

Available online at www.sciencedirect.com



Trans. Nonferrous Met. Soc. China 29(2019) 507-514

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn



Density of magnesium and magnesium-lithium alloys in solid and liquid states

R. N. ABDULLAEV, R. A. KHAIRULIN, Yu. M. KOZLOVSKII, A. Sh. AGAZHANOV, S. V. STANKUS

Institute of Thermophysics, Siberian Branch of the Russian Academy of Sciences, Lavrentyev Avenue 1, 630090 Novosibirsk, Russia

Received 15 March 2018; accepted 23 August 2018

Abstract: New experimental data are presented on the density and thermal expansion of solid and liquid magnesium and ultralight magnesium–lithium alloys containing 23.03 and 30.02 at.% Li, respectively. The measurements were performed using the dilatometer method and the gamma-ray attenuation technique in the temperature range from 145 to 1244 K for magnesium and from 293 to ~1000 K for the alloys. The density changes during the solid–liquid phase transition were directly measured for Mg and the Mg₇₀Li₃₀ alloy. The temperature dependences and reference tables of the investigated volumetric properties were developed. A comparison of the obtained results with literature data was made. The study showed that the eutectic composition in the magnesium–lithium system differs from 23 at.% Li. The concentration dependence of molar volume of the magnesium–lithium liquid system was found to be almost linear in the interval of 0–30 at.% Li and deviated noticeably from the corresponding dependence for an ideal mixture.

Key words: density; melt; solid; magnesium; magnesium-lithium alloys; thermal expansion; interdiffusion

1 Introduction

Magnesium-based alloys are among the most lightweight structural materials. The addition of lithium to these materials makes them ultralight and promising for use in the aerospace industry [1,2]. Besides this, an increase in lithium content improves the plasticity and ductility of the alloys [2,3]. Reliable data on the physicochemical characteristics of the Mg-Li system are necessary for predicting the properties of new materials containing magnesium and lithium. However, there is little information in the literature regarding the volume properties of the Mg-Li alloys at elevated temperatures (above 400 K). Only one study was found [4] in which measurements of the thermal expansion of a solid alloy containing 12.7 at.% Li were made in the temperature range from 300 to 650 K. In other studies, the data on the volume properties were obtained only near room temperature. Crystal lattice parameters of several alloys were determined in Refs. [5-11], and the thermal expansion coefficients were measured in Ref. [12]. The density of molten magnesium-lithium alloys has not been measured to date. The reason for the lack of experimental data on the volumetric properties of the Mg-Li system above 400 K is apparently due to the chemical activity and high vapor pressure of lithium and magnesium at elevated temperatures. Most of the conventional techniques used to measure the density and thermal expansion coefficients are poorly suitable for such systems, especially in the liquid state.

The assessed Mg–Li phase diagram [13] has an eutectic point at 23 at.% Li and at 861 K, and exhibits a maximum on the liquidus curve at 30 at.% Li (865 K). Solid alloys with compositions close to 30 and 23 at.% Li are the most interesting from a practical point of view [2]. The purpose of this work is to measure the density and thermal expansion of magnesium and magnesium–lithium alloys of the eutectic and congruent compositions (Mg₇₇Li₂₃ and Mg₇₀Li₃₀) over a wide temperature range including both solid and liquid states. In addition, mutual diffusion in the liquid alloys is investigated at about 980 K.

2 Experimental

The density (ρ_r) of solid samples at room temperature (T_r =293.15 K) was determined using the Archimedean immersion method. Silicone oil was used as the reference fluid. The relative error in the value of ρ_r did not exceed 0.05%.

Thermal expansion of solid samples was measured

Corresponding author: R. N. ABDULLAEV; E-mail: abdullaev.rasul88@gmail.com DOI: 10.1016/S1003-6326(19)64959-9

using a DIL-402C dilatometer [14]. The measurements were made by a procedure analogous to that used previously in the study of thermal expansion of solid nickel [15]. The experimental data were recalculated into the relative expansion of the sample ε ,

$$\mathcal{E}(T_i) = \frac{L(T_i) - L(T_r)}{L(T_r)}$$

where $L(T_i)$ and $L(T_r)$ are the sample lengths at temperatures T_i and T_r , respectively.

The linear thermal expansion coefficient (LTEC, α) was found by numerical differentiation of the data on relative expansion:

$$\alpha(T_i) = \frac{1}{2} \left(\frac{\varepsilon_{i+1} - \varepsilon_i}{T_{i+1} - T_i} + \frac{\varepsilon_i - \varepsilon_{i-1}}{T_i - T_{i-1}} \right)$$

where $\varepsilon_i = \varepsilon(T_i)$. The temperature interval $(T_{i+1}-T_i)$ was ~1.5 K. To construct the smoothed $\alpha(T)$ dependence, the raw data were fitted with the following equation:

$$\alpha(T) = \sum_{i=0}^{\kappa} A_i \left(T - T_r \right)^i \tag{1}$$

If the behaviour of the LTEC was found to vary strongly with temperature, the investigated temperature range was divided into several regions, and the data in each region were approximated by separate polynomials of the form of Eq. (1). The smoothed $\varepsilon(T)$ dependence was found by integrating the $\alpha(T)$ curve. The temperature dependence of the density $\rho_c(T)$ of solid sample was calculated by using the $\varepsilon(T)$ dependence and the ρ_r value.

Volume properties of the melts and density changes during the solid–liquid transition were determined by measuring the attenuation of a narrow beam of gamma rays through the samples. The gamma-ray attenuation technique and the experimental setups (gammadensitometers) are described in detail elsewhere [16–18]. The relative density change during phase transition $\delta \rho_{\rm f}$ and the density $\rho_{\rm m}$ of the melt are calculated using the following formulae:

$$\delta \rho_{\rm f} = \frac{\rho_{\rm c}(T_{\rm f}) - \rho_{\rm m}(T_{\rm f})}{\rho_{\rm c}(T_{\rm f})} = \frac{\ln(J_{\rm L}/J_{\rm S})}{\ln(J_0(T_{\rm f})/J_{\rm S})}$$
(2)

$$\rho_{\rm m}(T) = \rho_{\rm m}(T_{\rm f}) \cdot \frac{\ln[J_0(T)/J(T)]}{\ln[J_0(T_{\rm f})/J_{\rm L}]} \cdot \frac{1 + \bar{\alpha}_{\rm g}(T_{\rm f})(T_{\rm f} - T_{\rm r})}{1 + \bar{\alpha}_{\rm g}(T)(T - T_{\rm r})} \quad (3)$$

where J and J_0 are the intensities of the radiation after passing through the measuring cell with and without the sample, respectively, T_f is the melting temperature, $\overline{\alpha}_g$ is the mean linear thermal expansion coefficient of the crucible material, and subscripts "S" and "L" indicate solid and liquid states at the melting temperature.

If the density of the solid phase and (or) the density

change during the solid-liquid transition are not measured for some reason, the density of the liquid can be calculated using another formula:

$$\rho_{\rm m}(T) = \frac{\ln[J_0(T)/J(T)]}{\mu d_{\rm r}[1 + \bar{\alpha}_{\rm g}(T)(T - T_{\rm r})]} \tag{4}$$

where d_r is the gamma-ray attenuation length at room temperature (the inner diameter of the crucible corrected for the gamma-ray beam diameter), and μ is the gamma-ray mass attenuation coefficient of the investigated material (and for alloys, this is calculated from the mass attenuation coefficients of the metals using the additivity rule).

The gamma-ray method also allows one to determine the density of solid materials. The ρ_c value is calculated using a formula:

$$\rho_{\rm c}(T) = \rho_{\rm r} \left\{ \frac{\ln \left[J_0(T)/J(T) \right]}{\ln \left[J_0(T_{\rm r})/J(T_{\rm r}) \right]} \right\}^{3/2}$$
(5)

However, the gamma-ray attenuation technique has a lower sensitivity and accuracy in comparison with the dilatometer method. Therefore, the results obtained by the gamma-ray method were not used to construct the $\rho_c(T)$ dependence. On the other hand, the advantage of gamma-densitometers is that they make it possible to scan the sample at different heights. This allows one to control the homogeneity of solid and liquid alloys and to detect possible defects (for example, shrinkage cavities and porosity) in the solid samples. Notice that Eqs. (2)–(5) are valid for isotropic and homogeneous materials.

At the first stage of this study, the density of magnesium and magnesium-lithium alloys was measured using the gamma-ray attenuation technique. For gamma ray sources, ampules with the cesium-137 isotope were used (a photon energy of 662 keV). Measuring cells were made from molybdenum. This metal does not interact with magnesium at temperatures up to 2600 K and is practically insoluble in liquid lithium up to 1000 K [19]. The cell contained a cylindrical crucible with a 37 mm in internal diameter and a height of 72 mm, and a cap with a thin-walled thermowell for the chromel-alumel thermocouple (type K). The magnesium and lithium were of 99.95% mass purity. The supplied by JSC "Solikamsk magnesium was Magnesium Works". The natural lithium was supplied by JSC "Novosibirsk Chemical Concentrates Plant". The samples were prepared in a glove box filled with high-purity argon (99.992 vol.%). The box was equipped with an electronic analytical balance and an arc-welding machine. The masses of the magnesium and lithium pieces were measured with an accuracy of 2-3 mg. The pieces of the metals were placed in the measuring cell

and the cap was hermetically welded to the crucible. The actual lithium content in the studied alloys was (23.03 ± 0.02) and (30.02 ± 0.02) at.%. The gamma-ray mass attenuation coefficients of the magnesium and lithium were experimentally determined by the method described in Ref. [18].

In the experiments with the alloys, the mutual diffusion in the melts was studied before the density measurement. The experimental technique is based on direct registration of the concentration and density profiles in an inhomogeneous liquid sample and their respective evolutions in time. The cell was installed in the furnace of the gamma-densitometer, and the latter was evacuated and filled with pure argon up to 0.1 MPa. The sample was then melted and heated to about 980 K, at which the diffusion test was performed. During isothermal holding, the concentration and density differences in the liquid alloy gradually decreased with time due to diffusion. The concentration and density profiles were determined by measuring the gamma-ray attenuation in the melt at different heights. The coefficient of mutual diffusion was derived from these data. A detailed description of the measurement technique and processing of experimental data of the diffusion experiments is given elsewhere [20,21]. The duration of one experiment was 5-6 h. The test lasted until the concentration difference over the sample height decreased to 4-5 at.%.

After completion of the diffusion test, the melt was thoroughly mixed by shaking the cell directly in the furnace of the gamma-densitometer. The density of the sample in liquid state and the density change during the phase transition were then measured in the courses of heating and cooling. After cooling down to room temperature, the resulting ingot was thoroughly scanned. The samples for the measurements of the density and thermal expansion of the solid material by the Archimedean, dilatometer and gamma-ray methods were cut from a defect-free part of the ingot.

3 Results

According to the measurements, the mutual diffusion coefficient for the liquid $Mg_{77}Li_{23}$ alloy is equal to $(9.8\pm1.6)\times10^{-5}$ cm²/s at 982.1 K. For the $Mg_{70}Li_{30}$ melt, it is $(11.4\pm1.0)\times10^{-5}$ cm²/s at 983.5 K.

Solidification of the melts occurred in a narrow temperature interval (less than 2 K). The measured liquidus temperatures $T_{\rm L}$ were equal to (921.5±1.0) K for Mg, (865.2 ± 1.5) K for Mg₇₇Li₂₃, and (867.9 ± 1.5) K for Mg₇₀Li₃₀. Scanning of the solid sample of the Mg₇₀Li₃₀ alloy showed its rather high macroscopic homogeneity. Density differences over the sample height did not exceed 0.4% at distances of 4-20 mm from the crucible bottom, which practically lies within the limits of the measurement error. However, the scanning of the sample containing 23 at.% Li revealed that the differences in density reached 6%. In this connection, it was not possible to measure the density of the solid Mg77Li23 alloy reliably. Segregation of the components of this alloy during crystallization is probably due to the fact that the coordinates of the eutectic point in the assessed Mg-Li phase diagram [13] are not exactly accurate. Notice that, according to different sources [8,22-27], the eutectic composition varies from 21.8 to 27 at.% Li, and the eutectic temperature lies in the range of 860-865 K.

The measured ρ_r values for the Mg and Mg₇₀Li₃₀ alloy were (1737.3±0.9) and (1456.3±0.4) kg/m³, respectively. According to literature data on the crystal lattice parameters [11,28,29], the density of solid magnesium varies from 1736.6 to 1737.5 kg/m³ at room temperature. The density of the Mg₇₀Li₃₀ alloy at 293 K lies in the range of 1455.3–1464.0 kg/m³ [5–8].

3.1 Results of dilatometric measurements

The dilatometric measurements of the thermal expansion coefficient of solid Mg and the Mg₇₀Li₃₀ alloy were made in the temperature intervals of 145–773 and 293–773 K, respectively. The $\epsilon(T)$ dependence for each specimen was investigated in several cycles of heating and cooling. The coefficients of the polynomials (Eq. (1)) for the smoothed $\alpha(T)$ dependencies are presented in Table 1. To construct the smoothed $\alpha(T)$, $\epsilon(T)$ and $\rho_c(T)$ dependencies up to the melting point, Eq. (1) was extrapolated in the second region.

3.2 Results of measurements by gamma-ray attenuation technique

The measured values of the relative density changes during the solid-liquid phase transition for the Mg and $Mg_{70}Li_{30}$ alloy were equal to $(4.89\pm0.17)\%$ and $(4.16\pm0.41)\%$, respectively. The density of the melts,

Table 1 Coefficients of Eq. (1) for temperature dependencies of LTECs of solid Mg and Mg₇₀Li₃₀ alloy

Sample	Region	Temperature interval/K	$A_0/10^{-6} \mathrm{K}^{-1}$	$A_1/10^{-8} \mathrm{K}^{-2}$	$A_2/10^{-11} \mathrm{K}^{-3}$	$A_3/10^{-13} \text{ K}^{-4}$
Mg	1	145-229	25.27	-0.549	-28.366	-2.259
	2	229-773	25.68	1.822	0.199	_
Mg ₇₀ Li ₃₀	1	293-491	38.36	0.980	_	_
	2	491-773	39.60	-1.169	7.673	_

within random measurement error of the gamma-ray method, linearly decreases with temperature in the investigated temperature ranges. The experimental points were approximated by the following equation:

$$\rho_{\rm m}(T) = \rho_{\rm m}(T_{\rm L}) + \frac{\mathrm{d}\rho_{\rm m}}{\mathrm{d}T} (T - T_{\rm L}) \tag{6}$$

The coefficients of Eq. (6) are given in Table 2.

Figures 1 and 2 present the experimental data on the density of Mg and Mg₇₀Li₃₀ alloy in the solid and liquid states. Tables 3–5 tabulate the temperature dependencies of the density (ρ), relative expansion (ε), LTEC (α), and volumetric thermal expansion coefficient

Table 2 Density data for liquid Mg and Mg-Li alloys

X^{a}	$T_{\rm L}/$	$ ho_{ m m}(T_{ m L})/$	$-(\mathrm{d} ho_{\mathrm{m}}/\mathrm{d}T)/$	Temperature
at.% Li	Κ	$(kg \cdot m^{-3})$	$(kg \cdot m^{-3} \cdot K^{-1})$	interval/K
0	921.5	1557.5±3.0	0.232 ± 0.006	921.5-1244
23.03	865.2	1356.6±5.4	0.232±0.016	865.2-1007
30.02	867.9	1294.3±5.6	0.220±0.015	867.9-1014

^a X is atomic composition of the alloy



Fig. 1 Temperature dependence of density of magnesium in solid and liquid states



Fig. 2 Temperature dependence of density of $Mg_{70}Li_{30}$ alloy in solid and liquid states

 $(\beta = -(d\rho/dT)/\rho)$ for magnesium and magnesium–lithium alloys in the solid and liquid states.

4 Discussion

Figure 3 shows a comparison of the measured data with literature data on the LTEC of solid magnesium. One can see that all $\alpha(T)$ dependencies are in good agreement with each other in the temperature range from 400 K to the melting point. At lower temperatures, the scatter in the data is noticeably higher than the reported errors. This discrepancy may be due to the fact that the low temperature thermal expansion of solids often depends on the purity and thermal history of the samples under study [15].

Figure 4 presents the LTECs of solid magnesium, lithium and some magnesium-lithium alloys. From this figure, it is seen that the LTEC of the alloys varies very little with concentration in the range of 0-13 at.% Li. According to Mg-Li phase diagram [13], the alloys with Li content up to 17 at.% are solid solutions of lithium in magnesium with a hexagonal close-packed crystalline structure. The alloys with a content of Li from 25 to 100 at.% are solid solutions of magnesium in lithium (body-centered cubic lattice). The change in the crystal structure leads to a sharp increase in the coefficient of thermal expansion. In the composition range from 30 to 100 at.% Li, the room temperature LTEC again increases smoothly slowly and with increasing lithium content [12].

The data on the density change of Mg during the solid–liquid phase transition are summarized in Table 6. The resulting $\delta \rho_{\rm f}$ value practically coincides with the value measured in Ref. [37] (where the measurement was also made by the gamma-ray method) and is in satisfactory agreement with that calculated using the Clausius–Clapeyron relation [28]. The method of unfed casting, as shown in Ref. [38], always underestimates density changes during solidification. In Refs. [35,36], the density of solid and liquid magnesium was measured by different methods. As a result, the $\delta \rho_{\rm f}$ value calculated in these studies cannot be reliable, because its error includes the errors of both measurements.

Figure 5 shows a comparison of data in the present study with literature data on the density of liquid magnesium. The $\rho_m(T)$ dependence from Ref. [37] mentioned above agrees with Eq. (6) within the summary measurement errors. However, the results of other studies are in poor agreement with each other and with the data presented here. It should be noted that calculating the relative density change on melting– crystallization using the data on the density $\rho_m(T_f)$ from Refs. [36,39–41] gives the $\delta \rho_f$ values lying in the range

R. N. ABDULLAEV, et al/Trans. Nonferrous Met. Soc. China 29(2019) 507-514

Phase	<i>T</i> /K	$\alpha / 10^{-6} \mathrm{K}^{-1}$	<i>E</i> /10 ⁻⁶	$\beta / 10^{-5} \mathrm{K}^{-1}$	$ ho/(kg \cdot m^{-3})$	$\varphi(\alpha,\beta)/\%$	$\Delta \mathcal{E}/10^{-6}$	$\varphi(ho)/\%$
	145	20.6	-3525	6.2	1755.8	7.4	64	0.05
	160	21.5	-3210	6.5	1754.1	4.1	50	0.05
	180	22.6	-2769	6.8	1751.8	1.9	42	0.05
	200	23.5	-2307	7.1	1749.4	1.8	33	0.05
	220	24.2	-1830	7.3	1746.8	1.7	25	0.05
	240	24.7	-1339	7.4	1744.3	1.6	17	0.05
	260	25.1	-841	7.5	1741.7	1.4	10	0.05
	273.15	25.3	-510	7.6	1739.9	1.2	6	0.05
	280	25.4	-336	7.6	1739.0	1.2	4	0.05
	293.15	25.7	0	7.7	1737.3	1.1	0	0.05
	300	25.8	176	7.7	1736.4	1.1	2	0.05
Solid	350	26.7	1490	8.0	1729.5	1.0	16	0.05
(HCP)	400	27.7	2849	8.3	1722.5	1.0	30	0.05
	450	28.6	4255	8.5	1715.3	1.0	44	0.05
	500	29.5	5708	8.8	1707.9	0.9	58	0.05
	550	30.5	7209	9.1	1700.2	0.8	71	0.05
	600	31.5	8758	9.4	1692.4	0.7	83	0.06
	650	32.4	10356	9.6	1684.4	0.8	95	0.06
	700	33.4	12002	9.9	1676.2	0.8	108	0.06
	750	34.4	13699	10.2	1667.8	0.8	121	0.06
	800	35.4	15445	10.5	1659.2	0.8	135	0.06
	850	36.4	17242	10.7	1650.4	0.9	150	0.07
	900	37.5	19090	11.0	1641.5	1.0	167	0.07
	921.5	37.9	19902	11.2	1637.5	1.0	175	0.07
	921.5	-	-	14.9	1557.5	2.7	_	0.19
	950	-	_	15.0	1550,9	2.7	_	0.20
	1000	-	_	15.1	1539.3	2.7	_	0.22
	1050	_	_	15.2	1527.7	2.7	_	0.24
Melt	1100	_	_	15.3	1516.0	2.7	_	0.26
	1150	_	_	15.4	1504.4	2.7		0.29
	1200	_	_	15.5	1492.8	2.7		0.31
	1244	_	-	15.7	1482.6	2.7		0.33

 Table 3 Smoothed values of volumetric properties of magnesium

 $\varphi(x)$ is the relative error in the value of x; $\Delta \varepsilon$ is the absolute error in the value of ε ; the confidence level is 95%

Table 4 Smoothed values of volumetric properties of Mg70Li30 alloy

Phase	<i>T</i> /K	$\alpha / 10^{-6} \mathrm{K}^{-1}$	$\epsilon/10^{-6}$	$\beta / 10^{-5} \text{K}^{-1}$	$\rho/(\mathrm{kg}\cdot\mathrm{m}^{-3})$	$\varphi(\alpha, \beta)/\%$	$\Delta \varepsilon / 10^{-6}$	$\varphi(ho)/\%$
	293.15	38.4	0	11.5	1456.3	3.1	0	0.03
	300	38.4	263	11.5	1455.2	2.9	8	0.03
	350	38.9	2181	11.6	1446.8	1.0	64	0.04
	400	39.4	4099	11.8	1438.5	1.0	84	0.04
	450	39.9	6017	11.9	1430.3	1.0	103	0.04
	500	40.5	7953	12.0	1422.1	0.9	123	0.05
Solid	550	41.7	10005	12.4	1413.5	1.1	142	0.05
(BCC)	600	43.2	12126	12.8	1404.6	1.3	165	0.06
	650	45.2	14335	13.4	1395.4	1.5	193	0.06
	700	47.5	16652	14.0	1385.9	1.7	227	0.07
	750	50.3	19096	14.8	1376.0	1.9	268	0.08
	800	53.4	21686	15.7	1365.5	2.1	316	0.10
	850	56.9	24442	16.7	1354.5	2.3	372	0.11
	867.9	58.2	25469	17.0	1350.5	2.4	396	0.12
	867.9	—	-	17.0	1294.3	7.0	—	0.43
	900	_	-	17.1	1287.3	7.0	_	0.47
Melt	950	_	-	17.2	1276.3	7.0	_	0.53
	1000	_	-	17.4	1265.3	7.0	_	0.60
	1014	_	-	17.4	1262.2	7.0	_	0.62

 $\varphi(x)$ is the relative error in the value of x; $\Delta \varepsilon$ is the absolute error in the value of ε ; the confidence level is 95%

Table 5 Smoothed values of volumetric properties of $Mg_{77}Li_{23}$ alloy

<i>T</i> /K	$\beta / 10^{-5} \text{K}^{-1}$	$ ho/(\mathrm{kg}\cdot\mathrm{m}^{-3})$	$\varphi(eta)/\%$	$\varphi(ho)/\%$
865.2	17.1	1356.6	7.0	0.40
900	17.2	1348.6	7.0	0.44
950	17.4	1337.0	7.0	0.51
1000	17.5	1325.4	7.0	0.57
1007	17.5	1323.7	7.0	0.58

 $\varphi(x)$ is the relative error in the value of *x*; the confidence level is 95%



Fig. 3 LTEC of solid polycrystalline magnesium as function of temperature



Fig. 4 Temperature dependencies of LTECs of solid polycrystalline Mg and $Mg_{70}Li_{30}$ alloy (Dashed parts of lines show extrapolation of dependencies to melting point)

of 2%-3%. These values are much less than the measured and calculated density changes given in Table 6. This indicates that there are large errors in the $\rho_m(T)$ dependencies from these studies. The likely reasons for this have already been mentioned in the introduction.

The compositional dependence of molar volume V(X) of the magnesium-lithium liquid system in the interval of 0-30 at.% Li is shown in Fig. 6. As can be seen, this dependency deviates noticeably from the

Table 6 Relative density change of magnesium during solid–liquid phase transition

sond inquiti phase trai	ISITIOII	
Source	Method	$\delta ho_{ m f}$ /%
Ref. [34]	UC	3.8
Ref. [35]	IM	3.97
Ref. [36]	IM	2.87
Ref. [28]	CC	4.45
Ref. [37]	GM	4.98±0.15
Present work	GM	4.89±0.17

UC: Method of unfed casting; IM: Independent measurements of the density of the solid and liquid phases; CC: Calculation by the Clausius–Clapeyron equation; GM: Gamma-ray method



Fig. 5 Relative deviations of published data on density of liquid magnesium from Eq. (6)



Fig. 6 Molar volume of liquid Mg–Li system at 950 K as function of composition

corresponding dependence for an ideal mixture (the latter has been constructed using data on the density of liquid lithium from Ref. [43]). The relative excess molar volume reaches -3.0% at 30 at.% Li (and for the solid Mg₇₀Li₃₀ alloy at room temperature, the excess volume is -4.3%). Note that the compositional dependencies of thermodynamic activity and enthalpy of mixing for the Mg–Li liquid system also demonstrate markedly non-ideal behaviour [22,44,45].

5 Conclusions

(1) New experimental data on the density and thermal expansion of solid and liquid magnesium and magnesium–lithium alloys containing 23.03 and 30.02 at.% Li were obtained. Values of the density and volumetric thermal expansion coefficient of liquid magnesium were refined. The temperature dependences and reference tables of the investigated volumetric properties were developed.

(2) The study showed that the eutectic composition in the magnesium–lithium system differs from 23 at.% Li.

(3) The concentration dependence of molar volume of the magnesium–lithium liquid system was found to deviate noticeably from the corresponding dependence for an ideal mixture. The relative excess molar volume reaches -3.0% at 30 at.% Li in the liquid state (and for the solid Mg₇₀Li₃₀ alloy at room temperature, the excess volume is -4.3%).

(4) The molar volume of the magnesium–lithium liquid system was found to be almost linearly dependent on the concentration in the interval of 0–30 at.% Li. Therefore, in the range of 0–30 at.% Li, the volume properties of liquid alloys of any composition can be estimated by linear interpolation between the values of the molar volumes for liquid Mg and the $Mg_{70}Li_{30}$ melt. The accuracy of such an estimate should be sufficient for practical purposes.

Acknowledgments

The study of solid Mg and $Mg_{70}Li_{30}$ alloy was carried out under state contract with IT SB RAS (AAAA-A17-117022850029-9); the study of volume properties of melts and density changes during the solid–liquid transition was financially supported by RFBR (Grant No. 16-38-00669).

References

- HAFERKAMP H, NIEMEYER M, BOEHM R, HOLZKAMP U, JASCHIK C, KAESE V. Development, processing and applications range of magnesium lithium alloys [J]. Materials Science Forum, 2000, 350: 31–42.
- [2] WU R, YAN Y, WANG G, MURR L E, HAN W, ZHANG Z, ZHANG M. Recent progress in magnesium–lithium alloys [J]. International Materials Reviews, 2015, 60: 65–100.
- [3] TROJANOVÁ Z, DROZD Z, KÚDELA S, SZÁRAZ Z, LUKÁČ P. Strengthening in Mg–Li matrix composites [J]. Composites Science and Technology, 2007, 67: 1965–1973.
- [4] KÚDELA S Jr, RUDAJEVOVÁ A, KÚDELA S. Anisotropy of thermal expansion in Mg and Mg₄Li-matrix composites reinforced by short alumina fibers [J]. Materials Science and Engineering A, 2007, 462: 239–242.
- [5] LEVINSON D W. On the lattice parameter of Mg–Li β alloys [J]. Acta Metallurgica, 1955, 3: 294–295.

- [6] HERBSTEIN F H, AVERBACH B L. The structure of lithium-magnesium solid solutions—I: Measurements on the Bragg reflections [J]. Acta Metallurgica, 1956, 4: 407–413.
- [7] BERRY R L P, RAYNOR G V. Structure of magnesium–lithium β-phase alloys [J]. Nature, 1953, 171: 1078–1079.
- [8] GRUBE G, ZEPPELIN H V, BUMM H. Electrical conductivity and phase diagrams of binary alloys. 11. Message. The lithium– magnesium system [J]. Berichte der Bunsengesellschaft für physikalische Chemie, 1934, 40: 160–164. (in German)
- [9] BUSK R S. Lattice parameters of magnesium alloys [J]. The Journal of The Minerals, Metals & Materials Society, 1950, 2: 1460–1464.
- [10] HARDIE D, PARKINS R N. Lattice spacing relationships in magnesium solid solutions [J]. Philosophical Magazine, 1959, 4: 815–825.
- [11] BECERRA A, PEKGULERYUZ M. Effects of lithium, indium, and zinc on the lattice parameters of magnesium [J]. Journal of Materials Research, 2008, 23: 3379–3386.
- [12] LYNCH R W, EDWARDS L R. Thermal-expansion coefficients and Grüneisen parameters of bcc Li–Mg alloys [J]. Journal of Applied Physics, 1970, 41: 5135–5137.
- [13] NAYEB-HASHEMI A A, CLARK J B, PELTON A D. The Li-Mg (lithium-magnesium) system [J]. Bulletin of Alloy Phase Diagrams, 1984, 5: 365–374.
- [14] KOZLOVSKII Yu M, STANKUS S V. Thermal expansion of beryllium oxide in the temperature interval 20–1550 °C [J]. High Temperature, 2014, 52: 536–540.
- [15] ABDULLAEV R N, KOZLOVSKII Yu M, KHAIRULIN R A, STANKUS S V. Density and thermal expansion of high purity nickel over the temperature range from 150 K to 2030 K [J]. International Journal of Thermophysics, 2015, 36: 603–619.
- [16] STANKUS S V, KHAIRULIN R A. Measurement of the thermal properties of platinum in the temperature interval 293–2300 K by the method of penetrating radiation [J]. High Temperature, 1992, 30: 386–391.
- [17] STANKUS S V, KHAIRULIN R A. Density and phase diagram of the magnesium-lead system in the region of Mg₂Pb intermetallic compound [J]. Thermochimica Acta, 2008, 474: 52–56.
- [18] STANKUS S V, KHAIRULIN R A, POPEL P S. The technique of experimental determination of the density of solid and liquid materials by a gamma method [M]. Moscow: Standartinform, 2013. (in Russian)
- [19] SpringerMaterials-properties of materials [EB/OL]. https://materials. springer.com. 2018–02–28.
- [20] KHAIRULIN R A, STANKUS S V, KOSHELEVA A S. The interdiffusion in melts of tin-lead system of eutectic and near-eutectic composition [J]. High Temperature, 2008, 46: 212–217.
- [21] KHAIRULIN R A, STANKUS S V, SOROKIN A L. Determination of the two-melt phase boundary and study of the binary diffusion in liquid Bi-Ga system with a miscibility gap [J]. Journal of Non-crystalline Solids, 2002, 297: 120–130.
- [22] GASIOR W, MOSER Z, ZAKULSKI W, SCHWITZGEBEL G. Thermodynamic studies and the phase diagram of the Li–Mg system [J]. Metallurgical and Materials Transactions A, 1996, 27: 2419–2428.
- [23] SALDAU P, SCHAMRAY F. Equilibrium diagram of the magnesium–lithium system [J]. Zeitschrift für anorganische und allgemeine Chemie, 1935, 224: 388–398. (in German)
- [24] FREETH W E, RAYNOR G V. The systems magnesium-lithium and magnesium-lithium-silver [J]. Journal of the Institute of Metals, 1954, 82: 575–580.
- [25] SCHÜRMANN E, VOSS H. Investigation of the melting equilibria of Mg–Li–Al alloys [J]. Giessereiforschung, 1981, 33: 33–53.
- [26] SABOUNGI M L, HSU C C. Computation of isothermal sections of the Al-H-Mg system [J]. Calphad, 1977, 1: 237–251.

- R. N. ABDULLAEV, et al/Trans. Nonferrous Met. Soc. China 29(2019) 507-514
- [27] SAUNDERS N. A review and thermodynamic assessment of the Al–Mg and Mg–Li systems [J]. Calphad, 1990, 14: 61–70.
- [28] TONKOV E Y. Phase diagrams of the elements at high pressure [M]. Moscow: Nauka, 1979. (in Russian)
- [29] von BATCHELDER F W, RAEUCHLE R F. Lattice constants and brillouin zone overlap in dilute magnesium alloys [J]. Physical Review, 1957, 105: 59–61.
- [30] TOULOUKIAN Y S, KIRBY R K, TAYLOR R E. Thermophysical properties of matter [M]. Volume 12. New York, 1975.
- [31] PATHAK P D, DESAI R J. Thermal expansion of magnesium and temperature variation of negative second moment of its frequency spectrum [J]. Physica Status Solidi (A), 1981, 66: 179–182.
- [32] LU X G, SELLEBY M, SUNDMAN B. Assessments of molar volume and thermal expansion for selected bec, fcc and hcp metallic elements [J]. Calphad, 2005, 29: 68–89.
- [33] MEL'NIKOVA T N. Reviews of thermophysical properties of substances [M]. No. 6 (74). Moscow: IVTAN USSR, 1988. (in Russian)
- [34] PILLING N B, KIHLGREN T E. A method for study of shrinkage and its distribution in castings [J]. Trans Amer Found Assoc, 1932, 3: 201–216.
- [35] PELZEL E. Density measurements at high temperatures XI [J]. Zeitschrift für Metallkunde, 1940, 32: 7–9. (in German)
- [36] MCGONIGAL P J, KIRSHENBAUM A D, GROSSE A V. The liquid temperature range, density, and critical constants of magnesium [J]. The Journal of Physical Chemistry, 1962, 66: 737–740.

- [37] STANKUS S V, KHAIRULIN R A. Temperature and interphase changes in the density of magnesium in the solid and liquid states [J]. Tsvetnye metally, 1990, 9: 65–67. (in Russian)
- [38] STANKUS S V. Density change of elements on melting. Methods and experimental data [M]. Preprint No. 275. Novosibirsk: Institute of Thermophysics, 1991. (in Russian)
- [39] ARNDT K, PLOETZ G. The density of molten magnesium [J]. Zeitschrift für Physikalische Chemie, 1927, 130: 184–186. (in German)
- [40] PELZEL E, SAUERWALD F. Density measurements at high temperatures XII [J]. Zeitschrift f
 ür Metallkunde, 1941, 33: 229. (in German)
- [41] GEBHARDT E, BECKER M, TRAGNER E. About the properties of metallic melts. 10. The internal friction of liquid magnesium-lead alloys [J]. Zeitschrift für Metallkunde, 1955, 46: 90–94. (in German)
- [42] EDWARDS J D, TAYLOR C S. Density of magnesium from 20 to 700 °C [J]. Transactions of the AIME, 1923, 69: 1070–1075.
- [43] KHAIRULIN R A, ABDULLAEV R N, STANKUS S V, AGAZHANOV A S, SAVCHENKO I V. Volumetric properties of lithium–lead melts [J]. International Journal of Thermophysics, 2017, 38: 23.
- [44] SOMMER F. Thermodynamic investigation of liquid Li–Mg alloys [J]. Zeitschrift für Metallkunde, 1979, 70: 359–361.
- [45] SABOUNGI M L, BLANDER M. Electromotive force measurements in molten lithium-magnesium alloys [J]. Journal of the Electrochemical Society, 1975, 122: 1631–1634.

固态和液态镁及镁锂合金的密度

R. N. ABDULLAEV, R. A. KHAIRULIN, Yu. M. KOZLOVSKII, A. Sh. AGAZHANOV, S. V. STANKUS

Institute of Thermophysics, Siberian Branch of the Russian Academy of Sciences, Lavrentyev Avenue 1, 630090 Novosibirsk, Russia

摘 要:给出关于固体和液态的镁以及含 23.03 at.%和 30.02 at.% Li的超轻镁锂合金的密度和热膨胀率的新实验数据。采用膨胀计法和伽马射线衰减技术进行测量,测量的温度范围对于镁为 145~1244 K,对于镁锂合金为 293~1000 K。直接测量 Mg 和 Mg₇₀Li₃₀合金在固-液相变时的密度变化,建立体积性质与温度的关系和参考表。将所得结果与文献数据进行比较,结果表明,镁锂体系中的共晶成分不是 23 at.% Li。研究发现,在 0~30 at.% Li 范围内,液态镁锂体系的摩尔体积与浓度几乎呈线性关系,和理想混合物的明显不同。

关键词: 密度; 熔体; 固体; 镁; 镁锂合金; 热膨胀; 互扩散

(Edited by Bing YANG)

514