

Densities and Molar Volumes of Solid Lithium-Magnesium (Li-Mg) Alloys

W. Gasior, Z. Moser, and J. Pstruś
 Institute of Metallurgy and Materials Science
 Polish Academy of Sciences
 30-059 Kraków, Reymonta St. 25, Poland

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Densities of solid Mg and Li-Mg alloys were measured for five compositions of mole fractions of Li equal to 0.05, 0.1, 0.15, 0.20, and 0.25, respectively, by the dilatometric method. The curvilinear dependence of the density on temperature (room temperature up to 873 K) was observed for all investigated alloys. Results could be described by parabolic equations. The molar volumes of Li-Mg alloys were calculated from the density measurements. It has been found that the densities of solid Li-Mg alloys show positive deviations from linearity, and the molar volumes exhibit negative deviations from linear dependence for all samples in the experimental concentration range. It was possible to describe the dependence of density on temperature and concentration by a polynomial. Coefficients of thermal expansion were calculated and discussed. The density of the (Li) phase along the (Li)/[(Mg) + (Li)] boundary was calculated and described by a temperature-dependent polynomial of the third power.

Introduction

In the authors' earlier article on densities of the Al-Li alloys [98Gas], they summarized the previous references to Li alloys investigated by emf and calorimetric techniques. The starting point of these studies was the evaluation of binary Li alloys [76Smi] based on information from various references. Subsequent publications tend to concentrate on experimental studies of solid alloys to test phase equilibria predicted by phase diagram calculations or on extension of equilibrium thermodynamic studies to include diffusion. Diffusion data play an important role in solidification processes; thus solid-state diffusion should be taken into account in calculations of solidification paths. Diffusion phenomena are also crucial for obtaining alloys such as Li-Mg and Cu-Li by direct contact of pure components. In the case of Li-Mg or Cu-Li, the contact is with Li vapor [97Dud]; this method is promising in battery applications.

Precision of calculations of diffusion coefficients in any alloy requires a knowledge of the values of the molar volumes of components in the alloys. Therefore, having in mind studies on the Al-Li-Mg system and its constituent binaries, the authors have published data on densities and molar volumes of Al-Li [98Gas]. The present investigation continues with measure-

ments on Li-Mg solid alloys. It should be noted that density, compressibility, specific heat, and diffraction data for liquid Li-Mg alloys have been published by [80Rup].

Experimental

Density measurements of solid Li-Mg alloys were made dilatometrically by measuring changes in axial dimensions of cylindrical samples as functions of temperature. The measurements provide direct data for the linear expansion coefficients (α), which when multiplied by a factor of 3 yield values of the volume expansion coefficients (β) for randomly oriented polycrystalline materials. Volumes and densities were calculated at any given temperature with the following equations:

$$V = \pi (r_0 + \Delta r)^2 (h_0 + \Delta h) \quad (\text{Eq 1})$$

$$\rho = \frac{m}{V} \quad (\text{Eq 2})$$

$$V_m = \frac{M_{\text{Mg}} X_{\text{Mg}} + M_{\text{Li}} X_{\text{Li}}}{\rho} \quad (\text{Eq 3})$$

Table 1 Temperature Dependencies of Solid Li-Mg Alloys Together with Standard Deviations and Densities Calculated at 298.16, 600, and 850 K

| X_{Li} | $\rho = a + bT^2, \text{ g/cm}^3$ | $\sigma, \text{ g/cm}^3$ | $\rho_{298.16\text{K}}, \text{ g/cm}^3$ | $\rho_{600\text{K}}, \text{ g/cm}^3$ | $\rho_{850\text{K}}, \text{ g/cm}^3$ |
|-----------------|--------------------------------------|--------------------------|---|--------------------------------------|--------------------------------------|
| 0.00 | $1.7379 - 1.2555 \times 10^{-7} T^2$ | 0.0016 | 1.7267 | 1.6927 | 1.6472 |
| 0.05 | $1.6923 - 1.1375 \times 10^{-7} T^2$ | 0.0022 | 1.6822 | 1.6514 | 1.6101 |
| 0.10 | $1.6443 - 1.2900 \times 10^{-7} T^2$ | 0.0021 | 1.6328 | 1.5979 | 1.5511 |
| 0.15 | $1.6061 - 1.1690 \times 10^{-7} T^2$ | 0.0015 | 1.5957 | 1.5640 | 1.5216 |
| 0.20 | $1.5755 - 1.2128 \times 10^{-7} T^2$ | 0.0033 | 1.5647 | 1.5318 | 1.4879 |
| 0.25 | $1.5442 - 1.0745 \times 10^{-7} T^2$ | 0.0034 | 1.5346 | 1.5055 | 1.4666 |

where V is the sample volume, Δh and Δr are changes of height and radius of the sample after heating to T from T_0 arbitrarily chosen as 298.16 K, h_0 and r_0 are height and radius of the sample at the reference temperature T_0 , ρ is the density, V_m is the molar volume, M_{Mg} , M_{Li} are atomic masses of Mg and Li and X_{Mg} , X_{Li} are mole fractions of Mg and Li.

Measurements were made on cylindrical samples of 10 mm in diameter and 45 mm high. Changes of size were measured by a cathetometer with an accuracy of ± 0.002 mm. Measurements were performed on Mg of 99.99 wt.% purity. The Li used in the preparation of alloys was of 99.95 wt.% purity. The temperature was measured by a Pt-PtRh10 thermocouple. The alloys were prepared in a glove box with an atmosphere of high-purity argon in which the amounts of oxygen and water were lower than 1 ppm, and nitrogen (not detected) was removed by a titanium sponge contained in a separate purification system.

Results and Discussion

Results of the density measurements for solid Mg and solid Li-Mg alloys are shown in Fig. 1. It is seen that the temperature dependence of density for the alloys at all investigated compositions has a curvilinear character similar to that of pure Mg. Hence a parabolic equation of the following form:

$$y = a + bT^2 \tag{Eq 4}$$

was used to describe the temperature dependence of densities. Parameters a and b were evaluated by the least squares method. The fits to Eq 4 for all investigated compositions are presented in Table 1 together with the standard deviations and density values calculated at 298.16, 600, and 850 K. Experimental results obtained for Mg in this work show parabolic changes with temperature in contrast to results from [79Met], which have linear temperature dependence (the measurements were done only below 673 K) and are higher at the lowest and the highest temperature by about 0.01 and 0.015 g/cm³, respectively.

The equations in Table 1 were used to calculate densities for all compositions at 298.16, 400, 650, and 850 K. These were then used with the least squares method to evaluate a temperature/composition relation in the form:

$$\begin{aligned} \rho = & \rho_{Mg} (1 - X_{Li}) + \rho_{Li} X_{Li} \\ & + (-0.661 + 0.811 \times 10^{-3} T - 0.715 \times 10^{-6} T^2) X_{Li} \\ & + (9.431 - 0.895 \times 10^{-3} T + 0.715 \times 10^{-6} T^2) X_{Li}^2 \\ & + (-30.822 + 0.837 \times 10^{-4} T) X_{Li}^3 + 22.060 X_{Li}^4 \end{aligned} \tag{Eq 5}$$

(in g/cm³)

where ρ , ρ_{Mg} , and ρ_{Li} are the respective densities of Mg-Li alloys, magnesium, and lithium, T is the temperature in Kelvin, and X_{Li} is the mole fraction of Li. The estimated errors amounted to 0.014 g/cm³. From the data in [60Gme] the following dependence of the density of solid Li was calculated [98Gas] and used in our calculations:

$$\rho_{Li} = 0.5623 - 9.6869 \times 10^{-5} T \quad (\text{in g/cm}^3) \tag{Eq 6}$$

The densities and molar volumes calculated from Eq 5 and 3 at temperatures between 298.16 and 850 K are presented in Fig. 2 and 3. The density isotherms show for all investigated alloys a

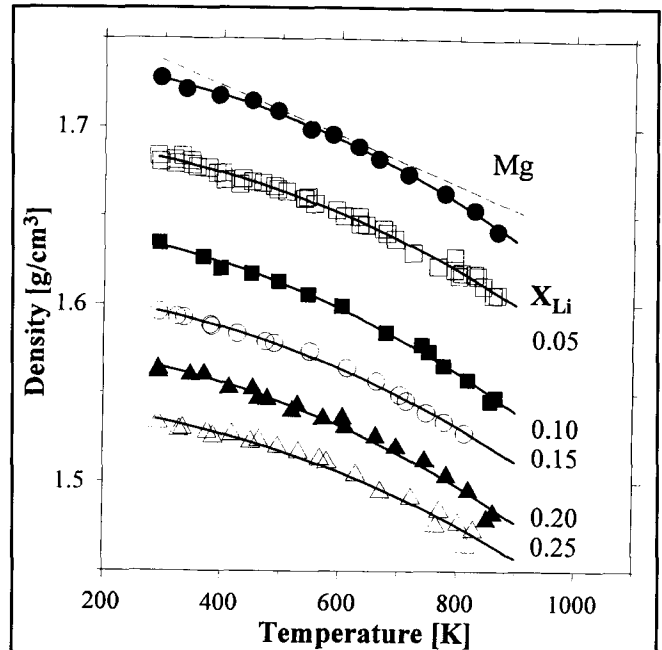


Fig. 1 Temperature dependence of the density of solid Li-Mg alloys. Data points, data from this study; solid line, calculated from the temperature dependence of densities (Table 1); dashed line, [79Met].

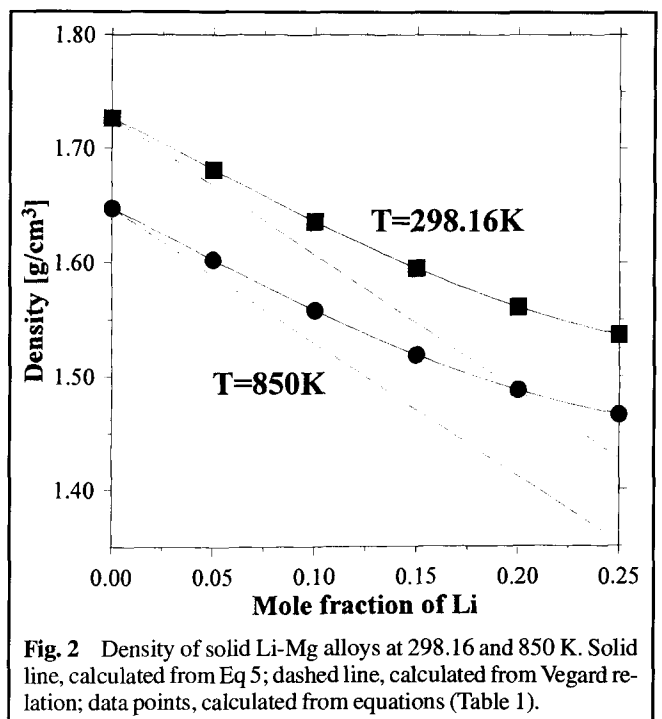


Fig. 2 Density of solid Li-Mg alloys at 298.16 and 850 K. Solid line, calculated from Eq 5; dashed line, calculated from Vegard relation; data points, calculated from equations (Table 1).

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positive deviation from additivity that increases gradually, reaching from 0.1 at 298.16 K to $\sim 0.115 \text{ g/cm}^3$ at 850 K at $X_{\text{Li}} = 0.25$.

Molar volumes of Li-Mg solid alloys calculated from the measured densities and from Eq 5 are presented in Fig. 3. Negative excess volume and its increase in absolute value with

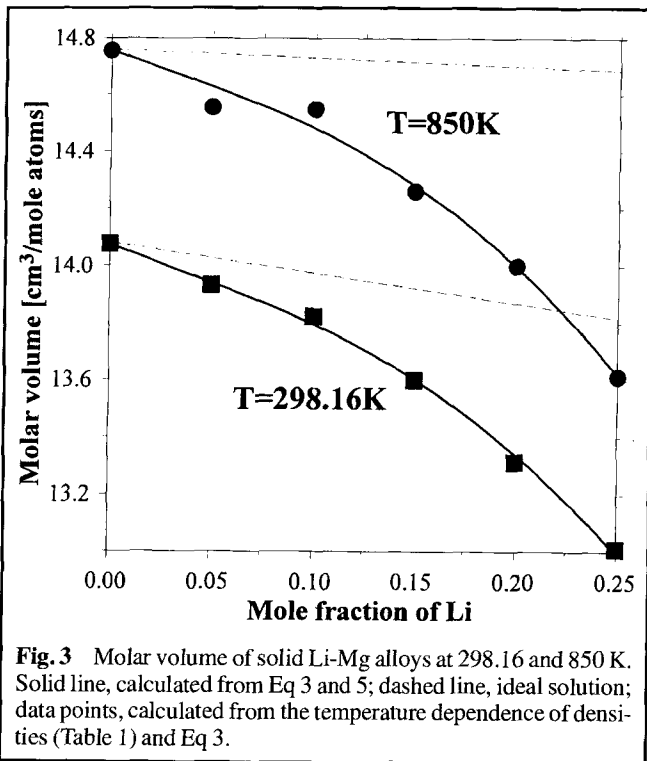


Fig. 3 Molar volume of solid Li-Mg alloys at 298.16 and 850 K. Solid line, calculated from Eq 3 and 5; dashed line, ideal solution; data points, calculated from the temperature dependence of densities (Table 1) and Eq 3.

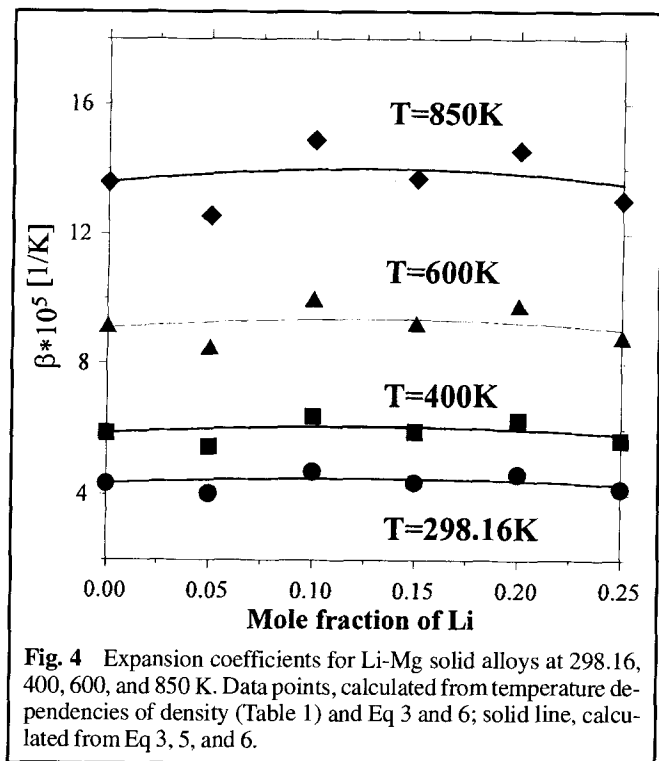


Fig. 4 Expansion coefficients for Li-Mg solid alloys at 298.16, 400, 600, and 850 K. Data points, calculated from temperature dependencies of density (Table 1) and Eq 3 and 6; solid line, calculated from Eq 3, 5, and 6.

concentration of Li are observed for all investigated solid solutions, and at 850 K this value is 7.5% of the value of an ideal solution for the highest Li content ($X_{\text{Li}} = 0.25$). In addition, molar volumes of alloys at all temperatures are much lower than for pure Mg. The molar volumes in the Al-Li system [98Gas] do not change substantially with the increase in concentration of Li from pure Al to $X_{\text{Li}} = 0.25$. The excess molar volume was found to be about 9% at $X_{\text{Li}} = 0.25$, which compares with 7.5% for a Mg-Li alloy with the same mole fraction. The small difference between the two systems is probably related to the differing structures of Mg(cph) and Al(bcc). It seems that both solid alloys at low concentrations of lithium show similar deviations from the linear behavior. However, it should be noted that in Al-Li alloys, addition of Li causes a greater decrease of density than in the Li-Mg alloys of this study.

From the molar volume dependence on temperature (Eq 3 together with Eq 5), the volume expansion coefficients were calculated from the defining relationship:

$$\beta = \frac{1}{V_0} \left(\frac{\delta V}{\delta T} \right)_p \quad (\text{Eq 7})$$

where β is the coefficient of the volume expansion, V_0 is the molar volume at $T = 298.16 \text{ K}$, T is the temperature, and V is the molar volume calculated from the equation describing V as a function of temperature.

The calculations of β were done at 298.16, 400, 600, and 850 K, and the calculated values are plotted in Fig. 4. Very small changes of β with Li concentrations are observed at all temperatures so, within experimental scatter, they can be assumed to be constant and equal to the β of pure Mg.

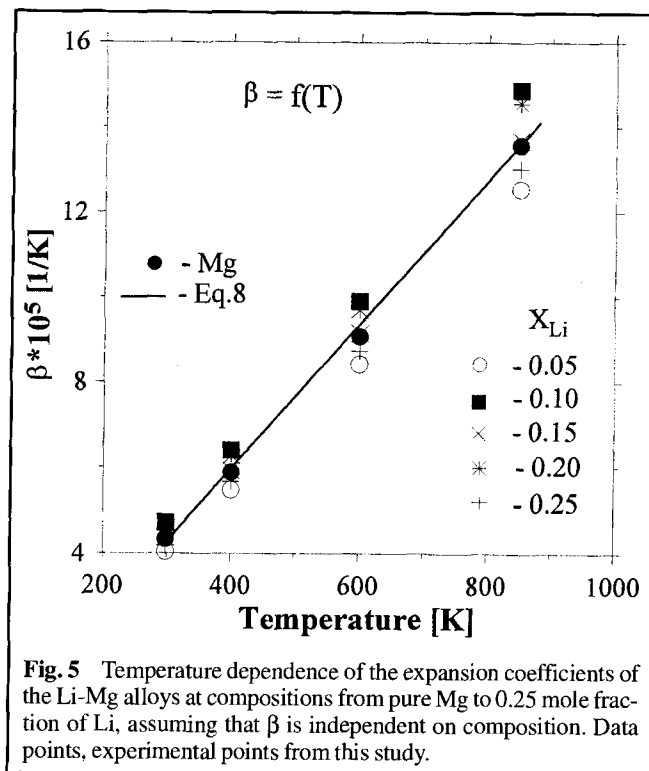


Fig. 5 Temperature dependence of the expansion coefficients of the Li-Mg alloys at compositions from pure Mg to 0.25 mole fraction of Li, assuming that β is independent on composition. Data points, experimental points from this study.

The dependence of β on temperature for all investigated solid solutions is presented in Fig. 5. To a good approximation, it can be assumed that the volume expansion coefficient is a linear function of temperature for Mg-Li alloys within $0 \leq X_{Li} \leq 0.25$, and this relation with the maximal error (at 850 K) lower than 10% may be described by the following equation:

$$\beta(T) \times 10^5 = -0.80633 + 0.0169509 T \quad (\text{Eq 8})$$

The volume expansion coefficients at $X_{Li} = \text{const}$ tend to increase with increasing temperature, and hence the second derivative of the molar volume and the derivative of β with respect to the temperature at constant pressure:

$$\left(\frac{\delta C_p}{\delta p}\right)_T = -T \left(\frac{\delta^2 V}{\delta T^2}\right)_p \quad (\text{Eq 9})$$

$$\left(\frac{\delta C_p}{\delta p}\right)_T = -TV_0 \left(\frac{\delta \beta}{\delta T}\right)_p \quad (\text{Eq 10})$$

have positive values. This indicates that in isothermal processes, for the investigated Li-Mg solid alloys, the specific heat C_p is a decreasing function of P , and that the increase of the pressure causes a decrease of C_p .

The measurements of the density were carried out for the alloys belonging to (Mg) and (Mg) + (Li) regions of the Mg-Li system, thus it was possible to calculate the density of the (Li) phase saturated with Mg, assuming a linear dependence of the density of the [(Mg) + (Li)] solid solutions on the mole fraction of constituent phases in the two-phase binary region ($Y_{(Li)}$, $Y_{(Mg)}$), and the densities ($\rho_{(Mg)}$, $\rho_{(Li)}$) of the (Mg) and (Li) phases, according to the following relations:

$$\rho_{[(Li) + (Mg)]} = \rho_{(Mg)} Y_{(Mg)} + \rho_{(Li)} Y_{(Li)} \quad (\text{Eq 11})$$

$$\rho_{(Li)} = (\rho_{[(Mg) + (Li)]} - \rho_{(Mg)} Y_{(Mg)}) / Y_{(Li)} \quad (\text{Eq 12})$$

The values of $Y_{(Mg)}$, $Y_{(Li)}$ were calculated with the lever rule applied to the [(Mg) + (Li)] region:

$$Y_{(Mg)} = (X_{Li}^{(Li)} - X_{Li}^{[(Mg) + (Li)]}) / (X_{Li}^{(Li)} - X_{Li}^{(Mg)}) \quad (\text{Eq 13})$$

where $X_{Li}^{[(Mg) + (Li)]}$ is the mole fraction of Li in the [(Mg) + (Li)] region and $X_{Li}^{(Li)}$, $X_{Li}^{(Mg)}$ are mole fractions of Li at the two-phase [(Mg) + (Li)] boundaries.

The temperature dependencies of $X_{Li}^{(Li)}$ and $X_{Li}^{(Mg)}$ were taken from the authors' earlier work [96Gas] and can be described in the temperature range of their experimental results by the equations:

$$X_{Li}^{(Mg)} = 0.1614 + 1.12 \times 10^{-5} T \quad (\text{Eq 14})$$

$$X_{Li}^{(Li)} = 0.3377 - 7.76 \times 10^{-5} T \quad (\text{Eq 15})$$

The density of the (Li) phase was calculated from Eq 11 to 13 in the temperature range 373 to 873 K and described by the parabolic equation as follows:

$$\rho_{(Li)} = 1.4937 - 5.368 \times 10^{-5} T - 1.23414 \times 10^{-7} T^2 \quad (\text{Eq 16})$$

(in g/cm³)

with the standard deviation of 0.0002 g/cm³.

Conclusions

Density measurements were made by the dilatometric method for solid Mg-Li alloys in the range of mole fraction below $X_{Li} = 0.25$ Li and starting from room temperature to 870 K. It has been found that the density isotherms exhibit positive deviations from additivity for all investigated alloys with the maximal deviation reaching 0.1 g/cm³ at $X_{Li} = 0.25$, which is the highest concentration of Li investigated in this study. The dependence of density on temperature and composition (X_{Li}) were evaluated using data of this study (Eq 5).

The isotherms of the molar volume of the solid Li-Mg alloys (Eq 3) all showed negative deviations from ideality, reaching ~7.5% of the value of ideal alloys at $X_{Li} = 0.25$.

Coefficients of volume expansion (Fig. 4) at any given temperature from 0 to 0.25 mole fraction of Li were found to be almost constant and equal to that of pure Mg at the same temperature.

The increasing values of the volume expansion coefficient with the increase of temperature for all investigated alloys indicate also a simultaneous decrease of the specific heat with the increase of the pressure under isothermal conditions (according to Eq 11).

With the error lower than 9%, the expansion coefficient can be approximated as a linear function of the temperature (Fig. 5), for all Mg-Li alloys over the composition range $X_{Li} = 0$ to 0.25.

The density of the (Li) phase along the (Li)/[(Mg) + (Li)] boundary was calculated and described by a temperature-dependent parabolic equation (Eq 16).

Acknowledgment

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