Mechanism of Dissolution of Magnesium and its Alloys in Sodium Chloride

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The mechanism of magnesium dissolution in sodium chloride of concentrations 0.01 M to 1.0 M was studied by potentiodynamic polarization method at a sweep rate of 1 mV/sec for pure and alloys A and B of magnesium. The anodic reaction order with respect to H^+ ions and anodic reaction order with respect to concentration of Cl^- ions were found. A suitable mechanistic sequence with formation of univalent magnesium by attack of chloride ions and rds as $Mg + Cl^- \, MgCl(ads)$ is proposed.

Key words: Anodic dissolution, magnesium and its alloys, potentiodynamic polarization.

Introduction

The studies of corrosion behaviour of magnesium and its alloys in both acidic and aqueous solutions are important since magnesium and its alloys are used as anode materials in magnesium – silver chloride cells and as sacrificial anodes for cathodic protection. The dissolution of magnesium in aqueous solution gives magnesium hydroxide due to the dissolution of the anode and liberation of hydrogen at the cathode. Many investigators reported the electrochemical behaviour of magnesium and its alloys in aqueous electrolytes. However the present work involves the dissolution of magnesium and its alloys in aqueous chloride solutions. The corrosion behaviour of magnesium and its alloys was studied by potentio-dynamic polarization method with different concentrations of sodium chloride from 0.01 to 1 M solution at a sweep rate of 1 mV/ sec. The variation of corrosion parameters with respect to H^+ ions and Cl^- ions were studied.

Experimental

The electrolytic magnesium obtained from commercial cells of 99.85% purity was used as pure magnesium electrode. A composition of 92% magnesium, 5% aluminium and 3% zinc was used as alloy A. Alloy B had a composition of 92% magnesium with 8% aluminium. These alloys were prepared by melting the constituents in a graphite crucible under salt surface layer and cast in the shape of cylindrical rods. All the three electrodes were turned into small rods with grooves and fitted into electrode assembly with the help of Teflon and copper rod. The exposed acting surface area of the working electrode was 0.6 cm². The electrodes were polished with 1/0, 2/0, 3/0, 4/0 emery papers and degreased with trichloroethylene. The common three-electrode cell was used for experimental measurements. Polarization measurements were carried out potentio-dynamically using Potentiostat EG&G PAR 173 in conjunction with Universal Programmer PAR 175. The potentials of the electrode were measured with respect to SCE. Experiments were carried out using 0.01 to 1 M NaCl solution prepared using analytical grade chemicals in double distilled water. Freshly polished, degreased specimens were used for each experiment and duplicate experiments were repeated for all concentration of solutions for magnesium and its alloys.

Results and discussions

The kinetics of magnesium dissolution reaction and hydrogen evolution for magnesium and its alloys in different concentrations of chloride are shown in Table 1. It is clear from the table that increase of concentration of chloride results in shift of corrosion potential in the negative direction for all the three electrodes. Magnesium – A alloy has low corrosion rate of 0.65 mA/cm² for one molar concentration of chloride whereas pure magnesium and alloy – B have higher corrosion rates namely 1.1 mA/cm² for the same concentration. The 'b_a' tafel slope varies from 65 mV to 100 mV where as 'b_c' has 120 ± 10 mV.

The variation of corrosion parameters with pH for pure magnesium and its alloys A & B in 0.5 M NaCl is shown in Table 2. It is very clear that increase of pH from 6 to 10 results in decrease of corrosion rates whereas the shift in corrosion potential is comparatively less. This is due to the high stability of the oxide film in alkaline conditions with increase of pH.

Table 1. Corrosion parameters for pure magnesium and its alloys A & B in sodium chloride.

Chloride concn. (M)	E_{cor} (V vs SCE)	b_a (mV)	b_c (mV)	I_{cor} (mA/cm^2)
Pure Mg				
0.01	-1.418	84	122	0.03
0.25	-1.595	94	128	0.22
0.50	-1.625	90	123	0.45
1.0	-1.637	99	129	1.10
Alloy – A				
0.01	-1.445	65	117	0.01
0.25	-1.579	72	120	0.27
0.50	-1.581	69	130	0.47
1.0	-1.599	80	129	0.65
Alloy – B				
0.01	-1.492	66	122	0.02
0.25	-1.569	71	124	0.21
0.50	-1.590	74	124	0.50
1.0	-1.614	75	128	1.10

Table 2. Variation of corrosion parameters with pH for pure magnesium and its alloys A and B in 0.5 M sodium chloride.

pH	E_{cor} (V vs SCE)	b_a (mV)	b_c (mV)	I_{cor} (mA/cm^2)
Pure Mg				
6	-1.622	90	122	0.59
8	-1.629	93	124	0.31
10	-1.642	92	123	0.15
Alloy – A	-1.582	73	129	0.61
6	-1.608	72	127	0.41
8	-1.678	66	123	0.22
10				
Alloy – B	-1.488	76	128	0.90
6	-1.582	69	126	0.31
8	-1.678	69	119	0.06
10				

The mechanistic parameters for pure magnesium and its alloys A & B dissolution and hydrogen evolution reaction in NaCl are shown in Table 3. Pure magnesium and alloy A had anodic tafel slope of 90 ± 10 mV where as alloy B had only 70 ± 6 mV slope. The cathodic tafel slope were same for pure magnesium and alloy A whereas it was 125 ± 10mV for alloy B. The anodic reaction order with respect to hydrogen ions were 0.40 to 0.16 and 0.15 respectively for pure and alloys A & B magnesium. The anodic reaction orders with respect to chloride concentration were 0.78, 0.92 and 0.86

respectively. The cathodic reaction orders with respect to hydrogen ions were 0.17, 0.20 and 0.35 respectively.

Table 3. Mechanistic parameters for pure magnesium and its alloys A & B dissolution and hydrogen evolution reaction in sodium chloride.

Parameters	Experimental		
	Pure Mg	Alloy – A	Alloy - B
Anode tafel slope (mV)	90 ± 10	90 ± 10	70 ± 6
Cathode tafel slope (mV)	120 ± 10	120 ± 10	125 ± 10
$\left[\dfrac{\partial \log ia}{\partial pH}\right]_{Cl-,-1500mv}$	-0.42	-0.16	-0.15
$\left[\dfrac{\partial \log ia}{\partial \log Cl^-}\right]_{H^+,-1500mV}$	0.78	0.92	0.86
$\left[\dfrac{\partial \log ic}{\partial pH}\right]_{Cl^-,-1700mV}$	-0.17	-0.2	-0.35

The positive reaction orders with respect to hydrogen ions and chloride ions suggest that both species participate in the rate of magnesium dissolution reaction. Based on the experimental results of Tafel slope and reaction orders, the kinetics of magnesium dissolution and hydrogen evolution can be written by the following rate equations. The anodic magnesium dissolution reaction can be given as

$i_a = Ka \, (H^+)^{0.42} (Cl^-)^{0.78} \exp^{(0.75FE/RT)}$

And the cathodic hydrogen evolution reaction as

$i_c = Kc \, (H^+)^{0.17} \exp^{(-FE/2RT)}$

at $E = E_{cor}$, ia=ic=I_{cor} and hence the dependence of E_{cor} and I_{cor} with (H$^+$) and (Cl$^-$) ions is given by

$E_{cor} = E^*cor + (RT/1.25F) \ln (H^+)^{-0.25}(Cl^-)^{-0.78}$
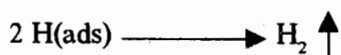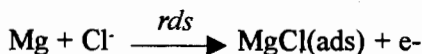
and $I_{cor} = K(H^+)^{0.27} (Cl^-)^{0.31}$

Similar rate equations can be written for alloy-A and alloy – B magnesium.

The experimentally observed variation of Ecor and Icor with respect to [H$^+$] and [Cl$^-$]ions for pure magnesium and its alloys A and B are summarized in Table 4.

Table 4. Variation of Ecor and Icor with respect to [H+] and [Cl-] ions for pure magnesium and alloys A and B in sodium chloride.

Parameters	Experimental		
	Pure Mg	Alloy – A	Alloy - B
$\left[\dfrac{\partial Ecor}{\partial pH}\right]_{cl-}$ (mV)	-5.9	-7.	-39
$\left[\dfrac{\partial Ecor}{\partial \log Cl^-}\right]_p$ (mV)	-69	-58	-68
$\left[\dfrac{\partial \log Icor}{\partial pH}\right]$	-0.13	-0.09	-0.23
$\left[\dfrac{\partial \log Icor}{\partial \log Cl^-}\right]$	0.59	0.76	0.91

The positive reaction order values with respect to [H+] ions and [Cl-] ions indicate that both ions participate in the dissolution of magnesium in neutral medium. However the lower values of cathodic reaction order with respect to hydrogen ions suggest the direct participation of [H+] ions in the magnesium dissolution in not possible. Hence the mechanism of dissolution of pure magnesium and its alloys in NaCl solution take place with the chief participation of chloride ions and it can be written as

$$Mg + Cl^- \xrightarrow{rds} MgCl(ads) + e-$$

$$MgCl(ads) + H_2O \longrightarrow Mg^{2+} + Cl^- + OH^- + H\,(ads)$$

$$2\,H(ads) \longrightarrow H_2 \uparrow$$

The expected anodic tafel slope and anodic reaction order with respect to chloride for the above mechanism were 60 mV and 1 respectively. The mechanism involving the stepwise dissolution of magnesium and its subsequent oxidation by water to divalent magnesium are proposed. The mechanism is same for magnesium and its alloys since the addition of aluminium and zinc do not affect the dissolution rate of magnesium in aqueous electrolytes.

Conclusion

The magnesium dissolution in sodium chloride take place through the participation of both [H+] and [Cl-]ions but chiefly chloride ions take part in the dissolution mechanism, With the formation of univalent magnesium ion to MgCl(ads) as the intermediate species and subsequent oxidation to magnesium divalent ions by water with the evolution of hydrogen has been proposed.

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