

Acknowledgements: this work was supported by CICYT (Grant Mat.- 464/90) and Human Mobility framework of CEE (ERB-CIPA-CT-92-2110).

(Received: December 12, 1994
Revised form: June 12, 1995)

**INFLUENCE OF HALIDE IONS ON THE ELECTROCHEMICAL
BEHAVIOUR OF MAGNESIUM AT HIGH CONCENTRATIONS**

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SUMMARY

Magnesium, one of the lightest nonferrous metals assumes great importance due to many attractive structural, chemical and electrochemical features. The influence of the halide ions at concentrations ranging from 0.1 M to 2.0 M on the corrosion behaviour of primary magnesium has been investigated by galvanostatic polarisation and atomic absorption spectroscopy (AAS). The corrosion kinetic parameters namely open circuit potential (OCP), corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel constants (b_a and b_c) have been calculated from polarisation experiments. These data are interpreted to bring out the effects of the halide ions and their concentration on the corrosion of magnesium in these media. The amount of magnesium anode dissolved and estimated by the instrumental method has been compared with the electrochemical weight loss. The dissolution rate in the former is found to be more than in the latter. Suitable explanations have been forwarded for the excess dissolution of magnesium. The change in p^{H} observed during the polarisation at high current densities has also been investigated and explained suitably in this paper.

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KEY WORDS: corrosion behaviour, magnesium, halide ions, AAS, polarisation studies.

INTRODUCTION

Magnesium and its alloys are strategically essential due to their lightness, high strength to weight ratio and ennoblement in aqueous environments. Magnesium based alloys exhibit poor corrosion resistance by virtue of their position in the galvanic series. But due to the ennoblement in many environments to an extent of 1.0 V, they are used in alloying, metallurgy, transportation, batteries and in cathodic protection[1-5]. The demand for the metal is on the rise for various applications. Halides are present in various industrial environments and may cause corrosion to different tools and machineries. Hence an understanding of the corrosion behaviour of magnesium in different environments will help in combating corrosion in such environments[6,7]. An attempt has been made in this study to combine polarisation method with atomic absorption technique to obtain various corrosion data for the magnesium metal in aqueous NaF, NaCl, NaBr and NaI at different concentrations ranging from 0.1 M - 2.0 M.

EXPERIMENTAL

A three electrode polarisation system has been used to obtain corrosion data for magnesium in solutions of NaF, NaCl, NaBr and NaI at concentrations of 0.1, 0.25, 0.5, 1.0, 1.5 and 2.0 M. The working electrode was 99.87% w/w pure

magnesium with impurities such as Al 0.04, Si 0.04, Fe 0.03, Zn 0.005, Cr 0.005 and Mn 0.003% w/w. The active area of the test specimen was 0.3 cm². Saturated calomel electrode (SCE) and platinum foil were the reference and counter electrode respectively. Solutions of different concentrations were prepared by dissolving guaranteed grade chemicals in triple distilled water made by using quartz distillation apparatus. The metal turned into small cylindrical rods were polished with 1/0, 2/0, 3/0, 4/0 emery papers and degreased with acetone and fitted to a copper rod. The unexposed area of the electrode was masked by lacquer. About 130 ml of the 0.1 M NaF solution was taken in a double walled polarisation cell and the p^H was measured using a pencil type p^H tester. The test solution was stirred using a magnetic stirrer and the temperature was maintained at 30 ± 1 °C by circulation of water from a constant temperature water bath. The working electrode was connected to the negative terminal of the constant current generator for performing cathodic polarisation and other connections were made. The system was allowed to attain equilibrium and the open circuit potential was measured using a digital multimeter (HIL 2161) with reference to SCE. A constant current starting from 10 μA was impressed on the test electrode. The system was allowed to attain equilibrium condition and the steady state electrode potential was noted. Successively small increments of current up to 10 mA cm⁻² were applied and respective steady state potentials were measured. Fresh polished specimens were introduced into

the medium and connected to the positive terminal of the current generator and the anodic polarisation was performed. At the end of the experiment p^H of the solution was also noted. Similar procedure was repeated for all media. Sodium fluoride solutions of concentrations up to 0.5 M were used due to solubility limitations. The corresponding potential values for different applied currents were measured. These values were plotted in a semilogarithmic graph to get Tafel plots (Figs. 1-4) from which the corrosion current, corrosion potential and Tafel constants have been calculated and are given in the Table 1. Separate set of experiments were carried out with the same specimen in all media at a constant current density of 50.0 mA cm^{-2} and the concentration of magnesium in solutions were determined using AAS from which the dissolution rate of the magnesium was calculated. The dissolution rate of magnesium versus concentrations were plotted and the graph is given in Fig.5.

RESULTS AND DISCUSSION

Figs.1-4 show the polarisation curves for magnesium in NaF, NaCl, NaBr and NaI of different concentrations. It is evident from Fig.1 that predominant anodic polarisation is observed in fluoride medium and hence the behaviour is said to be under anodic control. In NaCl equal polarisation of anode and cathode is observed up to 0.25 M (Fig.2a) and the polarisation which is under mixed control later is changed into a cathodically controlled behaviour with increase in

Table 1 Corrosion kinetic parameters obtained from polarisation studies for magnesium in different media

Medium	C (M)	OCP (-V)	E_{corr} (-V)	I_{corr} (mA cm^{-2})	b_a (mV dec^{-1})	b_c	Change in p^H
NaF	0.10	1.21	1.20	0.10	40	35	0.1
	0.25	1.09	1.08	0.05	38	32	0.1
	0.50	1.02	1.00	0.02	32	30	0.1
NaCl	0.10	1.59	1.64	1.70	340	350	2.2
	0.25	1.60	1.67	2.90	300	320	2.5
	0.50	1.63	1.68	4.80	180	300	2.7
	1.00	1.65	1.70	5.70	150	260	2.9
	1.50	1.67	1.72	5.90	140	250	3.0
	2.00	1.68	1.75	6.20	130	220	3.2
NaBr	0.10	1.48	1.50	1.00	250	300	1.5
	0.25	1.52	1.55	1.40	190	260	1.6
	0.50	1.55	1.56	1.70	160	210	1.8
	1.00	1.62	1.59	2.00	140	180	1.9
	1.50	1.63	1.60	2.90	120	150	2.1
	2.00	1.66	1.61	3.20	100	140	2.3
NaI	0.10	1.45	1.49	0.90	200	250	0.7
	0.25	1.49	1.51	1.00	190	210	0.8
	0.50	1.50	1.52	1.20	170	180	1.0
	1.00	1.51	1.53	1.50	140	160	1.3
	1.50	1.52	1.54	1.80	120	140	1.5
	2.00	1.53	1.54	2.40	100	120	1.8

the concentration (Fig.2b). Magnesium is predominantly cathodically polarised in solutions of NaBr and NaI thereby exhibiting cathodically controlled behaviour at all concentrations as evident from Figs.3 and 4. These observations are also confirmed from the 'b_a' and 'b_c' values (Table 1) as 'b_a' is found to be less than 'b_c' in these solutions. The corrosion potential is shifted towards more negative values as Cl⁻, Br⁻ and I⁻ ion concentration increases, and this can be attributed to the localised attack of magnesium in all these environments.

Open circuit potential (OCP)

OCP is one of the important parameters to support the corrosion phenomena. The variation of OCP with increase in concentrations of different ions were given in Table 1. It is seen that OCP value increases with increase in concentrations ranging from -1.59 V to -1.68 V in NaCl, from -1.48 V to -1.66 V in NaBr and from -1.45 V to -1.53 V in NaI. But the reverse trend is observed in the fluoride medium and the OCP changes towards more positive values from -1.21 V to -1.02 V. The ennoblement in fluoride medium is due to the formation of a protective magnesium fluoride film on the magnesium surface, while in other cases the corrosion products formed are not stable and they dissolve resulting in enhanced corrosion.

Corrosion potential (E_{corr})

The corrosion potential obtained by the extrapolation of the Tafel plots is given in Table 1. E_{corr} values show a steady increase to more negative direction with increase in the concentration from 0.1 to 2.0 M in Cl⁻, Br⁻, and I⁻ media. But a different behaviour of changing potential to more positive values with increase in the concentration is observed in F⁻ solutions. The behaviour of magnesium in fluoride environment is predominantly governed by anodic reactions. In other media the mechanism is totally controlled by cathodic hydrogen evolution process.

Corrosion current (I_{corr})

It is evident from Table 1 that I_{corr} is increases linearly with increase in the concentration of Cl⁻, Br⁻ and I⁻ where as a gradual decrease with increase in concentration is

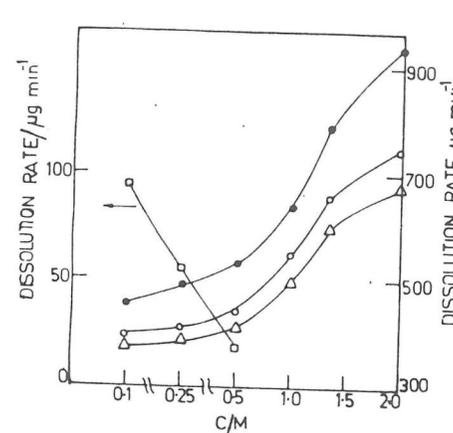


Fig. 5 Dissolution rate vs C plot for Mg
NaF (□), NaCl (●), NaBr (○) and NaI (△)

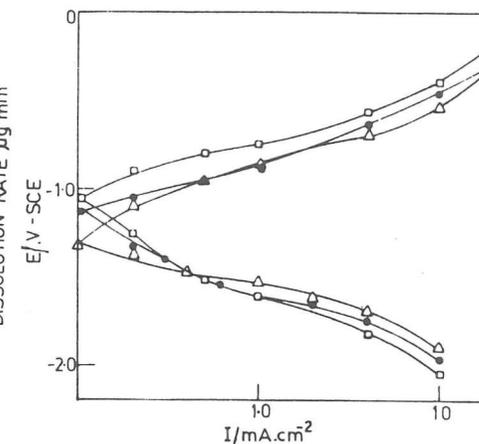


Fig.1 Polarisation plot of Mg in NaF

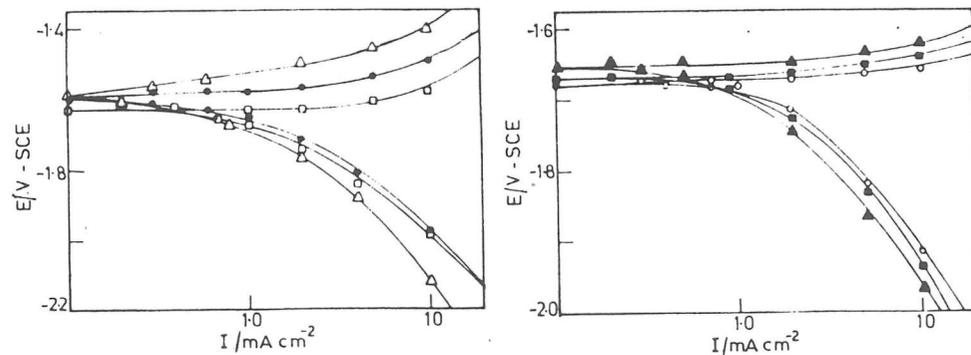


Fig.2a and 2b Polarisation plot of Mg in NaCl

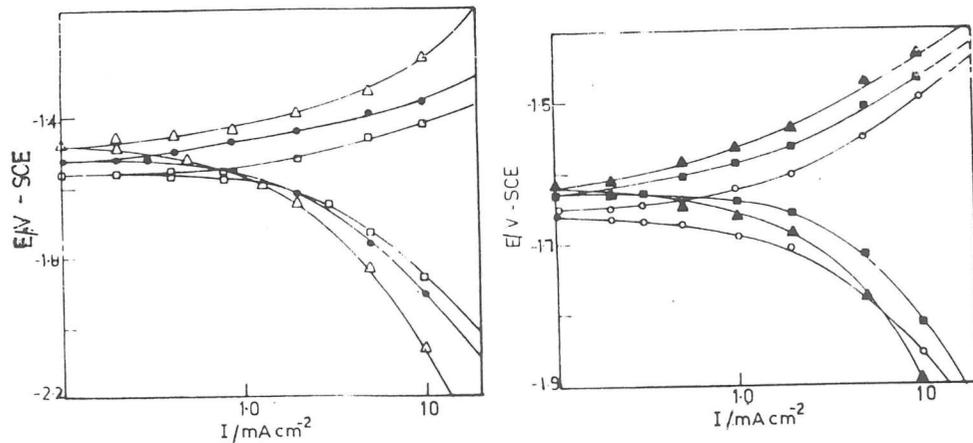


Fig.3a and 3b Polarisation plot of Mg in NaBr

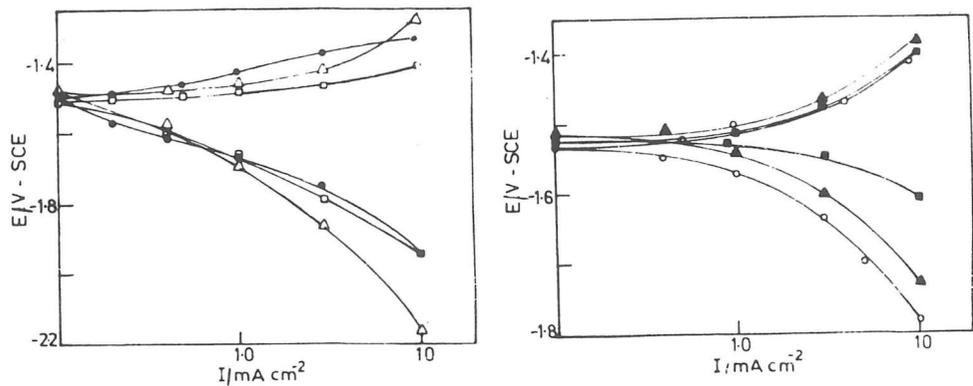


Fig.4a and 4b Polarisation plot of Mg in NaI
 (Δ) 0.1 M, (●) 0.25 M, (□) 0.5 M,

observed for fluoride ions. Lowest I_{corr} (0.02 mA cm^{-2}) value is obtained in 0.5 M fluoride medium and highest I_{corr} value (6.2 mA cm^{-2}) is obtained in 2.0 M NaCl. Similarly for NaBr and NaI corrosion currents are 1.0 to 3.2 mA cm^{-2} and 0.9 to 2.4 mA cm^{-2} respectively. The lower I_{corr} values of fluoride ion supports the inhibitive action of fluoride ion as the corrosion of magnesium. The relative stabilities of magnesium in halides on the basis of I_{corr} value may be given as $F^- \gg I^- > Br^- > Cl^-$. The chloride is found to be the most aggressive anion for magnesium which may be due to the pitting type of attack as well as to the formation of soluble salts in such environments.

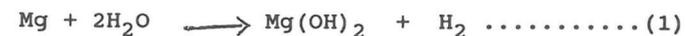
Dissolution rate

The dissolution rate calculated from the amount of magnesium present in the tested solution by AAS is plotted against concentration and is shown in Fig.5. It can be seen from the figure that the dissolution rate increases with increase in the concentration in all the media except in fluoride where a decrease is observed. The dissolution rate of magnesium in different media, other than fluoride medium can be graded on the basis of concentration as $2.0 > 1.5 > 1.0 > 0.5 > 0.25 > 0.1 \text{ M}$. A comparison of these rates with magnesium equivalent of corrosion current at respective concentrations reveals that the dissolution rate calculated from spectroscopic method is 2-3 times more than that observed by the polarisation method particularly at high concentrations. A maximum dissolution rate of magnesium (945 g min^{-1}) is

obtained in 2.0 M NaCl. At higher concentrations magnesium undergoes a pitting type of attack and also the formation of a soluble salt resulting in higher dissolution. The excess consumption of magnesium indicates that a portion has been dissolved nonfaradaically either as metal itself or as monovalent ions instead of divalent ions. It may also be due to the difference effect, loss of metal by disintegration, and damage of protective film promoted by aggressive anions. But in fluoride solutions the dissolution rate decreases with increase in the concentration and the lowest dissolution rate (16.5 g min^{-1}) is found in 0.5 M NaF. At higher concentrations a thick stable MgF_2 film is formed which breakdown further corrosion[8,9]. Both techniques confirm that Cl^- is the most aggressive anion and F^- is the least aggressive anion for magnesium.

Effect of p^{H}

The change in p^{H} of the solution during polarisation given in Table 1, shows a decrease in p^{H} with increase in concentration before polarisation in Cl^- , Br^- and I^- media. This change in p^{H} helps to decide the extent of attack on magnesium because the p^{H} of the electrolyte was found to influence the nature and growth of passive film. After polarisation a uniform increase in p^{H} is noticed in all media other than F^- medium. As corrosion proceeds, the metal surface experiences a local increase in p^{H} due to the removal of hydrogen ions from the evolution in the form of hydrogen gas and the formation of magnesium hydroxide / magnesium oxide according to the equations[10]



There is no appreciable change in pH before and after polarisation in fluoride medium which clearly supports the negligible dissolution of magnesium. It has been observed that the p^{H} increases with increase in concentration during polarisation and that this increase is in the order of $\text{NaCl} > \text{NaBr} > \text{NaI}$.

CONCLUSIONS

The open circuit potential and corrosion potential are negative and become more negative with increase in the concentration in solutions containing Cl^- , Br^- and I^- , but becomes more positive in solutions containing fluoride.

On the basis of corrosion current F^- ion behaves as an inhibitor and Cl^- ion acts as the most aggressive halide ion for magnesium.

The dissolution rate calculated by AAS is found to be much more than that obtained by the polarisation method and the excess dissolution may be due to spalling, particularly at higher concentrations.

p^{H} of the medium is observed to increase during polarisation because of the formation of $\text{Mg}(\text{OH})_2$ / MgO and evolution of H_2 in all halide solutions except those containing fluoride.

ACKNOWLEDGEMENT

Authors express their appreciation to their colleagues in the pyrometallurgy division for their excellent co-operation and to Director, Central Electrochemical Research Institute for his permission to publish the paper.

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(Received: January 30, 1995
Revised form: August 8, 1995)

ELECTROCHEMICAL INVESTIGATION OF β -ALKYLOXY SUBSTITUTED *meso*-TETRAPHENYLPORPHYRINS

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Abstract: The voltammetric behaviour of several β -alkyloxy substituted *meso*-tetraphenylporphyrins has been investigated. The first oxidation potential of all compounds depends strongly upon the substituent constant σ^+ . In contrast to this the second oxidation potential is insensitive to this constant. Furthermore, rate constants for the first anodic electron transfer process were determined. The estimated data confirm, that the distortion of the porphyrin chromophore induced by the substituents did not affect the electrochemical rate constant significantly.

Introduction:

Charge separation in photosynthetic organisms occurs in a chlorophyll-quinone-protein complex known as the photochemical reaction center. The structure of the photochemical reaction center of *Rhodospseudomonas viridis* was determined in 1984 by X-ray diffraction analysis.¹⁾ This investigation stimulated the synthesis of artificial model systems for photochemical reaction centers in the last years. Especially porphyrinic systems were synthesized for these investigations.²⁾ For the design and synthesis of new artificial model systems it is necessary to investigate the effect of different substituents on the chromophore properties. Especially it is necessary to get more information about the influence of substituent parameters on oxidation and reduction potentials and on spectroscopic properties.