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Solubility of Chloride in Molten Magnesium Metal

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The solubilities of chloride (Cl) in liquid magnesium (Mg) have been determined from the analysis of quenched samples of liquid Mg equilibrated with NaCl-$MgCl_2$ melts of different compositions at temperatures in the range 650-790 °C. As an example, the solubility of Cl in liquid Mg in contact with pure $MgCl_2$ at 735 °C was found to be approximately 18 ppm. The Cl solubility was found to be proportional to the square root of the $MgCl_2$ activity in the NaCl-$MgCl_2$ melt, indicating that $MgCl_2$ dissolved according to the reaction $0.5MgCl_2 + 0.5Mg(l) = MgCl$ (in Mg). The temperature dependency of the solubility also was measured. Thermodynamic values related to the dissolution of $MgCl_2$ in liquid Mg have been estimated.

1. Introduction

Some years ago, we reported on the activity coefficient of Na in magnesium (Mg) metal [2000Ros]. The equilibrium between NaCl-$MgCl_2$ melts and molten Mg then was measured. Samples of the equilibrated metal were analyzed for many elements, among them chloride (Cl). Recently, we reviewed these data and found that the Cl concentration in the metal varied systematically with the $MgCl_2$ concentration. This article reports these findings on the solubility of Cl in liquid Mg metal.

Such data are important since Cl impurities in Mg metal strongly affect its corrosion resistance. Lower Cl concentrations give lower corrosion. During the production and subsequent processing of liquid Mg, the metal is commonly in contact with molten Cl fluxes containing salts such as NaCl, $CaCl_2$, KCl, and $MgCl_2$. Cl impurities in the metal, both as dissolved Cl and as salt inclusions, may therefore be present. Careful processing can eliminate salt inclusions. Dissolved Cl is more difficult to remove, but the proper choice of a fluxing agent can reduce the amount. This choice relies upon thermodynamic data for Cl solubility. Here, such data are estimated. To our knowledge, the present solubility measurements of Cl in Mg metal are the first to be published.

2. Experimental

The experimental procedure, equipment, chemicals, and analytical method have previously been described [2000Ros]. Briefly, high-purity Mg metal was equilibrated with molten mixtures of dried $MgCl_2$ and NaCl of different compositions and temperatures above the melting point of Mg metal and the salt. The molten metal and molten salt were contained in a molybdenum crucible that was placed in a vertical furnace, which was placed inside an Ar-filled glove box. The melt was continuously stirred with a Mo stirrer. Metal samples were extracted at each salt composition and temperature. The samples were quenched and analyzed for many different elements by glow discharge mass spectroscopy. The Cl analyses are shown in Table 1.

Samples 4-7, 5-2, and 5-5 (Table 1) were excluded from the statistical analysis. These three samples showed both high Cl and high O concentrations. The O concentration was more than 10 times higher than those in the other samples, indicating some impurity, maybe in the form of an inclusion containing both oxide and Cl.

3. Results

The results can be analyzed within the frame of an equilibrium of the type:

$$1/2MgCl_2(l) + (1/y-1/2)Mg(l) = 1/yMgCl_y \text{ (in Mg)}$$

with

$$K = \frac{a_{MgCl_y}^{1/y}}{a_{MgCl_2}^{1/2} a_{Mg}^{1/y-1/2}} \quad \text{(Eq 1)}$$

Available standard state thermodynamic data for Cls are those of $MgCl_2$(s), $MgCl_2$(l), $MgCl_2$(g), and MgCl(g). Since data for MgCl(l) is unavailable, the pure standard state equilibrium constant of Eq 1 cannot be calculated. It is, however, possible to determine y in Eq 1 based on the present results. The activity of Mg is very close to one since high-purity electrolytically produced Mg metal was used [2000Ros], and the activity of $MgCl_2$ in the NaCl-$MgCl_2$ salt can be found from existing thermodynamic data. The activities of NaCl and $MgCl_2$ in the salt are determined by the composition in the NaCl-$MgCl_2$ system since the solubility of Mg metal in the salt is very low [1980Wyp]. In this work, the activities were taken from the FACT database [2002Fac]. They are given in Table 1. A Henrian activity coefficient of dissolved Cl is assumed since the solubility of

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Table 1 Cl Analysis of the Samples, Given in ppm by Weight and Mole Fractions (x_{Cl})

Run	Sample (a)	T (°C)	x_{NaCl}	x_{MgCl_2}	a_{NaCl}	a_{MgCl_2}	Cl (ppm)	$x_{Cl}/10^{-6}$
1	1	735	0.00	1.00	0.000	1.000	16	11.0
	2	735	0.20	0.80	0.024	0.749	11	7.5
	3	735	0.40	0.60	0.092	0.419	7.8	5.3
	5	735	0.70	0.30	0.483	0.050	3	2.1
	6	735	0.80	0.20	0.704	0.016	1.9	1.3
	7	735	0.83	0.17	0.763	0.011	1.3	0.9
2	1	735	0.00	1.00	0.000	1.000	20	13.7
	2	735	0.20	0.80	0.024	0.749	14	9.6
	3	735	0.40	0.60	0.092	0.419	4.8	3.3
	4	735	0.60	0.40	0.292	0.129	3.2	2.2
	5	735	0.70	0.30	0.483	0.050	1.6	1.1
	6	735	0.80	0.20	0.704	0.016	0.9	0.6
	7	735	0.83	0.17	0.763	0.011	1.2	0.8
3	1	735	0.00	1.00	0.000	1.000	23	15.8
	2	735	0.20	0.80	0.024	0.749	24.0	16.5
	3	735	0.40	0.60	0.092	0.419	9.5	6.5
	4	735	0.60	0.40	0.292	0.129	4.0	2.7
	5	735	0.70	0.30	0.483	0.050	2.6	1.8
	6	735	0.80	0.20	0.704	0.016	2.0	1.4
	7	735	0.83	0.17	0.763	0.011	1.2	0.8
4	1	735	0.00	1.00	0.000	1.000	18.0	12.3
	2	735	0.40	0.60	0.092	0.419	14.0	9.6
	3	652	0.40	0.60	0.079	0.407	5.0	3.4
	4	787	0.40	0.60	0.099	0.425	32.0	21.9
	5	658	0.55	0.45	0.203	0.175	2.8	1.9
	6	787	0.55	0.45	0.232	0.195	22.0	15.1
	7	787	0.70	0.30	0.493	0.055	30.0	20.6
	8	658	0.70	0.30	0.468	0.043	1.4	1.0
	9	735	0.70	0.30	0.483	0.050	4.1	2.8
5	1	735	0.00	1.00	0.000	1.000	21.0	14.4
	2	735	0.20	0.80	0.024	0.749	34.0	23.3
	3	735	0.40	0.60	0.092	0.419	10.0	6.9
	4	735	0.60	0.40	0.292	0.129	6.8	4.7
	5	735	0.70	0.30	0.483	0.050	70.0	48.0
	6	735	0.80	0.20	0.704	0.016	2.0	1.4
	7	735	0.83	0.17	0.763	0.011	2.0	1.4

(a) The composition of the molten salt, the temperature, and the activities of NaCl and $MgCl_2$ for each sample are also given (activities are calculated from the thermodynamic model implemented in FACT [2002Fac]).

Cl in the metal is very low. The equilibrium expression may thus be rewritten

$$\frac{K}{\gamma^{1/y}_{MgCl_y}} = \frac{x^{1/y}_{MgCl_y}}{a^{1/2}_{MgCl_2} a^{1/y-1/2}_{Mg}} \qquad \text{(Eq 2)}$$

Taking the logarithm of this expression and rearranging yields

$$\ln x_{Cl} = \ln y x_{MgCl_y} = y \ln \frac{K}{\gamma^{1/y}_{MgCl_y}} + \frac{y}{2} \ln a_{MgCl_2} + \ln y \qquad \text{(Eq 3)}$$

At constant T (and P), Eq 3 can be simplified to

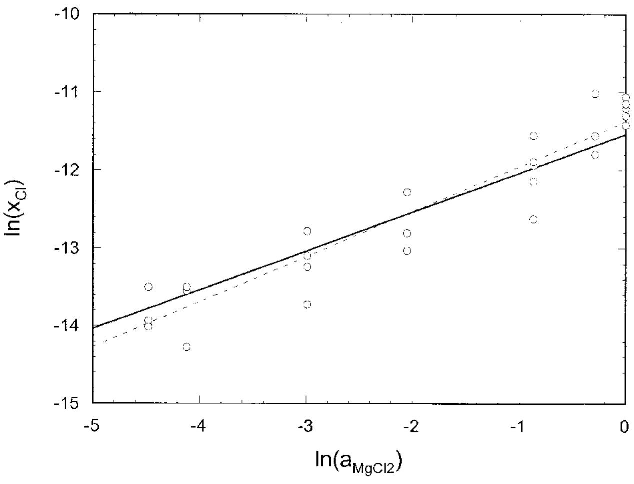

Fig. 1 Chloride concentrations in liquid Mg as a function of the $MgCl_2$ activity in the NaCl-$MgCl_2$ mixture at 735 °C. The full line represents concentrations proportional to $\sqrt{a_{MgCl_2}}$ and the dashed line is the linear regression.

$$\ln x_{Cl} = \text{Constant} + \frac{y}{2} \ln a_{MgCl_2} \qquad \text{(Eq 4)}$$

The slope of the plot of $\ln x_{Cl}$ vs. $\ln a_{MgCl_2}$ at a constant temperature should then be equal to $y/2$. Such a graph is shown in Fig. 1 for the results at 735 °C. The slope determined by linear regression is found to be 0.59 with a 95% confidence interval of 0.45-0.73. $y = 1.2$ suggests an unlikely Mg_5Cl_6 species. $y = 1$ seems like a more probable value, and a slope of 0.5 lies well within the 95% confidence interval. This is illustrated in Fig. 1, where a line with slope 0.5 is included. $y = 1$ suggests that Cl dissolves as single ions in the metal. The dissolution reaction then becomes

$$1/2MgCl_2(l) + 1/2Mg(l) = MgCl\ (\text{in Mg}) \qquad \text{(Eq 5)}$$

The experimental data also allow for the estimation of the temperature dependency of the Cl solubility. Rearranging Eq 3 with $y = 1$, and assuming that the regular solution theory (i.e., $\ln \gamma_{MgCl} = Ax^2_{Mg}/RT \approx A/RT$) holds for the dissolution of Cl in the metal, gives

$$R(\ln x_{Cl} - 1/2 \ln a_{MgCl_2}) = R \ln \frac{K}{\gamma_{MgCl}} = -\frac{\Delta H^\circ - A}{T} + \Delta S^\circ \qquad \text{(Eq 6)}$$

where the enthalpy and entropy refer to Eq 5 with MgCl in the pure liquid standard state. A plot of $R(\ln x_{Cl} - 1/2 \ln a_{MgCl_2})$ versus $1/T$ over a limited temperature range should give a straight line with slope ΔH°-A and intercept ΔS°. Such a plot is shown in Fig. 2. The results of the linear regression are shown in Table 2.

4. Discussion

Table 2 shows rather wide confidence intervals of both ΔH°-A and ΔS°. The significance of this is that using Eq 6

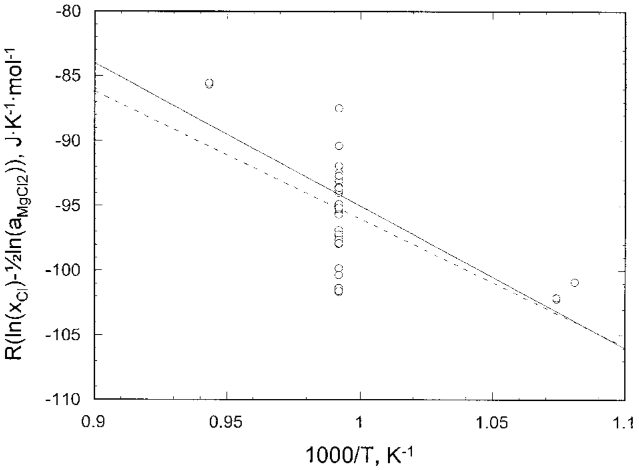

Fig. 2 The expression $R(\ln x_{Cl} - 1/2 \ln a_{MgCl_2})$ plotted vs. 1/T for all the measured chloride concentrations (except samples 4-7, 5-2, and 5-5). The dashed line is a linear regression line and the full line is drawn according to Eq 12.

Table 2 Results of the Determination of $\Delta H°$-*A* and $\Delta S°$ in Eq 6 by Linear Regression

	Value	95% CI (a)
$\Delta H°$-*A*, $J \cdot mol^{-1}$	96 476	53 558-139 394
$\Delta S°$, $J \cdot mol^{-1} \cdot K^{-1}$	0.1	−42.7-42.9
$\Delta H°$-*A* + $T\Delta S°$, $J \cdot mol^{-1}$	−96 000 (b)	−91 000-101 000

(a) For $\Delta H°$-*A* and $\Delta S°$ only the error found from the linear regression is included in the 95% confidence interval (CI) since the error from estimated standard deviations in the parameters ppm of Cl, *T*, and a_{MgCl_2} (20%, ±3 K, and $0.3 \cdot x_{NaCl}$, respectively [2000Ros]) calculated according to Box et al. [1978Box] hardly contributed to the errors. However, for the expression $-\Delta H°$-*A* + $T\Delta S°$, the errors in the parameters are included in the confidence interval since these contribute significantly.
(b) At 1008 K

and the results in Table 2 to calculate the Cl solubility at temperatures other than those in the current study will give rather uncertain solubilities. However, the confidence interval of the expression $-\Delta H°$-*A* + $T\Delta S°$ is much more narrow, and it is this expression that relates the solubility of Cl in liquid Mg to the $MgCl_2$ activity in the molten salt. The present data should therefore give good estimates of the Cl solubility in molten Mg when the temperature is similar to the ones in this study and the activity of $MgCl_2$ is known.

It is possible to improve the estimate of the Cl solubility over a wider temperature by comparing the present results with existing thermodynamic data for other monovalent Cls. This is done as follows.

Equation 5 can be split into three reactions,

$$1/2MgCl_2(l) + 1/2Mg(l) = MgCl(g) \qquad \text{(Eq 7)}$$

$$MgCl(g) = MgCl(l) \qquad \text{(Eq 8)}$$

$$MgCl(l) = MgCl(\text{in Mg}) \qquad \text{(Eq 9)}$$

Data exist for ΔG^0 of Eq 7 between 900 K and 1100 K [2002Fac]. They can be fitted well by a linear function of temperature:

Table 3 Entropies of the Reaction MCl(g) = MCl(l) for Some Monovalent Chlorides at 1000 K [2002Fac]

MCl	$\Delta S°$, $JK^{-1} \cdot mol^{-1}$
LiCl	−107.8
NaCl	−109.7
KCl	−108.6
CsCl	−106.0
CuCl	−106.8
AgCl	−114.9

$$\Delta G^0, J \cdot mol^{-1} = 239\,106 - 125.23T, R^2 = 0.99997 \qquad \text{(Eq 10)}$$

The $\Delta S°$ in Eq 6 is the sum of the entropies of Eq 7 and 8. This entropy is the same as the standard entropy of Eq 5, in which MgCl is in its hypothetical pure liquid standard state (i.e., $\Delta S°$ in Eq 5). If the regular solution model holds for Cl dissolution in liquid Mg metal (i.e., ideal entropy of mixing), the following equation can be formulated:

$$\begin{aligned}\Delta S°_{Eq\,8} &= \Delta S°_{Eq\,5} - \Delta S°_{Eq\,7}\\ &= 0.1 - 125.2\\ &= -125.1\ JK^{-1} \cdot mol^{-1}\end{aligned} \qquad \text{(Eq 11)}$$

The entropy of Eq 8 can be compared with the entropies of condensation of other gaseous monovalent Cls to their pure liquids. These are shown in Table 3, and all lie in the range −106 to −115 $JK^{-1} \cdot mol^{-1}$, which is ~15 $JK^{-1} \cdot mol^{-1}$ more positive than the one calculated in Eq 11.

The range of these entropies of condensation is quite narrow, and it is reasonable to assume that the entropy of condensation of MgCl should have a value similar to the others. Increasing $\Delta S°$ in Eq 5 to 15 $JK^{-1} \cdot mol^{-1}$ raises the $\Delta S°$ in Eq 8 by the same amount to 110 $JK^{-1} \cdot mol^{-1}$, which is in the center of the range of entropies of condensation. This adjustment is further justified when taking into consideration that the $\Delta S°$ in Eq 5 of 15 $JK^{-1} \cdot mol^{-1}$ is well within the confidence interval given in Table 2. Since the 95% confidence interval for the expression $-\Delta H°$-*A* + $T\Delta S°$ is quite narrow (Table 2), a change in the $\Delta S°$ of Eq 5 should be accompanied by a corresponding change in the $\Delta H°$-*A* value. Consequently, $\Delta H°$-*A* should be closer to $11 \cdot 10^4$ $J \cdot mol^{-1}$ to keep -$\Delta H°$-*A* + $T\Delta S°$ at the same value. The value of $11 \cdot 10^4$ $J \cdot mol^{-1}$ is well within the confidence interval of $\Delta H°$-*A* given in Table 2.

Based on the above, it is reasonable to assume that by using $\Delta S° = 15\ JK^{-1} \cdot mol^{-1}$ and $\Delta H°$-$A = 11 \cdot 10^4$ $J \cdot mol^{-1}$ in Eq 6, i.e.,

$$\begin{aligned}R(\ln x_{Cl} - 1/2 \ln a_{MgCl_2}) &= R \ln \frac{K}{\gamma_{MgCl}}\\ &= \frac{11 \cdot 10^4\ J \cdot mol^{-1}}{T} + 15\ JK^{-1} \cdot mol^{-1}\end{aligned} \qquad \text{(Eq 12)}$$

reasonable estimates of the Cl solubility in molten Mg over a relatively large temperature range should be possible as long as the $MgCl_2$ activity is known. A line drawn according to Eq 12 is included in Fig. 2 for comparison with the regression line.

5. Conclusions

The concentrations of Cl in liquid Mg equilibrated with NaCl-$MgCl_2$ melts of different compositions and temperatures in the range 650-790 °C have been measured. The solubility increases with the temperature and the square root of the $MgCl_2$ activity. The results suggest that Cl is dissolved as single Cl ions in the molten Mg.

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