

Thermodynamic Properties of Liquid Magnesium-Nickel Alloys

K. Micke and H. Ipsen*

Institut für Anorganische Chemie der Universität Wien, A-1090 Wien, Austria

Summary. Magnesium vapor pressures were determined over liquid Mg–Ni alloys for compositions $x_{\text{Mg}} > 0.65$ using an isopiestic method. Data points between 760 and 890 °C were evaluated to derive corresponding partial thermodynamic properties. The composition dependence of the magnesium activities in liquid alloys is shown for a temperature of 1073 K. Additionally, it is possible to obtain the shape of the liquidus curve between about 60 and 70 at% Mg from the results of the isopiestic measurements.

Keywords. Mg–Ni alloys; Mg–Ni system: thermodynamic properties; Mg–Ni system: phase diagram.

Thermodynamische Eigenschaften flüssiger Mg–Ni Legierungen

Zusammenfassung. Magnesiumdampfdrücke wurden mit Hilfe einer isopiestic Methode über flüssigen Mg–Ni-Legierungen mit einer Zusammensetzung $x_{\text{Mg}} > 0.65$ bestimmt. Aus experimentellen Punkten zwischen 760 und 890 °C wurden die entsprechenden partiellen thermodynamischen Eigenschaften abgeleitet. Es wird die Konzentrationsabhängigkeit der Magnesiumaktivitäten in flüssigen Legierungen bei 1073 K gezeigt. Zusätzlich kann aus dem Ergebnis der isopiestic Messungen der Verlauf der Liquiduskurve zwischen etwa 60 und 70 At% Mg ermittelt werden.

Introduction

Magnesium is an important component in different types of alloys which are of technical interest. Due to its low density it is used in various light alloys that are employed as construction materials in the transportation industry [1]. On the other hand, it is also used as an additive in different nickel-base alloys where it improves the mechanical properties and enhances their hot ductility [2].

In order to optimize the production process and the final properties of such materials which are generally multi-component alloys, a good knowledge of the thermodynamic properties and of the corresponding phase equilibria is of importance. Since the experimental determination of such information for systems containing more than three components becomes extremely tedious, very ambitious attempts have been made over the last two decades to predict thermodynamic properties and phase relationships of such materials from the corresponding properties of the binary and ternary systems from which they are composed.

In a recent attempt to optimize the binary Mg–Ni system [3] being a basic component of different higher-order magnesium alloys, it was again observed that the liquidus line in the composition range between 40 and 70 at% Mg cannot be fixed with certainty due to considerable discrepancies in the experimental data (*cf.* Ref. [4]). Additionally, any optimization of the phase diagram based on thermodynamic calculations is hampered by the fact that the necessary experimental thermodynamic information is rather limited, too [5, 6].

Thus, it was decided to start a thermodynamic investigation of liquid Mg–Ni alloys using an isopiestic vapor pressure method that had been employed successfully to determine partial thermodynamic properties of magnesium in ternary Cu–Mg–Ni alloys [7–9].

Experimental

The general principles of the isopiestic equilibration technique and its application to the measurement of magnesium vapor pressures have been described in detail in a number of previous publications [8–10]. Since magnesium reacts with most container materials at high temperatures, the entire isopiestic apparatus was made from pure iron (99.5%; Goodfellow, Cambridge, U.K.), with the crucibles and crucible holders machined from high-purity graphite (quality E506; Ringsdorff, Vienna, Austria). To prevent oxidation of the iron tube, the whole assembly was kept in an evacuated outer quartz container for the period of equilibration in the furnace.

Samples of 60 to 80 mg Ni were cut from a foil (0.125 mm thickness; 99.99%; Advent, Halesworth, U.K.) and weighed (± 0.05 mg) into the graphite crucibles; chips of high-purity magnesium were cut from a rod (15 mm diam.; 99.95%; Johnson-Matthey, Chemicals Ltd., London, U.K.) and loaded into the bottom of the iron apparatus to serve as the reservoir. After assembling the equilibration apparatus, it was evacuated down to 10^{-2} Pa through a thin-walled iron tube and finally closed by welding. Then the entire set-up was sealed within an outer quartz tube and inserted into a two-zone furnace. Further experimental details can be found in Refs. [8, 9].

The experiments lasted between 15 and 25 days, and the temperatures of each sample and of the reservoir were measured regularly by slowly raising a long Pt/Pt10%Rh-thermocouple inside an inner well. At the end, the whole assembly was quenched in cold water, and the outer quartz tube was broken to facilitate direct contact between the water and the iron container in order to achieve an optimum cooling rate. Sample and reservoir temperatures listed in Table 1 are those recorded immediately before quenching.

The compositions of the samples after equilibration were determined from their weight increase which was assumed to be caused by the uptake of magnesium. A number of representative samples were also checked by chemical analysis. For this purpose, the entire crucible containing the Mg–Ni alloy was heated for several hours in concentrated hydrochloric acid and the obtained solution was filtered. The remaining graphite crucible was boiled for extended periods in distilled water and the solution was filtered again. The filtrates were combined and used for analysis [11].

Nickel was precipitated with dimethylglyoxime, and its content was calculated from the mass of the precipitate after drying. The magnesium content was determined separately by complexometric titration using *EDTA* with Eriochrome Black T as indicator. The compositions found by wet-chemical analysis confirmed the values calculated from the weight increase of the samples.

Results and Discussion

A total of five successful experiments were evaluated, with sample temperatures varying between 764 and 886 °C and reservoir temperatures between 746 and 836 °C.

Table 1. Experimental isopiestic results for liquid Mg–Ni alloys; standard state: Mg(l)

Sample No.	at% Mg	T_s (K)	$\ln a_{\text{Mg}}(T_s)$	$\Delta\bar{H}_{\text{Mg}}$ (kJ·g-atom ⁻¹)	$\ln a_{\text{Mg}}(1073 \text{ K})$
Run 1 ($T_R = 1019 \text{ K}$; 17 days)					
1	79.77	1037	-0.267	-1.78	-0.260
2	77.40	1042	-0.335	-2.98	-0.325
3	74.60	1047	-0.409	-4.65	-0.397
4	71.61	1053	-0.489	-6.73	-0.474
Run 2 ($T_R = 1039 \text{ K}$; 20 days)					
1	81.53	1059	-0.295	-1.19	-0.293
2	79.16	1063	-0.344	-2.07	-0.342
3	76.42	1067	-0.407	-3.55	-0.405
4	74.05	1072	-0.469	-5.03	-0.469
5	71.10	1078	-0.558	-7.10	-0.562
6	60.01 ^a	1083			
Run 3 ($T_R = 1070 \text{ K}$; 17 days)					
1	78.41	1095	-0.338	-2.45	-0.344
2	75.31	1100	-0.410	-4.20	-0.422
3	71.96	1106	-0.488	-6.43	-0.510
4	57.91 ^a	1113			
Run 4 ($T_R = 1092 \text{ K}$; 15 days)					
1	80.55	1115	-0.295	-1.46	-0.301
2	77.44	1121	-0.371	-2.97	-0.385
3	74.12	1126	-0.427	-4.98	-0.454
4	71.05	1132	-0.508	-7.15	-0.550
5	67.59	1139	-0.588	(-10.50) ^b	-0.656
Run 5 ($T_R = 1109 \text{ K}$; 26 days)					
1	85.00	1124	-0.193	-0.64	-0.196
2	82.79	1128	-0.234	-0.93	-0.239
3	80.72	1132	-0.281	-1.42	-0.290
4	78.70	1136	-0.331	-2.30	-0.345
5	76.83	1138	-0.366	-3.32	-0.388
6	74.73	1142	-0.415	-4.55	-0.446
7	72.96	1146	-0.458	-5.72	-0.499
8	70.95	1149	-0.497	-7.20	-0.550
9	68.98	1152	-0.529	(-8.98)	-0.598
10	65.62	1156	-0.574	(-13.45)	-0.682
11	46.48 ^a	1159			

^a Samples in the (L + MgNi₂) two-phase field; ^b values in parentheses are from extrapolated curve in Fig. 2

The results and the experimental conditions are listed in Table 1. It is estimated that the uncertainty of the compositions is at most ± 0.20 at% and that of the temperatures approximately ± 2 K. The so-called equilibrium curves, which are plots of sample temperature *vs.* composition for each individual isopiestic run, are shown in Fig. 1. The curves are superimposed on the partial Mg–Ni phase diagram.

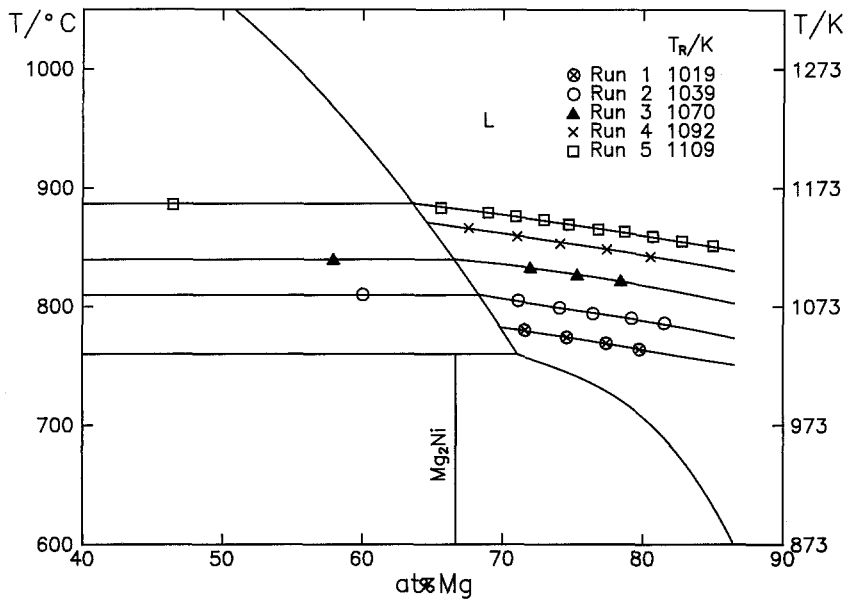


Fig. 1. Sample temperature vs. sample composition for five isopiestic experiments in the Mg–Ni system superimposed on the partial Mg–Ni phase diagram

Three samples in three different runs (No. 6/run 2, No. 4/run 3, No. 11/run 5) had compositions in the (L + MgNi₂) two-phase field after equilibration. According to the phase rule, the temperature of a tie-line defines also the boundaries of the corresponding two-phase field in a binary system, if the pressure is kept constant (in each isopiestic experiment, the pressure is constant and determined by the temperature of the magnesium reservoir). Consequently, three points on the liquidus line are defined by the intersections of the three tie-lines with the equilibrium curves in the liquid phase for runs No. 2, 3, and 5 (*cf.* Fig. 1): 810 °C at 31.5 at% Mg, 840 °C at 33.3 at% Mg, and 886 °C at 36.3 at% Mg. These values are in excellent agreement with the liquidus curve selected by *Jacobs* [3] and by *Nayeb-Hashemi and Clark* [4] for this composition range. It proves that the experimental liquidus data of *Haughton and Payne* [12] are clearly to be preferred over those by *Voss* [13].

Partial thermodynamic properties for liquid alloys were calculated as follows. The thermodynamic activity of Mg, a_{Mg} , in a sample at the temperature T_s is given by

$$a_{\text{Mg}} = p_{\text{Mg}}(T_s)/p_{\text{Mg}}^{\circ}(T_s) \quad 1$$

where $p_{\text{Mg}}(T_s)$ is the partial pressure of magnesium vapor over the sample at the sample temperature T_s and $p_{\text{Mg}}^{\circ}(T_s)$ is the vapor pressure of pure magnesium at the same temperature. Under equilibrium conditions, the partial pressure of magnesium in the entire tube is equal to the saturated vapor pressure of pure magnesium at the reservoir temperature T_R , and Eq. 1 becomes

$$a_{\text{Mg}} = p_{\text{Mg}}^{\circ}(T_R)/p_{\text{Mg}}^{\circ}(T_s). \quad 2$$

The necessary values for the vapor pressure of pure liquid magnesium in the temperature range of interest were taken from *Chase et al.* [14], and they were fitted

to the following equation:

$$\log(p_{\text{Mg}}^{\circ}/\text{bar}) = 5.0409 - 6876.2(\text{K}/T) \quad 3$$

Partial molar enthalpies of mixing for magnesium can be obtained from a plot of $\ln a_{\text{Mg}}$ vs. $1/T_s$ for compositions chosen at regular intervals (see for example *Hanninger et al.* [15]) according to

$$\partial \ln a_{\text{Mg}} / \partial (1/T_s) = \Delta \bar{H}_{\text{Mg}} / R \quad 4$$

However, the deduction of partial enthalpies from activity data over a rather limited temperature range, as in the present isopiestic experiments (less than 100 K for any composition), could involve considerable errors, especially when a noticeable scatter is observed for the temperature dependence of the activities.

Feufel and Sommer [17] measured integral enthalpies of mixing for liquid Mg–Ni alloys at temperatures around 1000 K by a calorimetric method, and from these partial molar enthalpies could be derived between 70 and 82 at% Mg by the method of intercepts. In order to obtain a better consistency with the calorimetric results, appropriate weighting factors were applied to the individual isopiestic runs for the calculation of $\Delta \bar{H}_{\text{Mg}}$ values. The obtained partial enthalpies are shown in Fig. 2 as a function of composition. The smoothed curve for $\Delta \bar{H}_{\text{Mg}}$ is shown as a dashed line below 70 at% Mg because it had to be extrapolated in a somewhat arbitrary way; the corresponding values in Table 1 are set in parentheses.

A comparison of the present experimental partial enthalpy values with literature results [6, 16–18] (*cf.* Fig. 2) shows reasonable agreement for the composition

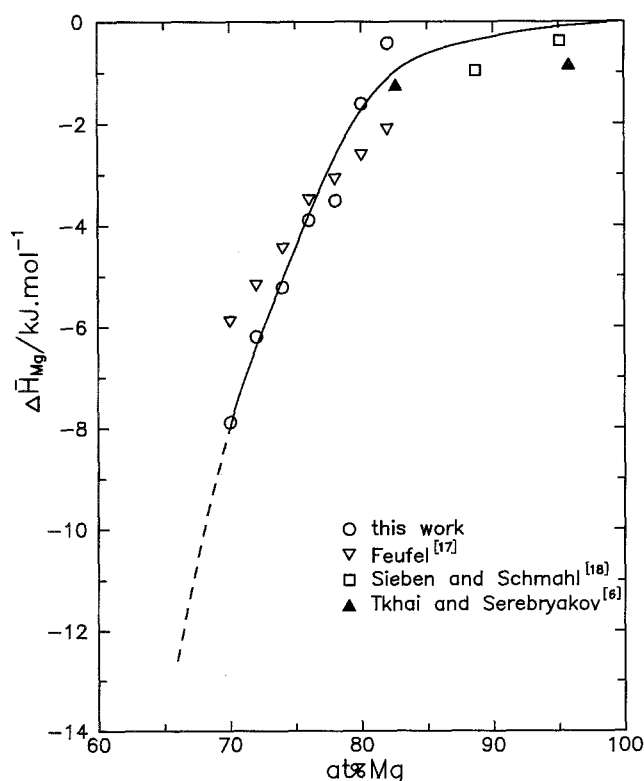


Fig. 2. Partial molar enthalpy of magnesium as a function of composition; standard state: Mg(l)

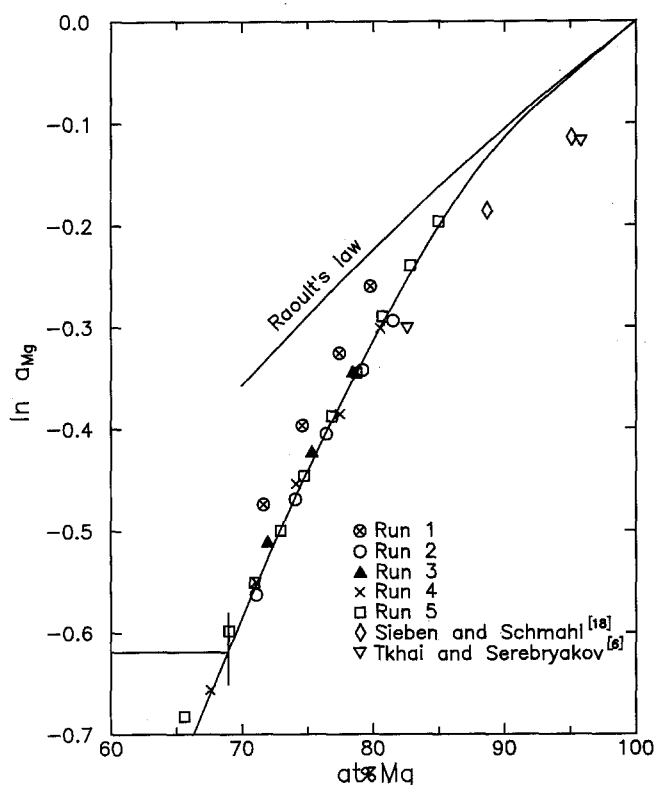


Fig. 3. Natural logarithm of magnesium activity at 1073 K as a function of composition; standard state: Mg(l)

range $x_{\text{Mg}} \geq 0.7$, especially if the original $\Delta \bar{H}_{\text{Mg}}$ values of *Sieben und Schmahl* [18] are taken. It should be mentioned that the values cited by *Hultgren et al.* [5] are considerably more negative, and it is not clear where this discrepancy comes from.

All experimental activity values, originally obtained for the individual sample temperatures, were converted to a common temperature of 1073 K by means of the integral form of Eq. 4; they are listed in Table 1. Figure 3 shows the composition dependence of $\ln a_{\text{Mg}}$ at 1073 K in liquid Mg–Ni alloys for magnesium contents of more than 65 at%. The curve is shown as a dashed line in the metastable range below 69 at% Mg (the phase boundary between the (MgNi₂ + L) two-phase field and the homogeneous liquid).

Literature data by *Sieben and Schmahl* [18] and by *Tkhai and Serebryakov* [6] are also included in Fig. 3. It can be seen that especially the values of $\ln a_{\text{Mg}}$ around 95 at% Mg are considerably more negative than our extrapolated curve. However, this large negative deviation from *Raoult's law* is somewhat surprising, since one would expect that any deviation reduces gradually to zero when approaching pure magnesium. Therefore, it is thought that the activity values obtained in the present investigation should be more reliable.

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