



Corrosion Behaviour of MLA Alloy by Potentiodynamic Polarization Studies

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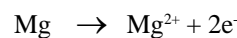
Abstract

Magnesium and its alloy have been increasingly used in many areas such as in automobiles, steel industries cathodic protection and in specialized battery systems. Recently many alloys with specified properties have been prepared for structural application also. These alloys have licurative properties such as high strength to weight ratio, better corrosion resistance, and better formability and cast ability. Lack of understanding about the corrosion behaviour of magnesium alloys prevented the application of such alloys in a scale as expected from their availability, hence this program has been under taken to show the interesting properties of the MLA alloy as well as the advantages and corrosion behaviour of these alloys. It has also been aimed at to popularized the use of these alloy in many aqueous environments. Basic understanding of the corrosion behaviour can only be obtained by carrying of polarization studies. Potentiodynamic method is one of the convenient techniques to collect corrosion data, by assessing the nature and extend of corrosion of these alloys appropriate protective methods can be devised. During this program Mg-11, Li-1.5, Al, alloys has been investigated by potentiodynamic polarization technique in NaCl, Na₂SO₄, NH₄Cl, MgCl₂ at concentration range from 0.05 to 2 M studied Open circuit potential and calculated corrosion current.

Keywords: Corrosion behavior; Corrosion current; Mg-Li-Al alloy; Open circuit pontential; Potentiodynamic polarization.

1. INTRODUCTION

Corrosion is simply defined as the destruction of materials under chemical or electrochemical action by the surrounding environment . Metallic corrosion (Inoue *et al.* 2002) is defined as the tendency of the metals to go to their original ore state. Corrosion entails the conversion of a metal from the atomic to ionic state, with the loss of one or more electrons. The anodic reaction produces positively charged metal ion and free electron in accordance with the reaction.



The term corrosion includes the metals, glasses, ionic solids, polymeric solids and composites with environment that include liquids, gases and non-aqueous electrolyte.

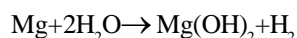
1.1 Importance of MLA alloys

Magnesium one of the lightest metals forms numerous lightweight alloys with Al, Zr, Zn, Mn, Li and rare earth metals. These alloys have varied application

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in structural automotive communication and industries. However the extensive corrosion anticipated of the alloys prevents the elaborative application online elapse scale hence in order to develop. However extensive corrosion these alloys prevents online elaborate scale once in order to develop better corrosion resistant and more useful alloys and understanding on the corrosion behavior (Baril *et al.* 2001) is essential. This program ensures the monitoring of metallic corrosion of the alloy in various aqueous by potentiodynamic (Andrei *et al.* 2002) studies. Mg and its alloys have the unique characteristics of low density and a good damping capacity. However, their corrosion resistance is poor and this restrict their applications. The progressive development of Mg corrosion in an aqueous solution in an atmosphere can be summarized as



The formed $\text{Mg}(\text{OH})_2$ film blocks the oxidation of the matrix. The dissolution rate at the open circuit potential generally decreases with an increasing Al content in alloy. An increase of the Cl^- content in the electrolyte strongly increases the dissolution rate at the open circuit potential. Electrochemical techniques have been used to study magnesium and its various alloys. Mg-Li-Al alloys (Han guk pusik, 1999) have been made of the inhibition efficiency of potassium chromate and n-butylamine in combating exposure due to the protective $\text{Mg}(\text{OH})_2$. MgCO_3 dissolution takes place in aqueous environments. Resulting in inferior performance. In neutral 0.1M NaCl and 0.1M Na_2SO_4 solutions, the alloys typically show active dissolution. The corrosion attack is localized and its morphology as well as the dissolution rate strongly depend on This work elucidates the electrochemical dissolution of Mg Li-Al alloy three chloride solution and one sulphate viz, NaCl, NH_4Cl , MgCl_2 and Na_2SO_4 at concentration range from 0.05 to 2.0M by potentiodynamic polarization (Stulikove *et al.* 2003) studies.

2. MATERIALS & METHODS

2.1 Material preparation

The MLA alloy (Mg-87.55%, Li-80%, Al-1.48%) electrode has been turned in to small rods with grooves and fitted in to the electrode assembly with the help of Teflon and copper rods. The exposed active surface area of the working electrode was 0.3 cm^2 . Rest of the area was marked by lacquer application. The refined magnesium electrode was polished with 1/0, 2/0, 3/0 and 4/0 emery papers and degreased with trichloroethylene. The unexposed area of the test electrode was masked by lacquer application, fitted in to the cell assembly and then introduced in to the cell.

2.2 Preparation of solution

The water used for the preparation and the dilution of solution was triple distilled using quartz distillation apparatus. Acids used for digestion and dissolution was of guaranteed reagent grade. Chemicals used for the preparation of electrolytic media were all guaranteed reagents. Sodium Chloride, Sodium Sulphate Ammonium Chloride and Magnesium Chloride (Matsubaraa and Toru, 2003) from Sarabhai M.chemicals. The required quantity of these chemicals were dissolved in triple distilled water to prepare a solution 2.0M. Lower concentration were made by dilution of the strong solution with triple distilled water.

2.3 Potentiodynamic polarization

A double walled three electrode assembly was for the polarization experiments. The tiny specimens made from the alloy were thoroughly polished, degreased and were used as working electrodes having an effective area of 0.3 cm^2 saturated calomel electrode (SCE) and platinum served as reference and counter electrode respectively. MLA specimens were turned, polished, degreased and embedded in Teflon fittings so as to expose 0.3 cm^2 , working electrode was lowered into the solution platinum electrode and SCE was positioned. Connection were given. The system was

allowed to attain equilibrium condition and the steady open circuit potential was noted. A constant potential at a sweep rate of 0.5 mv.sec^{-1} and the potentiograms both anodic and cathodic were recorded in all the four solution at concentration of 0.05, 0.1, 0.5, 1.0 and 2.0M by means of recorder. Measurements were carried out from -300mV to +300mV from open circuit potential potentiodynamically. Freshly polished, degreased specimens were used for each experiment and similar measurement was repeated for all other concentration, solution with the recording of respective plots. Corrosion current was calculated from the plots and the relationship between I_{corr} .

3. RESULTS & DISCUSSION

3.1 Potentiodynamic polarization

Potentiodynamic polarization is one of the widely practiced methods for resolving the corrosion criteria (Mat-Summurain *et al.* 2003) many metals especially magnesium based alloys. Such plots both anodic and cathodic obtained on polarization of the MLA alloys in NaCl, Na_2SO_4 , NH_4Cl and MgCl_2 at all concentration. Each one concentration are given in figs. 1-4. The corrosion parameters such as OCP, E_{corr} , I_{corr} , b_a and b_c derived from the plots are tabulated in Tables 1-4 for NaCl, Na_2SO_4 , NH_4Cl and MgCl_2 respectively. The furnished results are discussed thoroughly to bring are the salient features of the corrosion of the alloy in the selected solutions. The potentiodynamic polarization plots for the MLA in NaCl, solution at concentration of 0.05 given in fig.1. It can be seen that the polarization towards the cathodic side is more than the anodic side That is to say cathodic shift in potential is higher than is anodic shift from OCP (Augustin *et al.* 2001) for the same applied current density. As the applied current increase the electrode potential increases more rapidly in the cathodic region and slowly in the anodic region. From the potentiodynamic polarization plots are can say that both cathodic and anodic behavior are taking place differently for the MLA alloy in NaCl solution. Cathodic behavior predominates in the overall behavior in the dissolution of the alloy in NaCl. Hence it can said that

the polarization of the MLA electrode is controlled by cathodic behavior (Antonyraj *et al.* 1999).

Fig. 2, the potentiodynamic polarization plots of the MLA alloy electrode in Na_2SO_4 at 0.05. like wise fig. 3 & 4 for NH_4Cl and MgCl_2 respectively for 0.05 concentrations. From the shape of the plots it can be as contained that more or less identical behavior is exhibited by the alloy in NaCl, Na_2SO_4 and MgCl_2 . The polarization is cathodically controlled in all the three solutions. But a reversal of the control is observed in NH_4Cl solution as evident from fig 3. In these plots if is seen that anodic polarization is more than cathodic polarization. Hence these is a drastic change in electro chemical behavior of the alloy in NH_4Cl . The dissolution mechanism are current in this as a concentrations. Anodic dissolution behavior (Sakamoto and Sakdi Nobua, 2003) takes the lead in the dissolution of the alloy anode.

3.2 Open Circuit Potential (OCP)

Open circuit potential resulted for the system of an electrode in equilibrium with its aqueous environmental required with respect to a reference electrode. Normally in such measurement satisfied calomel electrode is used as the reference electrode. From the values of OCP the nature of the environment can be adjudged to some extent. This potential is the accurately measured value. The OCP values of MLA in NaCl solution at concentration 0.05, 0.1, 0.5, 1.0 and 2.0 M are tabulated in Table 1. It can be seen that all values are negative and increase with increase in concentration. Thus MLA electrode in 0.05 NaCl solution gives an OCP of -1.40V where as the same electrode in 2.0 M solution gives values of -1.60V. Similarly the OCP values of the MLA electrode in Na_2SO_4 , (Hollestin *et al.* 2003) NH_4Cl and MgCl_2 at all concentration of 0.05, 0.1, 0.5, 1.0 and 2.0 M are furnished in Tables 2-4 and respectively. These tables also show the same trend of increasing the negative values of OCP with increase in concentration trend OCP is resulted in the highest concentration of the medium. Thus in the Na_2SO_4 the value changes from -

1.25 V to -1.47V for a concentration change from 0.05 to 2.0 M as evident from Table 2. In the same manner which solution results a change from -1.78 to -2.02V and -1.50 to -1.75V respectively. The increased negative value with increased concentration may be due to the increased ionic concentration of the species constituting the double layer (Song and Atrens, 2002). The chloride ionic surrounding is formed to anodic a higher negative value than sulphate medium. Comparing all the OCP values given in all four tables its is noted that the higher OCP is resulted in NH_4Cl medium and lower in Na_2SO_4 , while other medium intermediate values are obtained.

3.3 Corrosion Potential (E_{corr})

Corrosion potential (Wang et al. 2003) is the potential calculated from the experimentally drawn polarization plots on extrapolation both of the anodic and cathodic lines, intercepts at a point. The potential corresponding to the intercepting point on the potential axis is the corrosion current. The Tables 1 to 4 give the corrosion potential value in all the four solution namely NaCl, Na_2SO_4 , NH_4Cl and MgCl_2 respectively for all the concentrations. The values are negative and increase with increase in concentration. The values are -1.42V to -1.6V in NaCl, -1.25V to -1.50V in Na_2SO_4 , -1.80V to -2.05V in NH_4Cl and -1.52V to -1.78 in MgCl_2 as evident from tables. The values are almost same as OCP. But the difference between OCP and E_{corr} is the former is experimentally observed and determined quantity from extrapolation. The significance of these quantities is same. A slight increase 20 to 30 mV observed in corrosion potential, particularly at higher concentration on the magnesium alloy surface during polarization may be due to the bubble formation on the magnesium alloy surface during polarization. An interesting observation noticed during the study that the potential one more positive in comparison to standard value of -2.37V vs NHE. An ennoblement results due to the film formed on the surface.

3.4 Corrosion Current (I_{corr})

Corrosion current is important parameters to assess the corrosion behavior of any material.

The quantity decides the extent of corrosion of the material in any medium. The changes of values are based on the corrosive medium. It can be determined by the extrapolation of the polarization lines obtained by the potentiodynamic polarization experiments. The I_{corr} value for MLA alloy in NaCl is given in Table 1. As seen it is increased with increase in concentration. The lower value of $4.2 \times 10^{-4} \text{ mAcm}^{-2}$ is resulted in the lower concentration of 0.05 M, on increasing the concentration of NaCl to 2.0 M the corrosion current is formed to increase to $3.2 \times 10^{-3} \text{ mAcm}^{-2}$. The increase in I_{corr} shows an enhanced corrosion of the alloy in higher concentrated solution. Thus 2.0 M are the most corrosion medium for the MLA alloy. It can also be seen that an order of increase in I_{corr} is resulted for an increase of concentration from 0.05 to 2.0M. The higher corrosion current observed for the alloy in higher concentration solution may be illustrated to the increase ionic concentration of the chloride ions generally Cl^- ion is assumed to be a highly corrosive species for metals especially magnesium.

Corrosion current values for the MLA alloy in Na_2SO_4 , NH_4Cl and MgCl_2 are provided in Table 2,3 and 5 respectively. The values clearly show the trend of increasing the I_{corr} with increasing in concentration. The I_{corr} values are 4.0 to $5.4 \times 10^{-4} \text{ mAcm}^{-2}$ in Na_2SO_4 , 4.2 to 6.0×10^{-4} in MgCl_2 and 4.7×10^{-4} to $3.5 \times 10^{-4} \text{ mAcm}^{-2}$ in NH_4Cl solution. Scrutiny of all the values given in tables shows that minimum values are obtained in Na_2SO_4 solution maximum I_{corr} is obtained in NH_4Cl solution the intermediate values in the other two namely NaCl and MgCl_2 . Aggressiveness of the chloride ions towards the corrosion of these magnesium alloy is evident from the I_{corr} values. Higher value obtained in the NH_4Cl may be the combined contribution of both chloride anion and NH_4^+ cation which is also considered to be an opposite cation towards magnesium in aqueous environments of the solution can be graded in the decreasing order as $\text{NH}_4\text{Cl} > \text{NaCl} > \text{MgCl}_2 > \text{Na}_2\text{SO}_4$.

3.5 Tafel slopes (b_a and b_c)

Potentiodynamic polarization of the MLA alloy results in both anodic plots and cathodic plots.

On taking the slopes of the observing result anodic Tafel (ba) and cathodic Tafel slope (bc). The values of ba and bc calculated for the specimen in NaCl, Na₂SO₄, NH₄Cl and MgCl₂ are furnished in table 1-4 respectively. In NaCl ba and bc values than ba indicate a cathodically controlled mechanism. On polarization for the same applied current more cathodic reaction take place. In short the result conclude a cathodically controlled process in NaCl, Na₂SO₄ and MgCl₂, while an anodically controlled in NH₄Cl.

Table 1. Corrosion parameters for MLA in NaCl

Conc. M	OCP (-v)	E _{corr} (-V)	I _{corr} mA/cm ²
0.05	1.40	1.4	4.2 x 10 ⁻⁴
0.1	1.47	1.47	4.2 x 10 ⁻⁴
0.5	1.50	1.5	5.7 x 10 ⁻⁴
1.0	1.55	1.55	7.8 x 10 ⁻⁴
2.0	1.6	1.6	3.2 x 10 ⁻⁴

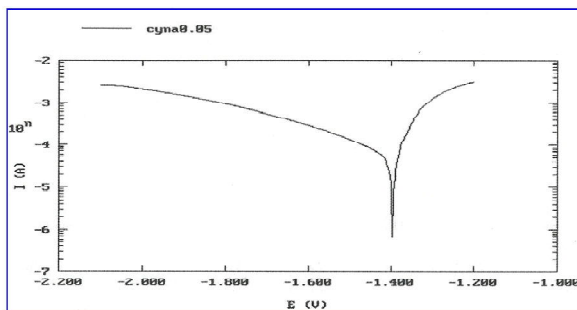


Fig. 1: Potentiodynamic polarization plot of MLA alloy in 0.05M NaCl

Table 2. Corrosion parameters for MLA in Na₂SO₄

Conc. M	OCP (-v)	E _{corr} (-V)	I _{corr} mA/cm ²	Tafel slopes (mv/dec)	
				ba	Bc
0.05	1.25	1.25	4.0 x 10 ⁻⁴	130	160
0.1	1.38	1.40	4.3 x 10 ⁻⁴	70	140
0.5	1.43	1.43	4.4 x 10 ⁻⁴	65	130
1.0	1.45	1.45	4.6 x 10 ⁻⁴	60	120
2.0	1.47	1.50	5.4 x 10 ⁻⁴	50	110

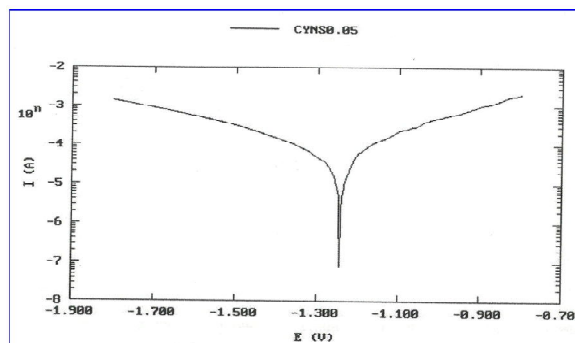


Fig. 2: Potentiodynamic polarization plot of MLA alloy in 0.05M Na₂SO₄

Table 3. Corrosion parameters for MLA in NH₄Cl

Conc. M	OCP (-v)	E _{corr} (-V)	I _{corr} mA/cm ² x 10 ⁻⁴	Tafel slopes (mv/dec)	
				ba	Bc
0.05	1.78	1.80	4.7	170	150
0.1	1.83	1.85	4.9	150	140
0.5	1.92	1.92	6.0	120	110
1.0	1.96	1.96	8.0	110	100
2.0	2.05	2.05	3.5	100	90

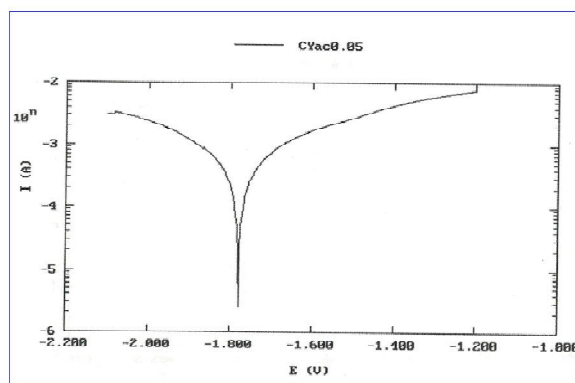
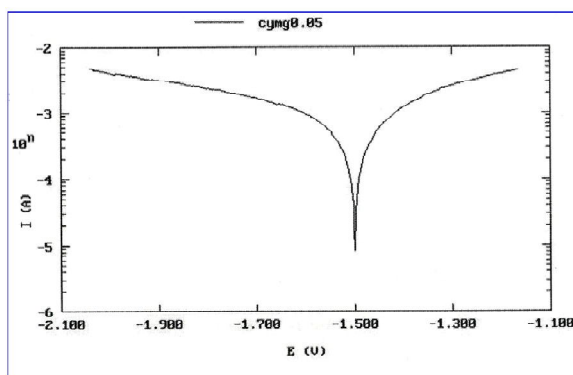


Fig. 3: Potentiodynamic polarization plot of MLA alloy in 0.05M NH₄Cl

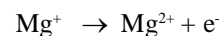
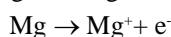
Table 4. Corrosion parameters for MLA in MgCl₂

Conc. M	OCP (-v)	E _{corr} (-V)	I _{corr} mA/cm ²	Tafel slopes (nv/dec)	
				ba	Bc
0.05	1.5	1.52	4.2x10 ⁻⁴	120	190
0.1	1.54	1.55	4.3x10 ⁻⁴	110	180
0.5	1.55	1.58	5.0x10 ⁻⁴	100	150
1.0	1.60	1.60	5.6x10 ⁻⁴	80	120
2.0	1.75	1.78	6.0x10 ⁻⁴	60	110

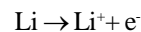
**Fig. 4: Potentiodynamic polarization plot of MLA alloy in 0.05M MgCl₂**

3.6 Criteria of corrosion

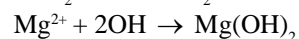
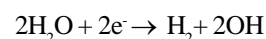
Corrosion of the metals is an electrochemical process manipulated by both anodic and cathodic process propagated by the electrons. The corrosion of the MLA alloy in the selected aqueous solution to also an energetically used process taking place by the dissolution of the alloy and evolution of hydrogen. On polarization both these reaction will take place but at different rates. The corrosion of MLA alloy in this solution may be on film-centered mechanisms. As far as the dissolution of the alloy at the anode is concerned for pure Mg in can be either a bivalent Mg²⁺ ion or monovalent Mg⁺ ion.



On polarization with a particular applied current all the metals may ionic and paris into the solution according to the following ionic reaction.



The cathodic reaction enabling the H₂ evolution can be written as follows.



4. CONCLUSION

It has been possible to arrive at the following important conclusion from the Potentiodynamic polarization of the MLA alloy in four different solutions. The open circuit potentials are all negative and range from -1.3V to -2.0V. The value is found to become more negative with increase in concentration. The corrosion potentials are also negative and almost equal to OCP and negative value enhances with concentration. Corrosion current is observed to increases with concentration. From the I_{corr} values the corrosivity of the solution is graded in the order as NH₄Cl > NaCl > MgCl₂ > Na₂SO₄. bc is noticed to be higher than ba in NaCl Na₂SO₄ and MgCl₃ and hence a cathodically controlled mechanism while an anodically controlled dissolution is interred in NH₄Cl solution.

REFERENCES

- Andrei, M., Eliezer, A. and Bonora, PL. Gutman, *Mater. Sci. and corrosion*, 53(7), 455(2002).
- Antonyraj, A., Augustin, C. O., *Bull. Eletro chem.* 15. 135(1999).
- Augustin, C. O., Antonyraj, A. and Sing, R. K., *Corr. reviw*, 19, 4(2001).
- Baril, Genevieve, Blank, Christine, Pebebe and Naden *Electrochemical Society*, 16(2001).

- Han guk pusik, *Corrosion science society of karee*, 28, 175(1999).
- Hollestin, Fruk, Wiedmann and Renate, *Surface and Coating Tech*, 162, 261(2003).
- Inoue. H., Sugabera, K., Yamamoto, E. and Eliezer, A. *Corrosion Science*, 44, 603(2002).
doi:10.1016/S0010-938X(01)00092-0
- Matsubaraa and Toru, *Jpn.Kokai Tokky koho*, 1, 371(2003).
- Mat-Summura, Sadaharu, Kawabe and Tokeshi Saito 64, 492(2003).
- Sakamoto and Sakdi Nobua Jpn. *Kokai Tokkyo Koho* 53, 471(2003).
- Song, G. L. and Atrens, A., *Corr. Sci. and Tech.*, 31, 106(2002).
- Stulikove, I., Smola, B., Von Buch, F. and Mordike, *Material Wissenchalf and Werkstofftechnik*, 34, 261(2003).
- Wang, Yanping, Yeshuang, Werijing and Zhu, *Material Wissenchalf and Werkstofftechnik*, 34, 178(2003).