ARCHIVES OF METALLURGY
Volume 48 2003 Issue 4

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DENSITY AND MOLAR VOLUME OF Al-RICH Al-Li-Mg SOLID ALLOYS

GĘSTOŚĆ ORAZ OBJĘTOŚĆ MOLOWA STAŁYCH STOPÓW Al-Li-Mg O DUŻYM STĘŻENIU ALUMINIUM

Using the dilatometric method the densities of the solid Al-Li-Mg alloys were measured for two constant values of $t = 0.85$ and 0.95, where $t = X_{Al}/(X_{Al} + X_{Mg})$ and for Li concentrations changing from 0 to 0.25 mole fraction. The experiments were carried out in the temperature ranges: 293–818 K and 293–718 K for $t = 0.05$ and 0.15, respectively. The temperature dependences of density were described by the parabolic equation of the form $y = a + bT + cT^2$. The parameters a, b, and c were calculated using the least squares method. It was found that the density isotherms for $t = 0.95$ show slight negative deviation from the linear behaviour, while for $t = 0.85$ an almost linear change is observed when plotting the density from Al-Mg alloys to pure Li density. The molar volume isotherms of Al-Li-Mg solid alloys calculated at the same temperatures as for the density are characterised by slow decreasing with the increase of Li content, except that calculated at 700 K for $t = 0.85$ showing an opposite trend.

Stosując metodę dylatometryczna zmierzono gęstość stałych stopów Al-Li-Mg dla stopów charakteryzujących się stałym stosunkiem aluminium do magnezu ($t = X_{Al}/(X_{Al} + X_{Mg})$ wynoszącym 0.95 oraz 0.85 (X_{Al}, X_{Mg} – ułamkami molowe Al oraz Mg). Pomiary prowadzono dla stopów, w których stężenie litu zmieniało się od 0 do 0.25 ułamka molowego oraz w zakresie temperatur od 293–818 K dla $t = 0.95$ oraz od 293–718 K dla $t = 0.85$. Zmiany gęstości z temperaturą zostały opisane zależnościami parabolicznymi postaci $y = a + bT + cT^2$ a parametry a, b i c zostały wyliczone metodą najmniejszych kwadratów. Obliczone izotermy gęstości w 293 K oraz 800 K dla $t = 0.95$ oraz w 293 K i 700 K dla $t = 0.85$ charakteryzują się słabym ujemnym odstępstwem od zmiany liniowej między gęstością stopu dwuskładnikowego Al-Mg i gęstością Li. Natomiast, wyznaczone w tych samych temperaturach izotermy objętości molowej pokazują nieznaczny spadek z zawartością litu z wyjątkiem izotermy dla T = 700 K oraz $t = 0.85$, która charakteryzuje się bardzo słabą wzrostową tendencją.

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1. Introduction

Thermodynamic studies on Li alloys were initiated at the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences in 1972, and later in Ref. [1] the evaluations for binary Li alloys were published. Subsequently, emf and calorimetric measurements were undertaken to collect additional binary data, mainly in co-operation with Max-Planck Institute in Stuttgart, Germany, and such studies are now being continued on ternary systems: Al-Li-Cu and Al-Li-Mg at Al-rich alloys. The following binary systems were investigated: Li-Sn [2], Li-Al [3], Li-Zn [4,5], Li-In [6], Li-Tl [7], Li-Bi [8], Li-Sn [9,10], Li-Mg [11] and Li-Pb [12]. In 1991, after completing the measurement of the enthalpy of mixing of liquid Al-Li-Mg alloys [13], the studies were extended by including the measurement of the Li activities and enthalpies of formation of ternary phases by the Al solution calorimetry [14]. These studies were intended to obtain data for phase diagram calculations and they are continued. Studies on Al-Li-Cu comprising emf of solid and liquid alloys were completed and used for phase diagram calculations [15].

In 1996, chemical diffusion studies on constituent binaries and on ternary Al-Li-Mg alloys were started with the aim to extend of subsequent emf, galvanostatic, and potentiometric equilibrium measurements. The molar volume or the density values are needed for precise calculations of the chemical diffusion coefficients. In the following papers the density and the molar volumes of solid binary alloys were investigated: Al-Li [16], Li-Mg [17] and Al-Mg [18]. These data were used for chemical diffusion coefficients studies in subsequent publications: Al-rich Mg alloys [19], Mg-rich Li alloys [20], Al-rich Li alloys [21]. For the latter system, the experimental chemical diffusion coefficients were used for comparison with modeling [22].

This article presents densities and molar volumes of solid Al-rich Al-Li-Mg alloys. The resulting data will be used in subsequent publications for calculation of chemical diffusion coefficients and next, when combined with previous information on phase equilibria, will be applied in the analysis of solidification processes.

2. Measurements

The investigations of the density of Al-Mg-Li solid alloys were conducted using the dilatometric method based on the measurements of changes in axial dimensions of cylindrical samples as functions of temperature. The height of the sample was measured with the accuracy ± 0.0005 cm. The scheme of the apparatus is presented in Fig. 1. Before starting the experiment with the Al-Li-Mg solid alloys the apparatus was calibrated and tested using high purity aluminium and copper. It was estimated that the measurement error of the density was equal to about 1%. The main assumption of this method is that the thermal expansion coefficient of the polycrystalline material (Al-Li-Mg alloy) is the same in all directions. The density and the molar volume of the investigated alloys were calculated using the following equations:

$$\rho = \frac{4m}{\pi D^2 H} \qquad [1]$$

$$V = \frac{M_{Al} X_{Al} + M_{Li} X_{Li} + M_{Mg} X_{Mg}}{\rho} \qquad [2]$$

where: ρ is the density, V is the molar volume, m is the weight of the sample, D and H are radius and height of the cylindical sample, X with the Al, Li or Mg subscripts denotes the mole fractions, and M with the same subscripts refers to the atomic weights of the marked metals.

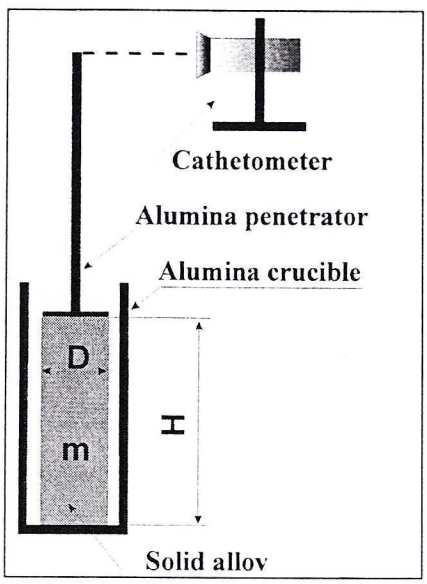


Fig. 1. Scheme of a dilatometric measurement of density

The alloys were prepared in a glove-box with continuous circulation of argon in which the amounts of oxygen and water were lower than 1ppm, and nitrogen (not detected) was removed by a titanium sponge contained in a separate purification system. The graphite crucibles were used for the preparation of alloys, and liquid alloys were poured out into the graphite cylindrical mould and next cooled very slowly. After mechanical processing, the height and diameter of samples were measured and next, they were used in the experiments. The diameters and height of samples were 12 and 50 mm, respectively. The measurements were carried out in the high purity $Ar + H_2$ gas atmosphere, additionally purified from oxygen and moisture by Ti-sponge and molecular sieve. Moreover, in the course of the experiment alumina crucible with the sample of the alloy (Fig. 1) was hold in the magnesium tube to protect the alloy sample from the reaction with the rest of oxygen and moisture.

3. Results and discussion

The dilatometric measurements of density were conducted starting from room temperature to lower than solidus temperature of Al-rich alloys of the Al-Mg system (T_{max} = 818 K). Because curvilinear dependence of the density on temperature was observed, the experimental results of the density measurements were described by parabolic equations of the form $y = a + bT + cT^2$, and a, b and c parameters were calculated using the least squares method. The obtained equations for t = 0.95 and 0.85 are reported in Tables 1 and 2 together with the standard deviations and the densities calculated at 298 K, 500 K and 800 K, for $t = 0.95$, while for $t = 0.85$ for the same first two temperatures and at 700 K due to the shape of the solidus temperature. The densities vs. temperature calculated from equations in Tables 1 and 2 (continuous lines) and the measured data (different designated points) are shown in Figures 2 and 3.

TABLE 1

Temperature dependences of density of solid Al-Li-Mg alloys for t = 0.95 together with standard deviations (σ) and density (ρ) calculated at T = 298 K, 500 K and 800 K

XLi	$\rho = a + bT^2$ [g/cm^3]	σ [g/cm^3]	$\rho_{298\ K}$ [g/cm^3]	$\rho_{500\ K}$ [g/cm^3]	$\rho_{800\ K}$ [g/cm^3]
0.0	$2.6278 - 3.14*10^{-5}T - 1.63*10^{-7}T^2$	0.0031	2.6039	2.5714	2.4985
0.05	$2.5347 - 7.68*10^{-6}T - 1.79*10^{-7}T^2$	0.0029	2.5165	2.4861	2.4140
0.10	$2.4429 - 1.47*10^{-5}T - 1.52*10^{-7}T^2$	0.0047	2.4250	2.3976	2.3339
0.15	$2.3365 + 9.85*10^{-6}T - 1.79*10^{-7}T^2$	0.0048	2.3235	2.2967	2.2298
0.20	$2.2420 + 1.63*10^{-5}T - 1.70*10^{-7}T^2$	0.0009	2.2317	2.2077	2.1462
0.25	$2.1450 - 1.04*10^{-5}T - 1.26*10^{-7}T^2$	0.0023	2.1307	2.1083	2.0560

TABLE 2

Temperature dependences of density of solid Al-Li-Mg alloys for t = 0.85 together with standard deviations (σ) and density (ρ) calculated at T = 298 K, 500 K and 700 K

XLi	$\rho = a + bT^2$ [g/cm^3]	σ [g/cm^3]	$\rho_{298\ K}$ [g/cm^3]	$\rho_{500\ K}$ [g/cm^3]	$\rho_{700\ K}$ [g/cm^3]
0.0	$2.4904 - 5.64*10^{-5}T - 1.18*10^{-7}T^2$	0.0044	2.4631	2.4327	2.3931
0.05	$2.3871 + 1.60*10^{-5}T - 2.06*10^{-7}T^2$	0.0008	2.3736	2.3436	2.2974
0.10	$2.3208 + 9.98*10^{-6}T - 1.66*10^{-7}T^2$	0.0029	2.3090	2.2843	2.2465
0.15	$2.2178 - 1.62*10^{-5}T - 1.36*10^{-7}T^2$	0.0025	2.2009	2.1757	2.1398
0.20	$2.0704 + 1.552*10^{-5}T - 3.14*10^{-7}T^2$	0.0022	2.0888	2.0695	2.0252
0.25	$2.0247 + 6.81*10^{-5}T - 2.80*10^{-7}T^2$	0.0021	2.0201	1.9888	1.9352

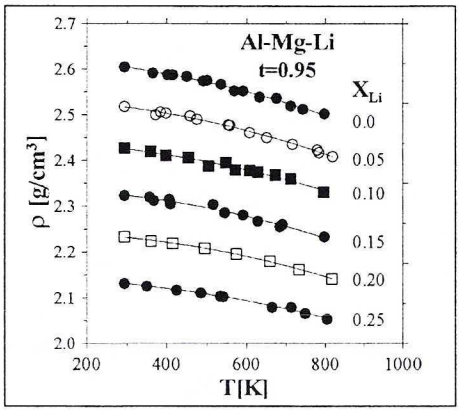


Fig. 2. Temperature dependences of density of solid Al-Li-Mg alloys for t = 0.95. Continuous lines represent values calculated from equations reported in Table 1. Points indicate the experimental data

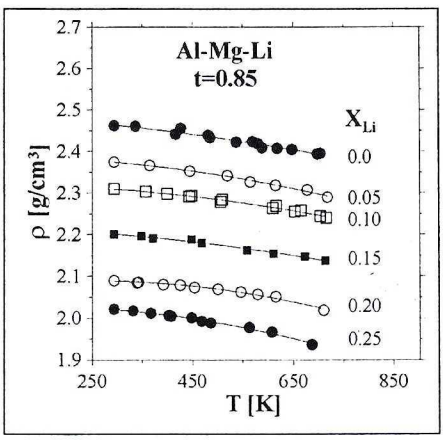


Fig. 3. Temperature dependences of density of solid Al-Li-Mg alloys for t = 0.85. Continuous lines represent values calculated from equations reported in Table 1. Points indicate the experimental data

The equations in Tables 1 and 2 and the calculated densities for all compositions at the same temperatures as above, for both $t = 0.95$ and $t = 0.85$, were next used to evaluate the temperature-composition relations in the form:

t = 0.95

$$\rho = 2.6278 - 3.14*10^{-5}*T - 1.63*10^{-7}*T^2 + \\ + (2.213*10^{-4}*T - 1.9425)*X_{Li}\ [g/cm^3] \quad [3]$$

t = 0.85

$$\rho = 2.4904 - 5.64*10^{-5}*T - 1.18*10^{-7}*T^2 + \\ + (-1.54*10^{-5}*T - 1.7702)*X_{Li}\ [g/cm^3] \quad [4]$$

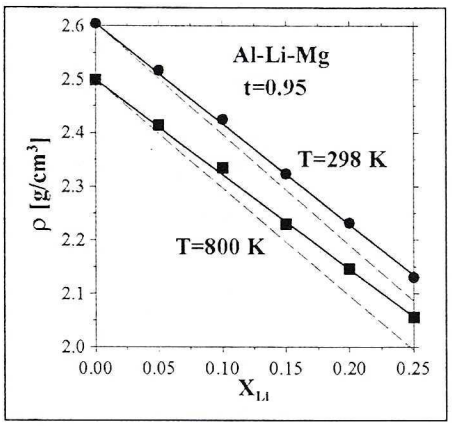


Fig. 4. Density isotherms of Al-Li-Mg solid alloys for t = 0.95 at 298 K and 800 K. Dotted lines show the linear changes of the density from Al-Mg (X_{Mg} = 0.05) to pure Li, continuous lines exhibit values calculated from Eq. 3, while the circles and squares show the density values calculated using equations from Table 1

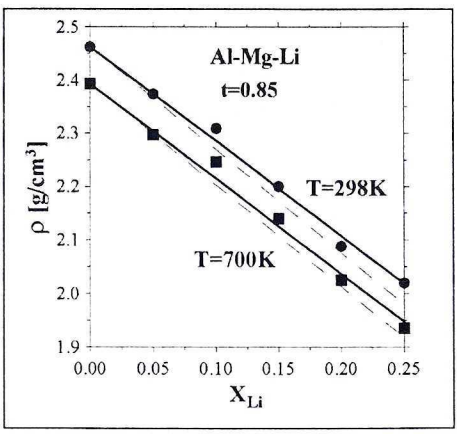


Fig. 5. Density isotherms of Al-Li-Mg solid alloys for t = 0.85 at 298 K and 700 K. Dotted lines show the linear changes of the density from Al-Mg (X_{Mg} = 0.15) to pure Li, continuous lines exhibit values calculated from Eq. 4, while the circles and squares show the density values calculated using equations from Table 2

In Figs. 4 and 5 there are presented the isotherms of density. In Fig. 4 they are plotted for t = 0.95 at the temperatures 298 K and 800 K, while in Fig. 5 for t = 0.85 at the temperatures 298 K and 700 K. The isotherms for t = 0.95 show weak positive deviations from the additive changes between binary Al-Mg solid alloy (containing 0.05 mole fraction of Mg) and pure lithium. These deviations are comparable with those for Al-Li system [16] and are not higher than 0.1 g/cm^3 at room temperature. At 800 K the deviations are slightly higher for the most Li-rich alloys and at X_{Li} = 0.25 the deviations amount about 5.5% of the additive value. Isotherms in Fig. 5 exhibit such small deviations from the additive changes, that they can be compared with experimental errors.

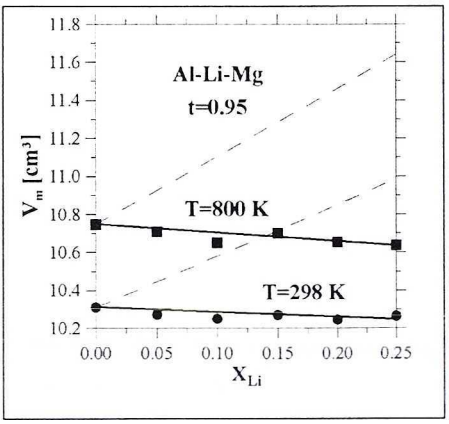
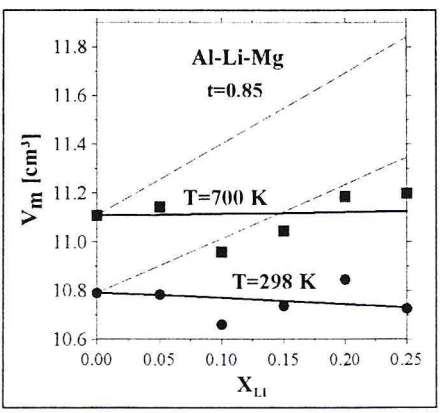


Fig. 6. Isotherms of the molar volume of Al-rich Al-Li-Mg solid alloys for t = 0.95 at 298 K and 800 K. Continuous lines show the values calculated using Eq. 3. Dotted lines show the linear changes of molar volume from Al-Mg (X_{Mg} = 0.05) to pure Li. Black circles and squares refer to the values calculated using equations from Table 1



Rys. 7. Isotherms of the molar volume of Al-rich Al-Li-Mg solid alloys for t = 0.95 at 298 K and 700 K. Continuous lines show the values calculated using Eq. 4. Dotted lines show the linear changes of molar volume from Al-Mg (X_{Mg} = 0.15) to pure Li. Black circles and squares refer to the values calculated using equations from Table 2

Basing on the equations (3) and (4) and those reported in Table 1 and 2, the molar volumes of the Al-Li-Mg solid alloys for t = 0.95 and 0.85 were calculated at room temperature and at 700 K (t = 0.85) and 800 K (t = 0.95) and they are shown in Figures 6 and 7. A better fit of experimental data points to the values calculated from Eqs. 3 and 4 is observed for t = 0.95 than for t = 0.85. In addition, a weak decrease of the molar volume with the increase of lithium content is observed for t = 0.95, while for t = 0.85 an opposite behaviour is visible. Maximal deviation from the additivity observed for both groups of

alloys (t = 0.95 and t = 0.85) and the most Li-rich alloys are found between $0.5 \div 0.9$ cm^3.This amounts to approximately $4 \div 8\%$ of the additive value.

4. Summarising

The density of Al-Li-Mg solid alloys was measured using the dilatometric method. The curvilinear dependence of density on temperature was observed for all investigated alloys and they were described by the parabolic equations using the least squares method and next, for both t values (0.05, 0.150) in the form of Eqs. 3 and 4 describing the density dependence on temperature and lithium concentration. Using Eqs. 3 and 4, the density isotherms were calculated and plotted for comparison with the linear changes between Al-Mg alloy (0.05, 0.15 mole fraction of Mg) and pure lithium.

The calculated density isotherms are characterised by linear decreasing of density with the lithium increase and very weak deviation from linear changes between the alloy Al-Mg ($X_{Mg} = 0.05, 0.15$) and pure lithium. Deviations are equal to 0.06 g/cm^3 for T = 800 K and t = 0.95 and their decrease is very close to zero for t = 0.85 and T = 700 K.

Molar volume isotherms of the Al-Li-Mg solid alloys show maximal deviations from linearity, (at the range of $0.5 \div 1$ cm^3) for alloys of highest lithium concentration. At t = 0.95 the molar volume isotherms decrease with the lithium content, and for t = 0.85 the same tendency is at 298 K and very slight opposite tendency (practically constant value of V_m) at 700 K.

Comparing our results of the molar volume measurements for the Al-Li and Al-Mg solid Al-rich alloys [16, 18], one can find, that the molar volume of Al-Li solid alloys at 800 K are lower than that of Al-Mg. Assuming that the molar volume of the (Al) phase of Al-Li-Mg system change additively, addition of Li to Al-Mg alloys with t = 0.95 should cause the decrease of the molar volume of Al-Li-Mg alloys in this (Al) one phase region. When the lithium concentration of the ternary Al-Li-Mg alloy (t = 0.95) is higher than the limiting concentration of the (Al) phase [23] the new (AlLi) phase will be present in Al-Li-Mg alloys and two phase, (Al) and (AlLi) will exist in these alloys. Because the molar volume of the (AlLi) phase is lower than that of the (Al) phase (recalculated from the density of the AlLi phase [16]) it should cause the slight decrease the molar volume of the Al-Li-Mg alloys for constant value of $t = X_{Al}/(X_{Al} + X_{Mg}) = 0.95$ in comparison to the Al-Mg alloy.

The Al-Mg alloys with the higher Mg concentration ($t = X_{Al} = 0.85$), at 700 K are the two phase alloys with the (Al) and (Al_3Mg_2) phases in which some amount of Li can dissolve [23]. Addition of lithium to these binary alloys cause that beside of the cited (ternary) phases new one will form. Depending on the Li concentration the ternary solid alloys will compose with (Al) and (Al_3Mg_2) by low Li content and with (Al), (Al_3Mg_2), ($Al_{22}Mg_{17}$) and (Al_2LiMg) ternary phases for higher Li concentrations [23]. It is very difficult to discuss influence of any phase on the molar volume without knowledge on the discussed property of these phases. One can only conclude that almost constant value of molar volume of the Al-Li-Mg solid alloys at 700 K is of the effect of very close values of the molar volumes of the intermetallic phases being in the equilibrium.

Density and molar volumes presented in this study for Al-Li-Mg alloys will be used for the calculations of the chemical diffusion coefficients in the future investigations.

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REVIEWED BY: WOJCIECH ZAKULSKI
Received: 17 November 2003.