THE MAGNESIUM–MAGNESIUM CHLORIDE SYSTEM. A CHRONOPOTENTIOMETRIC STUDY[1]

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The mode of dissolution of magnesium in molten magnesium chloride contacted with Mg–Pb alloys was studied at 750° using anodic chronopotentiometry. Relative amounts of magnesium dissolved in its chloride were determined as a function of magnesium activity in the alloy. According to the law of mass action a linear dependence of magnesium solubility on a_{Mg} indicates Mg_2^{2+} ion as the reaction product and a parabolic dependence indicates Mg^+ ion. It was found that the amount of magnesium dissolved in its chloride was directly proportional to the magnesium activity in the metal phase, *i.e.*, a linear dependence, indicating Mg_2^{2+} ion formation. Due to the corrosive nature of the $Mg–MgCl_2$ system, a special apparatus was used so that only the inert metals tantalum and molybdenum came in contact with the melt. Purification procedures for materials and conditions for proper equilibration and measurement were established and are reported. The basic equation of chronopotentiometry, $i\tau^{1/2} = nF\pi^{1/2}D^{1/2}C/2$, was found to hold and at given magnesium activities the product $i\tau^{1/2}$ did not vary with the current, indicating the validity of the analytical technique. The diffusion coefficient of the Mg_2^{2+} ion was calculated and found to be 5.3×10^{-6} cm.^{2}/sec. at 750°.

Introduction

It is well known that many metals will dissolve to some extent in their own molten halide salts. A variety of techniques has been employed to study such systems in an effort to determine the form of the excess metal in the salt. Investigations include solubility studies,[2] electrical conductivity measurements,[3,4] e.m.f. measurements,[5] magnetic susceptibility,[6] polarographic,[7] and spectral studies,[8] for a number of metal–metal halide systems.

The Mg–MgCl₂ system has been studied by Zhurin,[9] Rogers, *et al.*,[10] and Bukun and Ukshe.[11] These investigators measured the solubility of magnesium in its chloride at various temperatures and in the latter two investigations the change of solubility of magnesium as a function of magnesium activity was determined. Still discrepancies remain, *i.e.*, the solubilities determined by Zhurin and by Bukun and Ukshe were two to three times as great as those determined by Rogers, *et al.*, and furthermore, the mode of dissolution of magnesium in its molten chloride was not definitely established. It was, therefore, believed useful to make further studies on this system.

Two possible modes of dissolution of magnesium in its chloride are

$$Mg + Mg^{2+} \longrightarrow 2Mg^+ \qquad (1)$$

or

$$Mg + Mg^{2+} \longrightarrow Mg_2^{2+} \qquad (2)$$
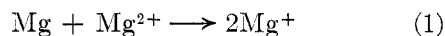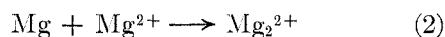
where the reaction product of either reaction is termed a subhalide ion. Since the solubility of excess magnesium in its chloride is low, less than 1 mole %, the activity of the subhalide ion formed can be assumed to be

proportional to its concentration. It, therefore, follows from the law of mass action that the solubility of magnesium in its chloride would be proportional to the square root of the activity a_{Mg} of magnesium in the case of reaction 1, but directly proportional to a_{Mg} in the case of reaction 2. The same conclusion would hold if reactions 1 and 2 were formulated in terms of molecular species. Thus, by varying the activity of magnesium, a_{Mg}, using a suitable alloy, and measuring the relative solubilities of magnesium, the mode of dissolution of magnesium in its chloride may be ascertained. Although one is unable to distinguish between reaction 2 and the possibility of Mg dissolving in the melt as Mg atoms by this experiment, evidence accumulated on other subhalide systems indicates that the latter mechanism is unlikely.

An *in situ* analysis for dissolved magnesium has the advantage of measuring the solubility under the actual condition of equilibrium as opposed to the previous investigations where samples were quenched and later chemically analyzed for excess magnesium content. Egan[7] has utilized the technique of anodic polarography to determine relative amounts of excess lead dissolved in its chloride, but because of the corrosive nature of the Mg–MgCl₂ system, a microelectrode did not appear feasible. Instead, anodic chronopotentiometry was found to be a suitable method for determining relative amounts of excess magnesium dissolved in molten magnesium chloride at 750°. Topol and Osteryoung[12] have utilized anodic chronopotentiometry in their study of the Bi–BiBr₃ system.

From the basic equation of chronopotentiometry

$$i\tau^{1/2} = nF\pi^{1/2}D^{1/2}C/2 \qquad (3)$$

where i is the current density in amp./cm.^{2}, τ the transition time in seconds, n the number of electrons transferred per ion, D the diffusion coefficient in cm.^{2}/sec., and C the concentration in moles/cm.^{3}, it follows that the product $i\tau^{1/2}$ is proportional to concentration and may be used to determine relative solubilities. Denoting this product at $a_{Mg} = 1$ by $(i\tau^{1/2})_0$, it follows that in the case of reaction 1

$$\frac{i\tau^{1/2}}{(i\tau^{1/2})_0} = a_{Mg}^{1/2} \qquad (4)$$

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(2) (a) J. D. Corbett and S. von Winbush, *J. Am. Chem. Soc.*, **77**, 3964 (1955); (b) E. A. Ukshe and N. G. Bukun, *Russ. Chem. Rev.*, **30**, 90 (1961).

(3) H. R. Bronstein and M. A. Bredig, *J. Phys. Chem.*, **65**, 1220 (1961).

(4) G. W. Mellors and S. Senderoff, *ibid.*, **64**, 294 (1960).

(5) L. E. Topol, S. J. Yosim, and R. A. Osteryoung, *ibid.*, **65**, 1511 (1961).

(6) N. H. Nachtrieb, *ibid.*, **66**, 1163 (1962).

(7) J. J. Egan, *ibid.*, **65**, 2222 (1961).

(8) C. R. Boston and G. P. Smith, *ibid.*, **66**, 1178 (1962).

(9) A. I. Zhurin, *Metallurg*, **10**, No. iv, 87 (1935).

(10) P. S. Rogers, J. W. Tomlinson, and F. D. Richardson, "Physical Chemistry of Process Metallurgy," Interscience Publishers, Inc., New York, N. Y., 1961, p. 909.

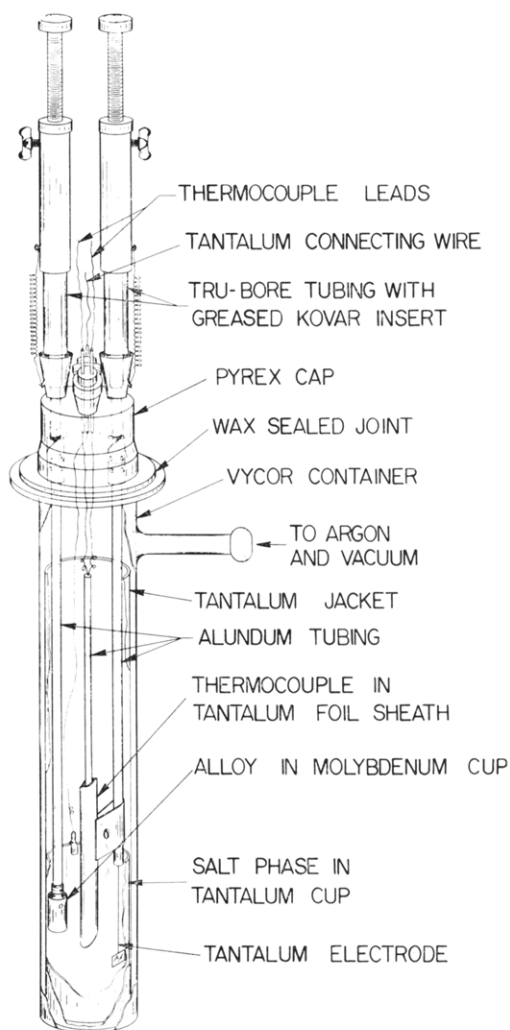(11) N. G. Bukun and E. A. Ukshe, *Russ. J. Inorg. Chem.*, **6**, 465 (1961).

(12) L. E. Topol and R. A. Osteryoung, *J. Phys. Chem.*, **66**, 1587 (1962).

Fig. 1.—Chronopotentiometric cell used for the study of the Mg–MgCl₂ system.

whereas in the case of reaction 2

$$\frac{i\tau^{1/2}}{(i\tau^{1/2})_0} = a_{\mathrm{Mg}} \qquad (5)$$

A plot of $i\tau^{1/2}/(i\tau^{1/2})_0$ vs. activity of magnesium, a_{Mg}, would yield a parabola for reaction 1 and a straight line for reaction 2.

Experimental

The magnesium chloride used in this investigation was a by-product of the production of titanium and was initially anhydrous. It was further purified by passing dry HCl gas through the powder for 24 hr. at less than 100° and for 6 hr. more while the temperature of the salt was raised above its melting point, 708°. The salt thus obtained was filtered through fine quartz frits and stored under dry argon until used. Spectrographic grade magnesium metal was in the form of one-quarter-inch rods. The surface of the rods was filed to remove the oxide film and the metal used directly. The lead metal used in the Mg–Pb alloys was filtered in the molten state through a coarse Pyrex frit to remove the insoluble oxide.

The chronopotentiometric cell used is shown in Fig. 1. The salt phase, MgCl₂, was contained in a large tantalum cup and the alloys were contained in a small molybdenum cup; a hole in the side of the small cup, below the surface of the salt, furnished contact of the alloy with the salt phase. The indicator electrode was a small tantalum foil of known area suspended in the salt from a thin tantalum wire. The temperature was measured with a Chromel–Alumel thermocouple protected with a tantalum sheath and immersed in the salt phase. The indicator electrode, the small molybdenum cup, and the thermocouple were attached with Alundum tubing to movable Kovar inserts in the Pyrex
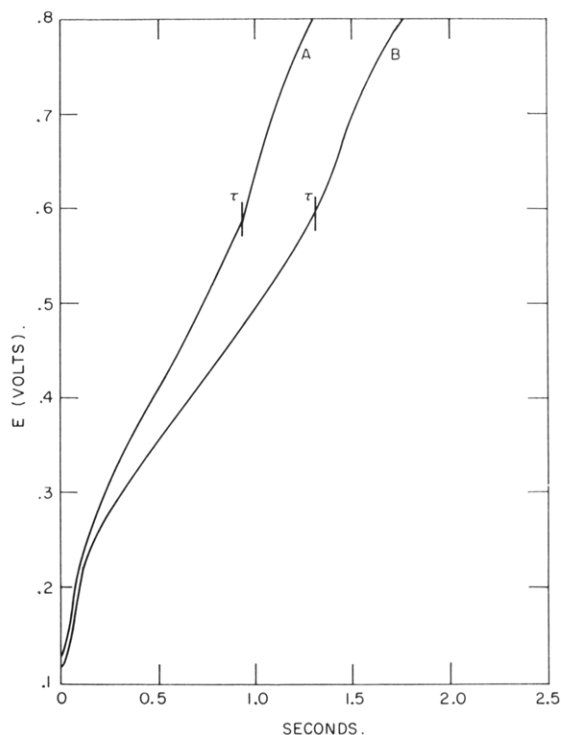

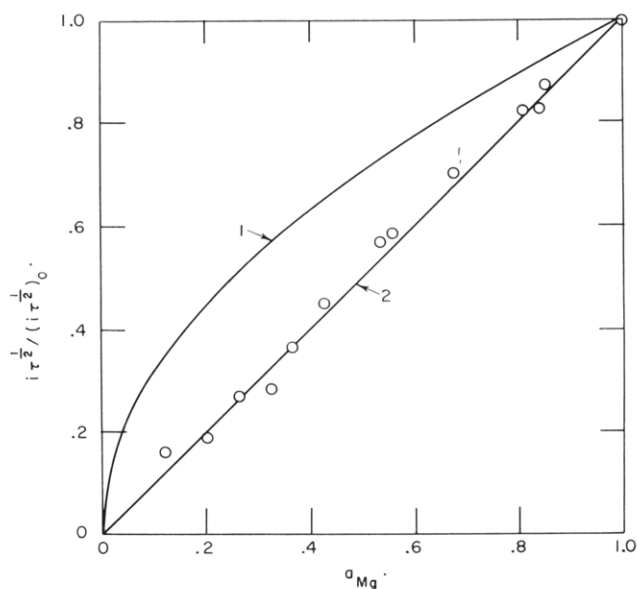Fig. 2.—Typical anodic chronopotentiograms obtained in the Mg–MgCl₂ system.

Fig. 3.—A plot of $i\tau^{1/2}/(i\tau^{1/2})_0$ vs. a_{Mg}: curve 1 corresponds to the formation of Mg⁺; curve 2 corresponds to the formation of Mg₂²⁺.

cap, to permit vertical positioning of these components. Electrical contact was made to the Kovar inserts from the electrodes with small tantalum wires inside the Alundum tubing. The large tantalum cup and the entire electrode assembly were contained in a tantalum jacket to protect the outer Vycor container from attack by magnesium vapor. The cell was contained in a resistance furnace maintained at the proper temperature. All metal components in contact with the metal–salt system were cleaned by induction heating in a fast pumping, high vacuum system.

Anodic chronopotentiograms were obtained by passing a known constant current between the tantalum indicator electrode and the large tantalum cup, which served as the counter electrode while measuring the potential between the indicator electrode and the molybdenum cup, the reference electrode, as a function of time. The constant current was furnished by an all-electronic current regulator designed by the Instrumentation Division of Brookhaven National Laboratory and the potential–time curves were recorded on a Leeds and Northrup High Speed

Speedomax G recorder which had a pen speed of 0.25 sec. full scale and chart speed of 2 in./sec.

Transition times for the chronopotentiograms obtained were read from the chart recordings with an estimated accuracy of ±0.025 sec. The alloy–salt systems were equilibrated for at least 12 hr. before chronopotentiometric measurements were made. Measurements taken at times greater than 12 hr. (up to 18 hr.) always gave the same results, ensuring true equilibration between salt and alloys.

Results and Conclusions

Anodic chronopotentiograms for the oxidation of the subhalide ion in magnesium chloride were obtained for a series of Mg–Pb alloy compositions at 750°. Figure 2 shows typical anodic chronopotentiograms obtained. Transition times were measured from the current onset to the potential break where the potential shifted rapidly to the more positive value of the limiting reaction. In practice, the potential at this potential break was measured for several anodic chronopotentiograms and subsequent transition times for that composition were measured to this point. It was found that at a given alloy composition the product $i\tau^{1/2}$ was indeed a constant for varying current densities, indicating the validity of the analytical technique. The final $i\tau^{1/2}$ for each composition was an average of twelve or more measurements at various current densities.

When anodic chronopotentiograms were taken of magnesium chloride equilibrated with pure lead, $a_{Mg} \cong 0$, a potential holdup was noted. A "residual" $i\tau^{1/2}$ was calculated by measuring the time necessary to achieve the predetermined potential when a constant current was passed. This background is probably due to oxidizable impurities in the salt. The various $i\tau^{1/2}$ values were corrected for this residual product as shown in Table I. Figure 3 shows the plot of $i\tau^{1/2}/(i\tau^{1/2})_0$ vs. a_{Mg}. Activities of magnesium in Mg–Pb alloys determined by Schmal and Sieben[13] and by Lantratov[14] were used. Curve 1 is the plot expected for the formation of Mg^+ ion, reaction 1, while curve 2 corresponds to the theoretical plot for reaction 2, the formation of Mg_2^{2+} ions. The experimental points fall on the straight line, curve 2, confirming that magne-

(13) N. Schmal and P. Sieben, "Physical Chemistry of Metallic Solutions and Intermetallic Compounds," National Physical Laboratory Symposium, No. 9, Paper 2K, England, 1958.

(14) M. F. Lantratov, *Russ. J. Inorg. Chem.*, **4**, 636 (1959).

sium dissolves in its chloride to form Mg_2^{2+} ions. Strangely, Bukun and Ukshe hypothesize the formation of Mg^+ ions (MgCl), although a plot of their data shows the three experimental points they obtained on a straight line.

TABLE I

x_{Mg}	a_{Mg}	$i\tau^{1/2} \times 10^2$ amp. sec.$^{1/2}$/ cm.^{2}	$i\tau^{1/2} \times 10^2$ corrected amp. sec.$^{1/2}$/ cm.^{2}	$\dfrac{i\tau^{1/2}}{(i\tau^{1/2})_0}$
1.000	1.000	2.22	1.60[a]	1.000
.901	0.850	2.01	1.39	0.868
.897	.842	1.94	1.32	.825
.875	.810	1.93	1.31	.820
.801	.672	1.74	1.12	.700
.751	.552	1.56	0.94	.587
.741	.534	1.54	.92	.575
.699	.424	1.35	.73	.456
.677	.367	1.20	.58	.362
.663	.325	1.07	.45	.282
.631	.261	1.05	.43	.269
.591	.200	0.92	.30	.188
.448	.118	.88	.26	.162
.000	.000	.62[b]	.00	.000

[a] Value of $(i\tau^{1/2})_0$. [b] Residual $i\tau^{1/2}$.

Cooled samples were analyzed for dissolved magnesium by measuring the hydrogen evolved when the samples were dissolved in water. The solubility of magnesium in its chloride at 750° found in this manner was 17% lower than the extrapolated value obtained from the data of Rogers, et al., whereas the values of Zhurin as well as Bukun and Ukshe were much higher, by a factor of 2 or 3. It is felt by the authors that the values of Rogers and co-workers are the most accurate. Using their extrapolated value for the solubility of Mg in $MgCl_2$ at 750° of 0.23 mole %, the diffusion coefficient of the Mg_2^{2+} ion was calculated using eq. 3 and was found to be 5.3×10^{-6} cm.^{2}/sec. This is similar to diffusion coefficients of other ions in fused salts.