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VAPOUR COMPOSITION AND ACTIVITIES IN Mg–Zn LIQUID ALLOY AT 923 K

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ABSTRACT

Vapour species effusing from a magnesia Knudsen cell containing Mg–Zn alloy at 923 K were condensed on a water cooled copper plate. The equilibrium composition of the vapour phase over the alloy was determined from chemical analysis of the condensate. The activity coefficients of both components in the alloy have been derived from the data using a modified Gibbs-Duhem relation. The ratio of saturation vapour pressures of pure Zn and Mg obtained from the analysis of alloy data agree well with values from the literature, providing an internal check on the accuracy of data obtained in this study. Both components of the alloy exhibit negative deviations from Raoult's law. The concentration-concentration structure factor of Bhatia and Thornton at zero wave vector, evaluated from the measurements, indicate the presence of $MgZn_2$ type complex in the liquid state. The associated regular solution model has been used for the thermodynamic description of liquid Mg–Zn alloys.

INTRODUCTION

A number of commercial magnesium alloys contain up to 5% zinc. Thermodynamic data on Mg–Zn alloys are of interest in minimizing material loss during alloying and optimizing the recovery of magnesium from scrap and waste by vacuum distillation. The phase diagram shows the presence of five intermetallic compounds [1]. Only one of these $MgZn_2$ melts congruently at 861 K; others decompose incongruently at lower temperatures. Early thermodynamic measurements on this system have been evaluated by Hultgren et al. [2]. Their evaluation relies heavily on closely agreeing emf measurements of Terpilowski [3], 923 K, $X_{Zn} = 0.2$ to 0.965, and Chiotti and Stevens [4], 673–1023 K, $X_{Zn} = 0.365$–0.948. The evaluated data agree only approximately with the zinc vapour pressure measurements of Kozuka et al. [5], 1043–1143 K $X_{Zn} = 0.2$–1.0. The free energy of mixing at equiatomic composition obtained by Kozuka et al. is 1.4 kJ per gram atom more

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positive than that recommended by Hultgren et al. at 923 K. The enthalpy of mixing obtained by Kawakami [6], 1073 K, $X_{Zn} = 0.265–0.776$, by the use of direct reaction calorimetry has been rejected in the evaluation [2] because Kawakami's results have been found to be incorrect in other systems. No other calorimetric work is available in the literature for the liquid phase.

Since the zinc content of magnesium distilled from scrap is usually higher than that calculated from the selected data of Hultgren et al. [2], measurements have been undertaken on the composition of the vapour phase in equilibrium with Mg–Zn alloys. Analysis of these data suggests that negative deviation from ideality in the Mg–Zn system is slightly less than that suggested by emf studies.

APPARATUS AND PROCEDURE

Approximately 40 g of the alloy was prepared in situ by melting pure metals of 99.99 + purity in a magnesia crucible fitted with a lid containing a Knudsen orifice. The orifice diameter varied from 0.3 to 0.7 mm. The magnesia crucible was supported inside an internally heated vacuum resistance furnace as shown in Fig. 1. Radiation shields made of molybdenum foil were placed around the heating elements. The outer steel shell of the

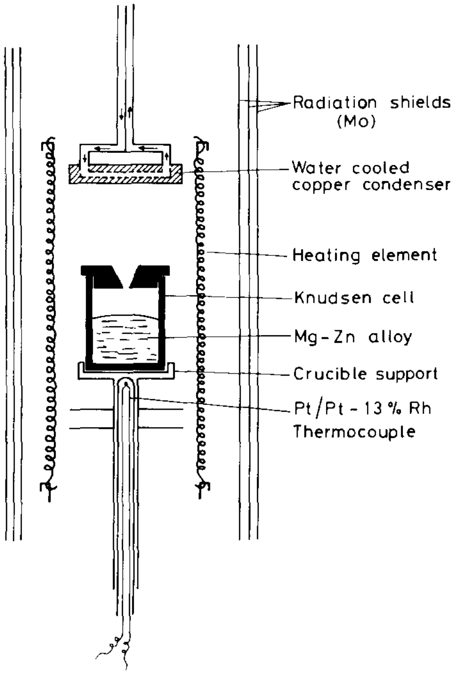

Fig. 1. A schematic diagram of the apparatus.

furnace was water cooled. The magnesia crucible was placed in the hot zone of the furnace such that the temperature of the lid was 2 K above that of the melt. This prevented condensation of the vapour near the Knudsen orifice. The temperature of the alloy was measured by a calibrated Pt/Pt + 13% Rh thermocouple placed immediately below the crucible. The temperature of the furnace was controlled to ± 1.5 K. The vacuum system consisted of an oil diffusion pump backed up by a mechanical rotary pump. Typical pressures inside the furnace were of the order of 10^{-3} Pa.

The alloy was first prepared by melting the component metals at 1000 K. The temperature was then reduced to 923 K. After temperature stabilization, a water cooled copper collector plate was lowered into the hot zone. Approximately 0.5–0.8 g of condensate were collected on the copper plate during each run. At the end of the experiment the condenser plate was withdrawn from the hot zone and the power supply to the furnace was switched off. The concentrations of magnesium and zinc in the condensate and the alloy were determined at the end of each experiment by atomic absorption spectrophotometry and volumetric method. The line at 2852.1 Å was used for the determination of magnesium, while the line at 2138.6 Å was chosen for zinc analysis. Volumetric methods were mainly used for concentrated alloys and for confirmation. Analytical results showed a small loss of zinc (less than 0.8%) from the alloy due to preferential vaporization during the experiment. The average values, representing the composition midway through each run, were used in data analysis.

The vapour pressures of magnesium and zinc at 923 K are 421 and 3673 Pa, respectively. These pressures are ideal for the application of the transpiration technique for determination of activities, but the reactivity of alloy components gives rise to experimental difficulties. The flow of vapour through the orifice at pressures prevailing over Mg–Zn alloys at 923 K would strictly be governed neither by the Knudsen equation for molecular flow nor by the equation for viscous flow. The pressures correspond to a transition region between the two regimes. However, provided the evaporation surface is greater than one hundred times the orifice area, the vapour phase inside the cell would be in equilibrium with the alloy. This is confirmed, as the composition of the condensate was independent of the orifice diameter. Thus the use of techniques for determination of vapour composition permits activity determination under conditions where the Knudsen equation is not strictly valid.

The compositions of the condensate (C) and of the vapour phase (N) in equilibrium with the alloy, expressed using molar concentration variables, are summarized in Table 1. They are related by the expression

$$\frac{C_{\mathrm{Zn}}}{C_{\mathrm{Mg}}} = \frac{N_{\mathrm{Zn}}}{N_{\mathrm{Mg}}}\left(\frac{M_{\mathrm{Mg}}}{M_{\mathrm{Zn}}}\right)^{1/2}$$

where M_i is the molecular weight of i. The activity coefficients of both

TABLE 1

Composition of the condensate and of the equilibrium vapour

Composition of liquid alloy X_{Zn}	Composition of condensate		Composition of equilibrium vapour	
	C_{Zn}	C_{Mg}	N_{Zn}	N_{Mg}
0.0333	0.0541	–	0.0858	0.9142
0.1270	0.2234	0.7766	0.3205	0.6795
0.2460	0.4477	0.5523	0.5710	0.4290
0.3750	0.6576	0.3424	0.7590	0.2410
0.5200	0.8282	0.1718	0.8880	0.1120
0.6280	–	0.0876	0.9447	0.0553
0.7470	–	0.0324	0.9800	0.0200
0.8600	–	0.0109	0.9933	0.0067
0.9500	–	0.00267	0.99837	0.00163

components in the alloy are derived from the equilibrium vapour phase composition using a modified Gibbs-Duhem relation [7]

$$\log \gamma_{Mg} = -\int_{X_{Mg}=1}^{X_{Mg}} X_{Zn} \mathrm{d}\left[\log\left\{\frac{a_{Zn}}{a_{Mg}} \frac{X_{Mg}}{X_{Zn}}\right\}\right] \tag{1}$$

As the activity of a component is directly proportional to the partial pressure (assuming ideal gas behaviour) of the corresponding monomeric gas species, which in turn is directly proportional to the vapour phase composition, eqn. (1) can be modified as

$$\log \gamma_{Mg} = -\int_{X_{Mg}=1}^{X_{Mg}} X_{Zn} \,\mathrm{d}\left[\log\left\{\frac{N_{Zn}}{N_{Mg}} \frac{X_{Mg}}{X_{Zn}}\right\}\right] \tag{2}$$

Similarly

$$\log \gamma_{Zn} = -\int_{X_{Zn}=1}^{X_{Zn}} X_{Mg} \,\mathrm{d}\left[\log\left\{\frac{N_{Mg}}{N_{Zn}} \frac{X_{Zn}}{X_{Mg}}\right\}\right] \tag{3}$$

The integration plot for deriving activity coefficients is shown in Fig. 2. The internal consistency of this plot can be easily verified. The composition (X'_{Zn}) at which the area generated by the integral

$$-\int_{X_{Zn}=0}^{X'_{Zn}} X_{Zn} \,\mathrm{d}\left[\log\left\{\frac{N_{Zn}}{N_{Mg}} \frac{X_{Mg}}{X_{Zn}}\right\}\right]$$

is equal to the area generated by the integral

$$\int_{X_{Zn}=1}^{X'_{Zn}} (1 - X_{Zn})\mathrm{d}\left[\log\left\{\frac{N_{Zn}}{N_{Mg}} \frac{X_{Mg}}{X_{Zn}}\right\}\right]$$

the activity coefficients are equal and therefore value of the function on the

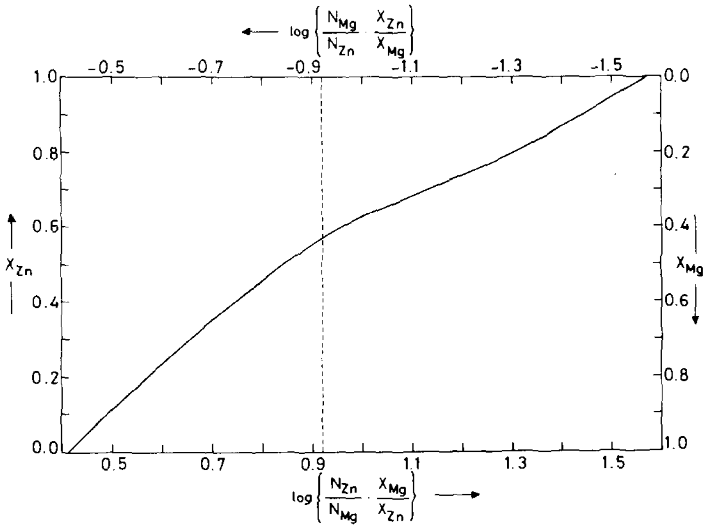

Fig. 2. A modified Gibbs-Duhem integration plot for determination of activities of Mg and Zn in the Mg–Zn solution at 923 K.

X-axis is equal to $\log(p^0_{Zn}/p^0_{Mg})$, where p^0_i is the vapour pressure of pure i. The equal area point occurs at $X_{Zn} = 0.56$, and therefore the value of $\log(p^0_{Zn}/p^0_{Mg})$ from alloy measurements at 923 K is 0.92 which is in good agreement with the value of 0.94 reported in the evaluation of Hultgren et al. [8]. The activities of magnesium and zinc in the binary Mg–Zn alloy

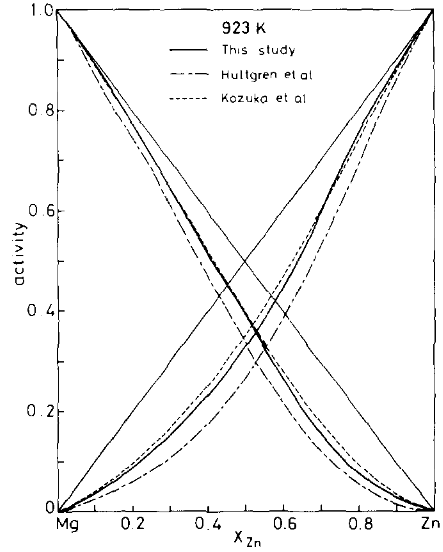

Fig. 3. Activity–composition relationship in the Mg–Zn binary alloy at 923 K and comparison with the literature.

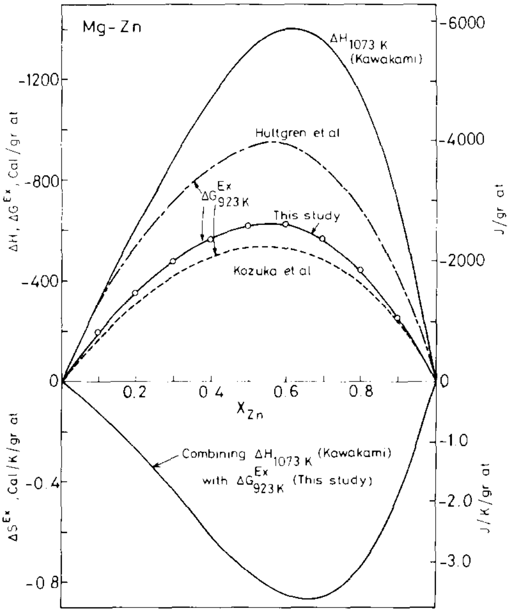

Fig. 4. Excess Gibbs energy, enthalpy and entropy of mixing in the Mg–Zn alloy.

obtained in the present study at 923 K are shown in Fig. 3 and the excess Gibbs energy as a function of composition is shown in Fig. 4. Activities of both components exhibit negative deviations from Raoult's law indicating a

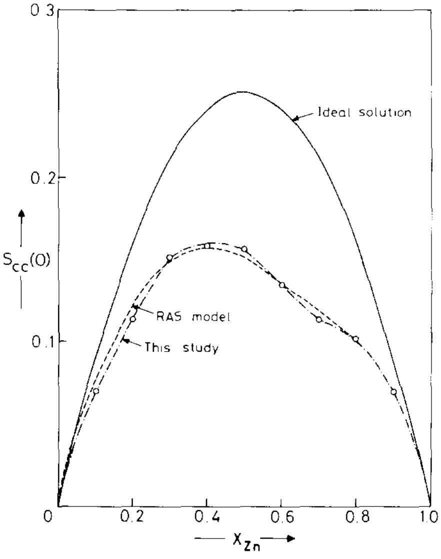

Fig. 5. Bhatia-Thornton concentration–concentration structure factor at zero wave vector, $S_{cc}(0)$, for Mg–Zn alloys at 923 K.

tendency for compound formation. The concentration–concentration structure factor of Bhatia and Thornton at zero wave vector can be calculated from the activity data [9]

$$S_{cc}(0) = (1 - X_{Mg})\left[\frac{\partial \ln a_{Mg}}{\partial X_{Mg}}\right]_{T,P}^{-1} \tag{4}$$

The derived values are shown in Fig. 5. The structure factor is related to the mean square thermal fluctuation in composition [9]

$$S_{cc}(0) = \bar{N}\langle(\Delta C)^2\rangle \tag{5}$$

where $\bar{N}$ is the average number of particles in a fixed volume V and (ΔC) is the mean-square thermal fluctuation in concentration. The structure factor at zero wave vector exhibits a dip at $X_{Zn} \sim 0.7$ compared with the value for an ideal solution, suggesting the presence of a complex of the type $MgZn_2$ in the liquid state.

DISCUSSION

Comparison with the literature

Earlier thermodynamic studies on Mg–Zn binary liquid alloys are listed in the compilation of Hultgren et al. [2]. Their selected values for activities and Gibbs energies are based on the emf studies of Terpilowski [3] and Chiotti and Stevens [4]. The activities of both the components and the integral Gibbs energies of mixing reported in the evaluation of Hultgren et al. [2] are shown in Figs. 3 and 4, respectively. The present study shows less negative deviations from ideality. Chiotti and Stevens [4] used tantalum cups to contain both the reference electrode and the alloy. Tantalum forms several intermetallic compounds with zinc [10]. Also their measurements only covered a limited range of composition, $X_{Zn} = 0.365–0.948$, so that the integral properties derived using the Gibbs-Duhem equation have relatively large uncertainity. The activities of Zn in binary Mg–Zn liquid alloys were also determined by Kozuka et al. [5] using a carrier gas technique. Activities and integral Gibbs energies of mixing at 923 K, reported by Kozuka et al. [5] based on zinc vapour pressure measurements are also shown in Figs. 3 and 4. The results of this study fall between the values given by Kozuka et al. [5] and Hultgren et al. [2], but are closer to the former. The only calorimetric measurement available in the literature is that of Kawakami [6]. The entropy of mixing calculated from Kawakami's enthalpy data and free energy from the present study is also shown in Fig. 4. The minimum in excess entropy occurs at a composition close to that of the Laves phase $MgZn_2$.

Gibbs energy of the Laves phase $MgZn_2$

The Gibbs energy of mixing at the composition $X_{Zn} = 0.667$ obtained in the present study is extrapolated to the melting temperature of the intermediate phase (861 K) using the enthalpy data on liquid Mg–Zn alloys [6]. This is then combined with the enthalpy of formation of the compound $MgZn_2$ and enthalpies of fusion of pure Mg and Zn compiled by Hultgren et al. [2,8] to yield an expression for the free energy of formation of $MgZn_2$. The Gibbs energy of formation of the Laves phase, corresponding to the reaction $2Zn(s) + Mg(s) \rightarrow MgZn_2(s)$ in the temperature range 400 to 861 K is $\Delta G^{\ominus} = -33{,}562 + 10.231T$ (J mol^{-1}). The free energy of formation derived in the present study is 3.8 kJ mol^{-1} more positive than that recommended by Chiotti and Stevens [4].

Associated regular solution model

The thermodynamics of liquid Mg–Zn alloys can be described by an associated regular solution model [11]. The associated regular solution model postulates the existence of complexes in the liquid solution due to chemical interactions upon mixing of the components. The complexes will be in equilibrium among themselves and with the monomers of the pure components. The complexes and the monomers, termed species to differentiate from the components, obey a strictly regular solution behaviour, whereas the macroscopic components can exhibit non-regular behaviour. In the present study the associated regular solution model is examined in relation to a Mg–Zn liquid solution in which two monomers Mg and Zn are in equilibrium with the associated species $MgZn_2$. The absolute mole fractions of components, Zn (X_1) and Mg (X_2) are related to the species mole fractions X_{Zn}, X_{Mg} and X_{MgZn_2} by mass balance restrictions, given by

$$X_{Zn} = X_1\left[1 + 2X_{MgZn_2}\right] - 2X_{MgZn_2} \qquad (6)$$

and

$$X_{Mg} = X_2\left[1 + 2X_{MgZn_2}\right] - X_{MgZn_2} \qquad (7)$$

The equilibrium constant for the dissociation of the complex $MgZn_2 \rightleftharpoons 2Zn + Mg$ is given by

$$\begin{aligned}\ln K = {} & \ln\frac{X_{Zn}^2 X_{Mg}}{X_{MgZn_2}} + \frac{\omega_{Zn-Mg}}{RT}\left[2X_{Mg}(1 - X_{Zn}) + X_{Zn}\right] \\ & + \frac{\omega_{Zn-MgZn_2}}{RT}\left[2X_{MgZn_2}(1 - X_{Zn}) - X_{Zn}\right] \\ & + \frac{\omega_{Mg-MgZn_2}}{RT}\left[X_{MgZn_2}(1 - 2X_{Mg}) - X_{Mg}\right] \qquad (8)\end{aligned}$$

TABLE 2

Interaction energies and equilibrium constant corresponding to associated regular solution model for the system Mg–Zn at 923 K

Interaction energies (kJ mol^{-1})			K
$\omega_{\text{Zn-Mg}}$	$\omega_{\text{Mg-MgZn}_2}$	$\omega_{\text{Zn-MgZn}_2}$	
−8.8938	1.4604	2.0395	0.5805

The free energy of mixing for an associated regular solution is given by

$$\Delta G^{\text{m}} = \frac{1}{\left(1 + 2X_{\text{MgZn}_2}\right)}\left(X_{\text{Zn}}X_{\text{Mg}}\omega_{\text{Zn-Mg}} + X_{\text{Zn}}X_{\text{MgZn}_2}\omega_{\text{Zn-MgZn}_2} + X_{\text{Mg}}X_{\text{MgZn}_2}\omega_{\text{Mg-MgZn}_2}\right) + \frac{RT}{\left(1 + 2X_{\text{MgZn}_2}\right)} \times \left(X_{\text{Zn}} \ln X_{\text{Zn}} + X_{\text{Mg}} \ln X_{\text{Mg}} + X_{\text{MgZn}_2} \ln X_{\text{MgZn}_2}\right) + \frac{X_{\text{MgZn}_2}}{\left(1 + 2X_{\text{MgZn}_2}\right)} RT \ln K \tag{9}$$

The interaction energies ω_{ij} and the equilibrium constant for the dissociation of the complex MgZn_2 were determined by the procedure developed by Lele and Rao [12] using the values of activity coefficients at infinite dilution and one set of activity values for a concentrated solution following an iteration technique. The parameters so derived are listed in Table 2. The integral Gibbs energies of mixing for the Mg–Zn system at 923 K as a function of composition, estimated from an associated regular solution model using eqn. (9), are given in Table 3 for comparison with the values obtained in the present study. The concentration–concentration structure factor $S_{\text{cc}}(0)$ at the zero wave vector limit is given by

$$S_{\text{cc}}(0) = RT\left[\frac{\partial^2 G^{\text{m}}}{\partial X_1^2}\right]_{T,P}^{-1} \tag{10}$$

Using eqn. (9) in eqn. (10), following Bhatia and Hargrove [13], $S_{\text{cc}}(0)$ can be written as

$$S_{\text{cc}}(0) = \frac{S_{\text{cc}}}{1 + DS_{\text{cc}}} \tag{11}$$

Here

$$S_{\text{cc}} = \left(1 + 2X_{\text{MgZn}_2}\right)\left[\frac{\left(X'_{\text{Zn}}\right)^2}{X_{\text{Zn}}} + \frac{\left(X'_{\text{Mg}}\right)^2}{X_{\text{Mg}}} + \frac{\left(X'_{\text{MgZn}_2}\right)^2}{X_{\text{MgZn}_2}}\right]^{-1}$$

TABLE 3

Comparison of Gibbs energy of mixing for the Mg–Zn system at 923 K from experiment and associated regular solution model

X_{Zn}	$-\Delta G^m$ (J mol^{-1})	
	ARS model	Experimental
0.1	3539	3544
0.2	5678	5705
0.3	7040	7058
0.4	7755	7774
0.5	7906	7906
0.6	7545	7544
0.7	6694	6694
0.8	5321	5323
0.9	3308	3293

and

$$D = \frac{2}{RT(1 + 2X_{MgZn_2})}\left[\omega_{Zn-Mg}X'_{Zn}X'_{Mg} + \omega_{Mg-MgZn_2}X'_{Mg}X'_{MgZn_2} + \omega_{Zn-MgZn_2}X'_{Zn}X'_{MgZn_2}\right]$$

where a prime denotes differentiation with respect to X_1. From the known values of interaction energies ω_{ij} and K, $S_{cc}(0)$ was calculated as a function of concentration for the Mg–Zn system at 923 K. As shown in Fig. 5, the results calculated from the associated regular solution model are in good agreement with values derived directly from activity measurements.

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