copper.

4.4 Relationship between the charges corresponding to the deposition and dissolution of copper

The charges Q_{dep} and Q_p corresponding to the deposition and dissolution are obtained by the graphical integration of each scanning curve in the potential range of adsorbed and intermediate layer. The integration method is given in Fig. 9 (a), where Q_{dep} is obtained from the cathodic area C. In the estimation of the area C, the correction for the area due to the reduction of adsorbed oxygen and to the double layer charging was made by using the potential-current curves obtained in 1 N H_2SO_4 without Cu^{2+} . Q_p is obtained from the anodic area A which is estimated by making the correction for the area due to the oxygen adsorption and to the double layer charging. It is shown in Fig. 9 (b) that Q_p is approximately equal to Q_{dep} within the potential range where adsorbed and intermediate layers are formed. According to the Tindall's result³⁾ obtained with a platinum ring-disk electrode, the appearance of oxidation current due to the process $\text{Cu}^+ \rightarrow \text{Cu}^{2+} + e$ is limited

to the potential range of the deposition of bulk phase copper. His result is consistent with that of the present work. Thus, it follows that the current efficiency for deposition is little reduced by the process $\text{Cu}^{2+} + e \rightarrow \text{Cu}^+$ during the potentiostatic deposition of adsorbed layer and intermediate layer. However, under the galvanostatic deposition, the current efficiency for deposition was very low⁴⁾ during the growth of adsorbed layer which attained the half of full coverage. This difference should be elucidated by further studies.

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Technical Paper

The Initial Dissolution Rate of Magnesium Alloy in Neutral Chloride and Strong Acid Solutions

Masao HIROI*

The initial dissolution rates of Mg alloy (AZ-31B) were measured in aqueous solutions of KCl, NaCl, HCl, HClO_4 , H_2SO_4 , and HNO_3 in order to elucidate a relationship between the dissolution rate and concentration. The corrosion rate in the neutral chloride solution was obtained by extrapolating log (current density)-potential curves measured within 3 min from immersion of the specimens into the testing solution. Weight loss was measured by a pouring technique to determine the rate of dissolution in acids.

A plot of log (corrosion current density) vs. log (activity of chloride ion) yielded a straight line having a slope of about 0.34 in the chloride solutions. For the strong acids except HNO_3 , log (weight loss) increased linearly with an increase in log (mean activity of acid) in a concentration range between 0.1 and 2 N. The order of the reaction was 1.32~1.36 with respect to the activity of hydrogen ion, indicating that the rate of dissolution in strong acids was strongly influenced by anion at high concentrations.

An interpretation of the experimental results is proposed in terms of the theory of mixed potentials.

1 Introduction

Considerable work has been done in measuring the rate of dissolution of Mg and its alloy in salt and acid solutions^{1)~9)}. The relationship between the

dissolution rate and concentration, however, has not been elucidated and there is no adequate explanation for the apparent reaction order. Taking account of time-dependency of the dissolution rate, the author considers to use the initial dissolution rate as an experimental base for discussion and comparison.

The dissolution rate of Mg in acids at low concen-

* Chemical Laboratory, Kobe University of Mercantile Marine (Fukae-minami, Higashinada, Kobe)

trations has been reported to be first order with respect to H^+ concentration or total acid concentration, but there is little information in the literature on the dissolution of Mg at high acid concentrations. The purpose of this study was to elucidate a relationship between the dissolution rate of Mg alloy and concentration.

Roald and Beck⁵⁾ studied the dissolution of rotating Mg cylinders in HCl at acid concentrations up to 1.6 *N*. They observed that the dissolution rate at low concentrations was proportional to the acid concentration but at concentrations above 0.3 *N* the rate increased exponentially. They attributed the increase in rate constant at the higher concentrations to stirring effect due to the hydrogen bubbles, but the results were not clear-cut.

Wada⁷⁾ studied the dissolution of Mg in various salt solutions and proposed a dissolution mechanism involving an intermediate species of $Mg \cdot 2H^+$, whereas Perrault¹⁰⁾ proposed a mechanism involving MgH_2 .

The rotating disk and the tubular reactor are most frequently used for a study of the electrochemical reaction proceeding under significant diffusion control. In this study, a pouring technique was used in measuring the initial dissolution rate in acids.

2 Experimental

In all cases the metal specimens with the size of $2.5 \times 3.5 \text{ cm}^2$ were cut from commercial 1.3 mm sheet containing a nominal 3% Al and 1% Zn; ASTM designation AZ 31 B. After the metal surface was polished and cleaned by trichloroethylene, the coupon was covered with a plastic coating, leaving about 1.7 cm^2 of the surface exposed to the testing solution. The specimens were pickled in an acetic-nitrate pickle (266 ml acetic acid, 67 g sodium nitrate made up to 1 liter with distilled water), followed by rinsing in a stream of distilled water, and then dried.

Anodic and cathodic current-potential curves were measured in solutions of KCl and NaCl to obtain the corrosion current density (i_{corr}). The measurements were carried out in a conventional one-compartment electrolysis cell. Steady state potentials were measured for each current value through a Luggin capillary against a saturated calomel electrode (S.C.E.). The auxiliary electrode was a Pt screen. The solutions were deaerated with purified nitrogen and stirred with a magnetic stirrer.

Anodic and cathodic polarization measurements were carried out within 3 min from immersing the specimens in the corroding medium, because cathodic polarization curves were not reproducible when the speci-

mens were immersed over 5 min before the polarization measurement. The corrosion current density was reproducible to $\pm 4\%$.

Weight loss was measured by a pouring technique in measuring the initial dissolution rate in acids. Acidic solution was poured onto the specimens at pour rate of about 1 l/min from a tube of 7 mm diameter.

The relationship between the dissolution rate and pour rate is shown in Fig. 5, indicating that constant weight loss can be obtained at pour rate greater than 0.6 l/min.

The changes in acid concentration and the temperature increase of the solution due to rapid dissolution can be avoided by this technique. Deaeration of acidic solution was not achieved because the dissolution of Mg was not greatly affected by the presence of oxygen⁶⁾. The time of immersion varied from 5 or 120 seconds, depending on the dissolution rate.

After immersion the specimen was immediately washed with distilled water. Following drying and weighing, the area of the exposed surface was carefully measured and the dissolution rate in $\text{mg}/\text{cm}^2/\text{min}$ was evaluated. The dissolution rates were generally reproducible within $\pm 4\%$.

Except for the measurements to determine the heat of activation, the temperature of the test section was maintained at $25 \pm 0.2^\circ \text{C}$.

The activity of chloride ion (a_{Cl^-}) was calculated from the voltage of the cell (1)

3 Results

Typical cathodic and anodic polarization curves of Mg alloy in deaerated solutions of KCl and NaCl are shown in Fig. 1 and 2, respectively. The anodic polarization curves indicate that the potential is relatively insensitive to increasing anodic current. Robinson¹¹⁾ showed that this is true up to at least $1 \text{ mA}/\text{cm}^2$ in chloride and sulfate electrolytes. The electrode behavior can be explained by process of film damage and film repair^{11), 12)}.

Fig. 1 Polarization curves of Mg alloy in deaerated solutions of KCl

Fig. 2 Polarization curves of Mg alloy in deaerated solutions of NaCl

The cathodic polarization curves represent the hydrogen evolution reaction by the discharge of water. The cathodic Tafel slopes were 180~190 mV.

The concentration dependence of corrosion potential (E_{corr}) is shown in Fig. 3, which indicates that

$$\frac{dE_{\text{corr}}}{d(\log a_{\text{Cl}^-})} = -66 \text{ mV} \quad (2)$$

Fig. 3 Corrosion potential vs. the activity of Cl^- curve

●: KCl, ○: NaCl

A plot of $\log i_{\text{corr}}$ vs. $\log a_{\text{Cl}^-}$ yields a straight line as shown in Fig. 4.

$$\frac{d(\log i_{\text{corr}})}{d(\log a_{\text{Cl}^-})} \cong 0.34 \quad (3)$$

Fig. 4 Dependence of the corrosion on the activity of Cl^-

●: KCl, ○: NaCl

The difference of corrosion rate in KCl and NaCl solution is probably due to cation effect or slight

difference of pH.

In order to confirm the results obtained in the neutral chloride solutions, the rates of dissolution in acidic chloride solutions were measured at constant H^+ concentration varying concentration of Cl^- by addition of KCl. The results obtained in 0.2 N and 0.5 N HCl are shown in Fig. 6 and agree well with that obtained in the neutral chloride solutions. A plot of corrosion potential vs. $\log a_{\text{Cl}^-}$ indicated that corrosion potential was independent of H^+ concentration.

Fig. 5 Dissolution rate vs. pour rate curves in air-saturated solutions of HCl

●: 1 N HCl, ○: 0.5 N HCl

Fig. 6 Corrosion potential and dissolution rate vs. the activity of Cl^- (varied by addition of KCl) at constant H^+ concentration

●: 0.5 N HCl, ○: 0.2 N HCl

The dissolution rates of Mg alloy in HCl are shown as a function of the mean activity of HCl ($a_{\pm\text{HCl}}$) in Fig. 7. The mean activities of acid were calculated from the mean activity coefficients taken from Harned and Owen¹³⁾.

Fig. 7 Dissolution rate as a function of the mean activity of HCl in air-saturated solution

●: In stagnant solution
○: By pouring technique

The irregularity of the curve for stagnant solution is due to the temperature increase of the solution.

Logarithm of the initial dissolution rate (R_{dissoln}) was proportional to logarithm of the mean activity of HCl in a concentration range of 0.1~2 N.

$$\frac{d(\log R_{\text{dissoln}})}{d(\log a_{\pm\text{HCl}})} = 1.34 \quad (4)$$

The order of the reaction was 1.34 with respect to the proton activity (a_{H^+}), evidently indicating that the dissolution rate is not proportional to H^+ concentration and Cl^- strongly affect the dissolution rate at the higher concentrations. Butler and Frost¹⁴⁾ reported the order of the reaction for Fe dissolution in HCl to be 1.5 with respect to the proton activity at the higher concentrations (2~6 N).

The deviation from linearity above 2 N was probably due to the hydrogen evolution or the contribution of diffusion.

The logarithmic plots of the dissolution rate vs. the mean activity of acid are shown in Figs. 8 and 9. The slope of the line is 1.32 for HClO_4 and 1.96 for H_2SO_4 at a concentration range of 0.1~2 N. In all cases except HNO_3 , the apparent reaction order was 1.32~1.36 with respect to the proton activity.

Fig. 8 Dissolution rate vs. the mean activity of HClO_4 curve

Fig. 9 Dissolution rate vs. the mean activity of H_2SO_4 curve

The dissolution rates in HNO_3 are shown in Fig. 10. The rate of dissolution in HNO_3 is proportional to the concentration and considerably smaller than that in the other strong acid at same normality as

Fig. 10 Dependence of the dissolution of Mg alloy on the concentration of HNO_3

shown Fig. 11. These mean that the reduction of HNO_3 becomes dominant as cathodic reaction instead of the hydrogen evolution reaction¹⁷⁾.

Fig. 11 Arrhenius plot at 0.5 N

○: HCl, ●: H_2SO_4 ,
△: HClO_4 , ×: HNO_3

The change of the rate with temperature at 0.5 N is shown in Fig. 11. The apparent activation energy was determined from the slope of the log rate vs. $1/T$ plots. The results are given in Table 1 and the values found in this study agree with that found by other observers^{4),9)}. It seems that diffusion is rate-controlling step. However, if surface coverage with atomic hydrogen was high, a reaction between adsorbed H atoms or between adsorbed H atoms and a species in solutions might proceed with a much lower activation energy¹⁵⁾. The data do not permit distinguishing whether activation or diffusion is rate-controlling step.

Table 1 The apparent activation energy at 0.5 N

Acid	HCl	HClO_4	H_2SO_4	HNO_3
Activation energy (kcal/mole)	4.6	5.9	4.4	3.7

4 Discussion

When the hydrogen evolution reaction by the discharge of H^+ or water is the only cathodic reaction and diffusion process is unimportant, the following can be used^{16),18)}.

$$|i_{\text{dissoln}}| = i_{\text{evoln}} = (i_0)_\text{H} \exp \left[-\frac{\alpha_\text{H} F}{RT} (E_{\text{corr}} - E_{\text{e,H}}) \right] \quad (5)$$

where i_{dissoln} and i_{evoln} are current density for the metal dissolution and the hydrogen evolution reaction (h.e.r.), respectively, $(i_0)_\text{H}$ is the exchange current density of the h.e.r., α_H the transfer coefficient cor-

responding to the h.e.r., $E_{\text{e,H}}$ the equilibrium potential of the hydrogen electrode, and the other symbols have their customary meanings.

With $(i_0)_\text{H} = (i_0)'_\text{H} a_{\text{H}^+}^{(1-\alpha_\text{H})/2}$ ^{16),18)}, $dE_{\text{corr}}/d(\ln a_{\text{A}^{n-}}) \cong -RT/F$ (from Eq. (2)), and $dE_{\text{e,H}}/d(\ln a_{\text{H}^+}) = RT/F$, Eq. (5) can be written as

$$\begin{aligned} \log i_{\text{dissoln}} &= \log a_{\text{H}^+} + \alpha_\text{H} \log a_{\text{A}^{n-}} + \text{const} \\ &= (K_1 + \alpha_\text{H} K_2) \log a_{\pm \text{H}_n\text{A}} + \text{const} \end{aligned} \quad (6)$$

where $K_1 = d(\log a_{\text{H}^+})/d(\log a_{\pm \text{H}_n\text{A}})$, $K_2 = d(\log a_{\text{A}^{n-}})/d(\log a_{\pm \text{H}_n\text{A}})$, and $a_{\pm \text{H}_n\text{A}}$ is the mean activity of strong acid, H_nA .

K_1 and K_2 are considered to be constant in a given concentration range and were determined experimentally. α_H was estimated from Fig. 1 and 2 to be 0.33.

With $K_1 \cong 1$ and $K_2 \cong 1$ for HCl and HClO_4 ,

$$\log i_{\text{dissoln}} = 1.33 \log a_{\pm \text{HA}} + \text{const} \quad (7)$$

With $K_1 \cong 1.46$ and $K_2 \cong 0.76$ for H_2SO_4 ,

$$\log i_{\text{dissoln}} = 1.71 \log a_{\pm \text{H}_2\text{SO}_4} + \text{const} \quad (8)$$

For the neutral chloride solution

$$\log i_{\text{dissoln}} = 0.33 \log a_{\text{Cl}^-} + \text{const} \quad (9)$$

The apparent reaction order can be fairly well explained by Eq. (6) in the concentration range between 0.1 and 2 N.

The concentration dependence of the dissolution rate of Mg is schematically represented in Fig. 12. At infinite dilution, a reaction between water and Mg is dominant. As the acid concentration increases, the discharge of H^+ becomes dominant. At a concentration range (a-b), where E_{corr} is independent of the concentration of anion, the dissolution rate is proportional to H^+ concentration. At the higher concentrations (b-c), where E_{corr} varies with changing concentration of anion, the order of the reaction is 1.32~1.36 with respect to the H^+ activity.

In the neutral chloride solutions the order of the

Fig. 12 Schematic diagram of concentration dependence for Mg dissolution

①: Strong acid, ②: Neutral chloride salt

reaction is about 0.34 with respect to the Cl^- activity at the higher concentrations (greater than d).

Similar interpretation may be applied to the dissolution of other metals. Further studies with other metals are in progress to elucidate the dissolution mechanism of metals.

5 Conclusions

1) A linear relationship existed between $\log$ of corrosion current density of Mg alloy at initial stage and $\log$ of the Cl^- activity in the neutral chloride solution. A slope of the line was about 0.34.

2) The order of the rate of dissolution in strong acids except HNO_3 was 1.32~1.36 with respect to the H^+ activity, indicating that the rate was strongly influenced by anion at high concentrations.

3) The apparent reaction order can be accounted for on the assumption that anode potential in local element varies with changing concentration of anion.

4) A pouring technique may be considered to be useful for a study of rapid metal dissolution.

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Technical Paper

A Study of Polyelectrolyte Complexes. Polyethyleneimine-Polyacrylate and Polyethyleneimine-Polyvinylsulfate

Norio YUI*, Yoichi KUROKAWA* and Eigo MIURA*

An investigation has been made on the reaction of protonated polyethyleneimine and polyacrylate or polyvinylsulfate ion. A white colloidal precipitate was formed in highly dilute solution of polyions. Elementary analysis of the precipitate and the conductometric behaviors of polyelectrolyte solutions indicated that the reaction between polycation and polyanion in solution proceeds nearly stoichiometrically. The complex did not contain microions at all and had some crystalline order and also water absorptivity.

1 Introduction

It was previously found that polyelectrolytes with opposite charges formed a precipitate, so called a polyion complex, due to electrostatic attraction between them^{1),2)}. Michaels et al. studied on such a polyion complex as that prepared from sodium polystyrene sulfate and polyvinyl benzyl trimethyl ammonium chloride, and the properties of the complex^{2),3)}. However, the results reported so far related only to such a complex. In the present work, polyion com-

plexes of polyethyleneimine·HCl and sodium polyacrylate or potassium polyvinylsulfate were studied.

2 Experimental

Polyethyleneimine, sodium polyacrylate and potassium polyvinylsulfate were all of reagent grade and were used without further purification. Polyethyleneimine·HCl was prepared by neutralization of polyethyleneimine with hydrochloric acid solution, using phenolphthalein as an indicator. Dilute aqueous solution of polyanion salt (one gram per 100 ml water) was added dropwise under agitation to a dilute solu-

* Department of Applied Science, Faculty of Engineering, Tohoku University (Aoba, Aramaki, Sendai)