys, the physicochemical properties of pure elements (especially Al) have the greatest impact, irrespective of the method used to measure viscosity. In addition, the purity of elements and the experimental atmosphere (taking into account the high affinity of Al and Mg to oxygen), have a high impact on the obtained value of viscosity for the Al-Mg system.

Acknowledgments

This work was financed by the Ministry of Science and Higher Education of Poland, within the project No. 630/N Kanada/2009 "Using a new method for simultaneous measurement of surface tension, density and viscosity for use in soldering materials and new alloys for the automotive industry". Funding from the Natural Science and Engineering Research Council of Canada is also greatly acknowledged.

References

- 1. Bampton CC, Ghosh AK, Mahoney MW. In: Pearce R, Kelly L, editors. Superplasticity in aerospace aluminum. Southampton, UK: Ashford Press, (1985)
- P.A. Friedman, W.B. Copple, Superplastic response in Al-Mg sheet alloys, J. Mater. Eng. Perf., 13 (2004) 335–347
- H. Todaa, Z. Shamsudina, K. Shimizua, K. Uesugi, A. Takeuchi, Y. Suzuki, M. Nakazawac, Y. Aoki, M. Kobayashi, Cavitation during high-temperature deformation in Al–Mg alloys, Acta Materialia 61 (2013) 2403–2413

©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license

- T. Dursun, C. Soutis, Recent developments in advanced aircraft aluminium alloys, Mater. Des. 56 (2014) 862–871
- 5. M. Paliwal, I-H. Jung, The evolution of the growth morphology in Mg–Al alloys depending on the cooling rate during solidification, Acta Materialia 61 (2013) 4848–4860
- I.J. Polmear, Recent Developments in Light Alloys, Materials Transactions, JIM 37 (1) (1996) 12–31
- 7. ASM, Metals Handbook 10th Edition, 2 (1990) 455–479
- 8. A. H. Van den Boogaard, Thermally Enhanced Forming of Aluminium Sheet, PhD. Thesis, University of Twente (2002)
- M.J. Starink, L.F. Cao, P.A. Rometsch, A model for the thermodynamics of and strengthening due to co-clusters in Al–Mg–Si-based alloys, Acta Materialia 60 (2012) 4194–4207
- T. Gancarz, Physicochemical Properties of Sb-Sn-Zn Alloys, J. of Electron. Mater. 43 (2014) 4374-4385
- T. Gancarz, W. Gasior, H. Henein, Physicochemical Properties of Sb, Sn, Zn, and Sb–Sn System, Int. J. Thermophys. 34 (2013) 250-266
- T. Gancarz, W. Gasior and H. Henein, The Discharge Crucible method for making measurements of the physical properties of melts: an overview, Int. J. Thermophys., 35 (2014) 1725-1748
- S.J. Roach, H. Henein, A dynamic approach to determining the surface tension of a fluid, Can. Metall. Q. 42 (2003) 175-186
- 14. S.J. Roach, H. Henein, A New Method to Dynamically Measure the Surface Tension, Viscosity, and Density of Melts, Metall. Mater. Trans. B 36 (2005) 667-677
- E. Gebhardt, K. Ditering, Effect of alloying additions on the viscosity of aluminum, Z. Metallkde, 50 (1959) 379
- 16. W. F. Galo, T. C. Totemeier, Smithells Metals Reference Book, Eight Edition, Elsevier and ASM International, (2004)
- M. J. Assael, K. Kakosimos, R. M. Banish, J. Brillo, I. Egry, A. Nagashima, Y. Sato, W.
 A. Wakeham, Reference Data for the Density and Viscosity of Liquid Aluminum and Liquid Iron, J. Phys. Chem. Ref. Data 35 (2006) 285-300

©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license

18. K.C. Mills, Y.C. Su, Review of surface tension data for metallic elements and alloys: Part

1 – Pure metals, Int. Mater. Rev. 51 (2006) 329-351

- 19. Yu. V. Naidich, V. N. Eremenko, Fiz. Met. Metalloved. 11 (1961) 883-931
- 20. E. S. Levin, G. D. Ayushina, P. V. Geeld, M.A. Ryss, V.F. Seryii in Fiz. Khim. Poverh. yav. Temp. (ed. V.N. Eremenko), (1971) Kiev, Naukowv Dumka. 51
- 21. S. P. Yatsenko, V. I. Kononenko, A. L. Sukhman, Experimental Studies of the Temperature Dependence of the Surface Tension and Density of Sn, In, Al and Ga, High Temp. 10 (1972) 55-58
- 22. N. Eustahopoulos, J. C. Joud, P. Desre, J. M. Hicter, The wetting of carbon by aluminium and aluminium alloys, J. Mater. Sci. 9 (1974) 1233-1242
- 23. G. Lang, Effect of Added Elements on the Surface Tension of High-Purity Al, Aluminium, 50 (1974) 731-761
- L. Goumiri, J. C. Joud, P. Desre, J.M. Hicter, Tensions superficielles d'alliages liquides binaires présentant un caractère dimmiscibilité: Al-Pb, Al-Bi, Al-Sn et Zn-Bi, Surf. Sci. 83 (1979) 471-486
- 25. A. Pamies, C. Garcia-Cordovilla, E. Louis, The measurement of surface tension of liquid aluminium by means of the maximum bubble pressure method: the effect of surface oxidation, Metall. 18 (1984) 869-872
- 26. E. Rothwell, JIM, 90 (1961-62) 389-394
- 27. V.Z. Kisunko, I.A. Novokhatskii, A.Z. Beloborodov, Y.B. Bychkov, A.I. Pogorelov, Viscosity of Secondary Aluminum Alloys With Silicon, Manganese, Copper and Magnesium, Tsvetnte Metally (Non-Ferrous) 24 (1983) 84-85
- 28. A. Yakymovych, Yu. Plevachuk, V. Sklyarchuk, Influence of Zn and Al additions on viscosity of liquid Mg, Materials Science and Technology Conference and Exhibition 2013, Montreal, Quebec, Canada, Magnesium Technology, MS & T (2013) 1600-1605
- 29. M. Trybula, T. Gancarz, W. Gasior, Density, surface tension and viscosity of liquid binary Al-Zn and ternary Al-Li-Zn alloys, Fluid Phase Equilibr. 421 (2016) 39-48
- T.P. Yao, V. Kondic, The viscosity of molten tin, lead, zinc, aluminium, and some of their alloys, J. Inst. Met. 81 (1952–1953) 17

- ©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license
- 31. T. Gancarz, The physicochemical properties of liquid Ga-Zn alloys, Fluid Phase Equilibr.

442 (2017) 119-124

- T. Gancarz, Density, surface tension and viscosity of Ga-Sn alloys, J. Mol. Liq. 241 (2017) 231-236
- 33. J. Brillo, I. Egry, Density and excess volume of liquid copper, nickel, iron, and their binary alloys, Z. Metallkd. 95 (2004) 691-697
- 34. Y. Zhong, M. Yang, Z-K. Liu, Contribution of first-principles energetics to Al–Mg thermodynamic modeling, Calphad 29 (2005) 303–311
- 35. J.A. Butler, Proceedings of the Royal Society of London series A, CXXXV (1932) 348
- 36. P. Lianga, T. Tarfab, J.A. Robinsonc, S. Wagnera, P. Ochinb, M.G. Harmelinb, H.J. Seiferta, H.L. Lukasa, F. Aldingera, Experimental investigation and thermodynamic calculation of the Al-Mg-Zn system, Thermochimica Acta 314 (1998) 87-110
- 37. C. Garcia-Cordovilla, The surface tension of liquid pure aluminium and aluminium-magnesium alloy, J. Mater. Sci. 21 (1986) 2787–2792
- 38. L.Ya. Kozlov, L. M. Romanov, N. N. Pietrov, Prediction of multicomponent metallic melt viscosity, Izv. Vuzov. Chernaya Metall. 3 (1983) 7
- 39. D. Sichen, J. Bygden, S. Seetharaman, A model for estimation of viscosities of complex metallic and ionic melts, Metall. Mater. Trans. 25B (1994) 519-525
- 40. S. Seetharaman, D. Sichen, Estimation of the viscosities of binary metallic melts using Gibbs energies of mixing, Metall. Mater. Trans. 25B (1994) 589-595
- 41. G. Kaptay, Proc. of MicroCAD 2003 Int. Section Metall., Univ. of Miskolc, Hungary, (2003) 23
- 42. Z. Morita, T. Iida, M. Ueda, Liquid Metals, Ins. Phys. Conf. Ser. 30, Bristol (1977), 600
- 43. E. A. Moelwyn-Hughes, Physical Chemistry, Pergamon Pres, Oxford, 1961
- 44. W. Gasior, Z. Moser, Polska Metalurgia w Latach 2006-2010, 2010 (in Polish) ISBN 978-83-60958-64-3
- 45. W. Gasior, Viscosity modelling of binary alloys: Comparative studies, Calphad 44 (2014) 119-128
- 46. W. Nozdryov, W. Smremouso, W. Tekuche, J. Physic. Chem. (in Russian) 5 (1979) 1199-1202
- 47. F. Lihl, E. Nachtigall, A. Schwaiger, Z. Metallkd. 59 (1968) 213-219

©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license

- 48. T. Sato, S. Munakata, Studied on the viscosity of molten metals and alloys (III). The density of molten Sb-Sn and Pb-Sn Alloys and viscosity coefficients of molten Sb-Sn, Sb-Pb and Al-Cu alloys, Bull. Res. Inst. Miner. Dressing Metall. Tohoku Univ. 11 (1955) 183
- 49. W. YuQing, W. YuQin, B. XiuFang, Composition dependence of viscosity for $Al_{(1-x)}Mg_x$ ($0 \le x \le 0.1$) alloys, Chinese Sci. Bull.52 (2007) 1441-1445
- 50. W. Jones, W. Bartlett, The viscosity of aluminium and binary aluminium alloys, J. Inst. Met. 81 (1952-53) 145-152

Table 1. The coefficients and their standard deviation for the linear temperature dependency with density (ρ =A+B·T) for Al, Al-Mg, Al-Mg-Zn alloys. In addition, their density and standard deviations are calculated at 973 K.

	$\rho = A + B T, [\text{kg·m}^{-3}]$						
at. %	Α	δA	В	δB	ρ (973 K)	δho	
Al	2674.3	14.9	-0.31	0.01	2370.5	1.5	
A138.6Mg	2772.1	8.8	-0.80	0.01	1995.2	1.4	
A152.8Mg	2726.0	27.9	-0.99	0.03	1767.4	3.9	
Al63.2Mg	2441.3	11.4	-0.80	0.01	1662.4	2.8	
Al38.0MgZn1.85	2965.2	40.7	-0.93	0.05	2060.4	7.3	
Al51.7MgZn2.0	2882.4	32.9	-1.06	0.03	1851.0	3.9	
Al67.8MgZn2.0	2636.6	17.5	-0.94	0.02	1722.0	3.2	

©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license **Table 2.** The coefficients of linear temperature dependencies of surface tension (σ =A+B[·]T) for Al, Al-Mg, Al-Mg-Zn alloys. Standard deviations and surface tension values, calculated at 973

	1					
	$\sigma = A + B T, [mN m^{-1}]$					
at. %	A	δA	В	δB	σ (973 K)	$\delta \sigma$
Al	1036.1	11.1	-0.177	0.011	863.4	1.0
A138.6Mg	902.2	7.4	-0.228	0.009	680.2	1.2
A152.8Mg	845.5	8.2	-0.213	0.010	638.3	1.2
Al63.2Mg	769.2	6.9	-0.172	0.008	601.8	1.7
Al38.0MgZn1.85	926.7	9.9	-0.249	0.011	684.1	1.8
Al51.7MgZn2.0	879.3	9.4	-0.242	0.010	644.0	1.1
Al67.8MgZn2.0	798.9	9.4	-0.195	0.006	609.1	1.1

K.

©2017. This manuscript version is made available under the CC-By-NC-ND 4.0 license **Table 3.** Coefficients (A, E_a) of Arrhenius equations in relation to the temperature dependence of viscosity (η =A·exp(- E_a /RT)) for Al, Al-Mg, Al-Mg-Zn alloys. Standard deviations and viscosity values, calculated at 973 K.

	$\eta = A \cdot e^{E/RT}, [\text{mPa} \cdot \text{s}]$					
at. %	A	δA	Ε	δE	η (973 K)	δη
Al	0.191	0.001	14982.4	96.2	1.277	0.067
A138.6Mg	0.131	0.003	14710.6	54.6	0.838	0.059
A152.8Mg	0.144	0.004	14327.4	45.3	0.882	0.068
A163.2Mg	0.157	0.002	13046.4	47.1	0.817	0.047
Al38.0MgZn1.85	0.114	0.002	16928.9	58.5	0.920	0.047
Al51.7MgZn2.0	0.093	0.001	19124.5	70.5	0.991	0.004
Al67.8MgZn2.0	0.143	0.003	14975.1	49.3	0.912	0.008

Figure Captions

Fig. 1. Temperature dependence of the density of liquid Al compared with literature data.

Fig. 2. Temperature dependencies of the surface tension of liquid Al compared with literature data.

Fig. 3. Temperature dependence of Al viscosity. The equation describes average values based on data in the studies of Gebhardt et al. [15] and Yao et al. [26].

Fig. 4. Temperature dependence of density for Al, Al-Mg and Al-Mg-Zn alloys.

Fig. 5. Temperature dependence of surface tension of Al, Al-Mg and Al-Mg-Zn alloys.

Fig. 6. Temperature dependence of viscosity of Al, Al-Mg and Al-Mg-Zn alloys.

Fig. 7. Density isotherms at 973K of Al-Mg alloys compared with data from the Brillo model [31].

Fig. 8. Surface tension isotherms at 973K of Al-Mg alloys calculated by the Butler model [32].

Fig. 9. Viscosity of isotherms at 973K of Al-Mg alloys compared with literature data and different models.

















