CORROSION BEHAVIOUR OF DIFFERENT GRADES OF MAGNESIUM IN DIFFERENT ELECTROLYTES

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SUMMARY

Gasometric measurements and galvanostatic polarisation studies of different grades of magnesium in different electrolytes have been carried out at different current densities ranging from 0 - 100 mA cm^{-2}. A relationship between current density and the rate of hydrogen evolution has been observed. The predominant role of anions in corrosion and other unusual behaviour of magnesium in aqueous solutions of electrolytes have been confirmed in this investigation. Cations are also found to play a decisive role in the anomalous behaviour of magnesium in these solutions. The present study has made it possible to arrive at a new parameter called 'Transition current density' denoted by the symbol 'i_T' at which a transition from positive difference effect to negative difference effect or vice versa occurs. The dependence of this parameter on system variables has been explained suitably.

Key words: magnesium, difference effect, transition current density, aqueous environments.

INTRODUCTION

Magnesium like any other metal is susceptible to corrosion under certain service conditions. Eventhough

magnesium has a reputation of being an easily corrosive metal, it has also a good corrosion resistance, superior to steel in its resistance to atmospheric corrosion [1]. Hence an understanding of the electrochemical behaviour of magnesium is important.

The standard electrode potential Mg^{2+}/Mg = -2.37 V vs. SHE [2]. As with other electronegative metals, the absence of severe corrosion is explained by the formation of a protective film which inhibits the attack [3]. In many media the working electrode potential of magnesium varies from -1.4 to -1.6 V vs. SHE because of the ennoblement by presence of a protective film. The behaviour of magnesium in aqueous solution is characterised by an electrochemical corrosion. The attack depends on the aggressiveness of the medium, pH and temparature [4]. The film is usually $Mg(OH)_2$ which is more basic than hydroxides of other light metals and it is less soluble at pH 4 - 9. There will be protection until the pH reaches 10 due to the active potential. Corrosion of magnesium in aqueous solutions occurs predominantly by hydrogen evolution [5].

The unusual behaviour of magnesium in aqueous medium is ascribed to 'negative difference effect' transpassive behaviour, low efficiency in cathodic protection and apparent valency [6]. An electrochemical study of magnesium was carried out to find out the effect of current density, temparature and pH on the anodic and cathodic behaviour in buffered and unbuffered solutions [7]. Several workers have

reported the negative difference effect of magnesium and attributed it to the formation and deformation of a protective film on magnesium anode. They have also pointed out that the dissolution of magnesium anode proceeds electrochemically and the increased corrosion rate at low pH values could be due to polarisation of the anode by the break down of the magnesium hydroxide barrier and the depolarisation of the cathode by the increased availability of protons for discharge [8].

In the present study the corrosion behaviour of three grades of magnesium in electrolyte solutions of sodium chloride, sodium perchlorate, magnesium chloride and magnesium perchlorate at concentrations ranging from 0.05 M to 0.5 M, has been investigated using gasometric and galvanostatic polarisation measurements with an idea of understanding the anomalous behaviour of magnesium on dissolution in these electrolytes.

EXPERIMENTAL

Three different grades of the metal viz., 1) primary magnesium produced by fused salt electrolysis in the Central Electrochemical Research Institute, Karaikudi, India, referred as 'CECRI Mg', 2) an alloy of magnesium with zinc referred as 'ZnMg' and 3) super purity magnesium (Johnson & Matthey Chemicals Limited, England) referred as 'SpMg' have been used for the study in four electrolytes viz., NaCl, $NaClO_4$, $MgCl_2$ and $Mg(ClO_4)_2$ at concentrations of 0.05, 0.1, 0.2 and 0.5 M. The chemical composition of all the

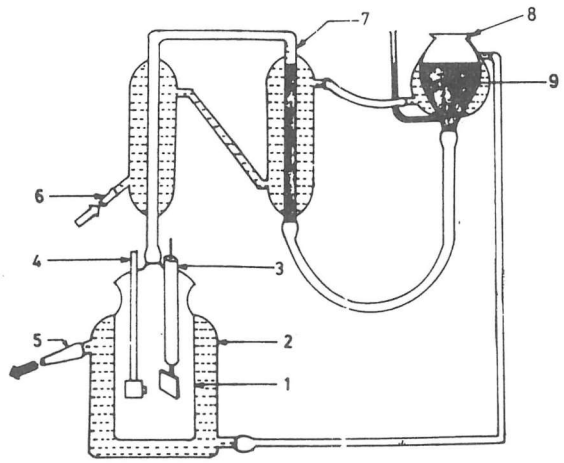
specimens was analysed by atomic absorption spectrophotometer, Perkin Elmer, using both flame and flameless techniques. The analytical report of the specimens is given in Table 1.

TABLE : 1 CHEMICAL COMPOSITION OF DIFFERENT GRADES OF MAGNESIUM

Sl.No.	Impurity	ZnMg (ppm)	CECRI Mg (ppm)	SpMg (ppm)
1	Aluminium	50	500	20
2	Bismuth	10	10	1
3	Calcium	10	20	10
4	Chromium	10	20	2
5	Copper	10	30	20
6	Iron	50	400	20
7	Lead	10	50	10
8	Manganese	10	30	10
9	Nickel	10	30	2
10	Silicon	20	340	10
11	Sodium	10	20	5
12	Zinc	5500	100	10
	Magnesium (%) (by difference)	99.430	99.845	99.989

Accurately weighed quantities of guaranteed grade chemicals were dissolved in triple distilled water to prepare 0.5 M solutions. Lower concentrations were obtained by the dilution of this solution with triple distilled water of conductivity 0.6 S cm^{-1} in a quartz distillation unit. Metal specimens were turned into tiny rods of 1.13 cm diameter with grooves and fitted into electrode assembly by means of a copper rod and Teflon sleeves. The exposed area of the working electrode was 1 cm^2, keeping rest of the area masked by lacquer.

A modified experimental cell set up (Fig 1) was used in this study. The modification has been done to collect the hydrogen gas liberated from the electrodes under non polarised and polarised conditions. The experimental set up consisted of a double walled polarisation cell, closed with an airtight ground glass lid having an opening for hydrogen and provisions to introduce the test electrode and the platinum elecrode to apply current. The outlet for hydrogen was connected to a eudiometer with liquid reservoir surrounded by glass jackets for the circulation of water. The thermoset (303 ± 1 K) water was circulated continuously through outer jackets of the polarisation cell and the eudiometer. The column liquid was 20% NaCl solution coloured by hydrochloric acid and methyl orange. All the flexible and ground glass joints were made leak proof using araldite sealings.



1. Reaction vessel
2. Outer jacket
3. Pt. electrode
4. Working Mg electrode
5. Water outlet tube
6. Water inlet tube
7. Graduated burette
8. Reservoir bulb
9. Coloured liquid

Fig.1 The set up for Gasometric measurements

Test specimens were thoroughly polished using 1/0, 2/0, 3/0 and 4/0 emery sheets and degreased with acetone. 150 ml of NaCl 0.05 M was taken in the polarisation cell, covered with an airtight lid carrying the test electrode (CECRI Mg) and platinum. The outlet from the lid was connected to the eudiometer by means of leak proof rubber tubing. The test electrode was connected to the positive terminal of the constant current generator. The initial level in the liquid column was noted after equalising with reservoir bulb (R1). Instantly, a digital stop watch was started. The hydrogen liberated for 30 minutes was collected by downward displacement of the liquid. The reading in the column was again noted (R2). The difference between the two readings (R2 - R1) gave the volume of hydrogen liberated at zero

current (Vo) for the specimen under unpolarised condition or open circuit value. A current density of 5 mA cm^{-2} was applied from a constant current generator. After 30 minutes the current was stopped and the reading was taken (R3). The difference between this reading and the initial reading (R3 - R1) gave the volume of hydrogen liberated for 30 minutes from the same electrode obtained by passing a constant current density of 5 mA cm^{-2}. The pressure from the system was released, the same measurement was repeated and the volume of hydrogen liberated was noted. The average of the two readings was taken as the correct volume of hydrogen liberated from the test electrode for 30 minutes at a constant current density of 5 mA cm^{-2} in 0.05 M NaCl (Vt). The same procedure was repeated for higher current density values and the total hydrogen evolved for each current density was measured up to 100 mA cm^{-2}. Duplicate experiments have been carried out to eliminate any error due to leakage in the system. Similar measurements were carried out for different concentrations of NaCl, $NaClO_4$, $MgCl_2$ and $Mg(ClO_4)_2$ for all specimens, taking all precautions and values of Vo and Vt were obtained for all the systems. From the volumes of hydrogen collected for each system in the absence of any impressed current (Vo) and by impressing a known current for the same system (Vt), the difference effect was calculated using the relationship

$$\triangle = (Vo + 6.97\ I) - Vt \qquad \ldots\ldots\ldots\ldots(1)$$

where the factor 6.97 converts the milliampere current flowing through the test electrode for one minute into cubic

millimetre (mm^3) of hydrogen at standard condition and I is substituted in milliampere-minute. Hence the unit of 'Δ' becomes $mm^3\ cm^{-2}\ min^{-1}$. Values of Vt were plotted against corresponding current density values. Straight line graphs were obtained, from which more Vt values with respect to many current density values were computed and difference effect was calculated up to 100 mA cm^{-2}. The difference effect versus I plot was constructed (Figs 2 to 7) from which the new parameter 'i_T' was computed. The dependence of 'i_T' on concentration was established graphically and given in Fig.8.

RESULTS AND DISCUSSION

It has been observed that Vo increases with increase in the concentration of electrolyte, and Vt the volume of hydrogen liberated during the polarisation in different concentrations of the above electrolytes also increases with increase in the extent of external polarisation at initial stages, but at high current densities almost same values are obtained indicating the absence of concentration dependence. The behaviour of magnesium in these electrolytes is shown to be electrochemical in nature with formation of magnesium ions at the anode and liberation of hydrogen at the cathode. It has been noticed that the consumption of magnesium anode measured in terms of hydrogen was very much higher than that predicted by Faraday for Mg^{2+} formation especially at high current densities. At a particular current density, Vt increases with increase in the concentration of the media.

These observations clearly show the effect of concentration and current density on the rate of hydrogen evolution. Generally the gas evolution in NaCl solution is found to be more than in other solutions for all specimens. In the case of 'SpMg', Vo is slightly lower than other two grades in all concentrations. It has been seen from this study that chlorides are more corrosive than perchlorates and sodium ion is more corrosive than magnesium ion. A comparison of Vt values for different electrolytes show the decreasing order of aggressiveness as NaCl > $MgCl_2$ > $NaClO_4$ > $Mg(ClO_4)_2$. This enunciates that anions contribute more towards the electrochemical dissolution but at the same time cations also have a significant role to play in the anomalous behaviour of Mg in these electrolytes.

Fig.2 shows the dependence of difference effect on current density for 'ZnMg' in NaCl and $NaClO_4$. In NaCl at low current densities a positive difference effect (PDE) is observed for all concentrations. As current density increases it is found to increase a little, then starts to decrease, becomes zero and finally changes into negative difference effect (NDE). Similar trend is shown by 'ZnMg' in $NaClO_4$ also, whereas the same electrode in $MgCl_2$ and $Mg(ClO_4)_2$ exhibits only negative difference effect as evidenced from Fig.3. At a low current density a negative difference effect is exhibited whose value is found to increase with increase in current density as well as with concentration. The behaviour of 'CECRI Mg' in NaCl and $NaClO_4$ is shown in Fig.4. Initially at low current densities

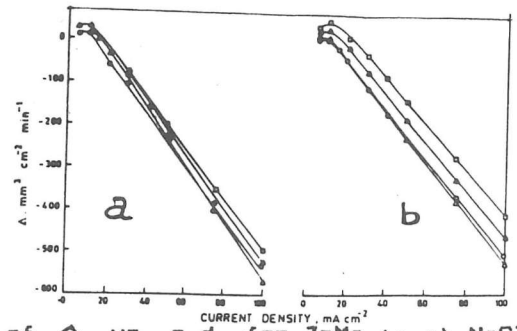


Fig.2 Plot of △ vs. c.d. for ZnMg in a) NaCl, b) $NaClO_4$

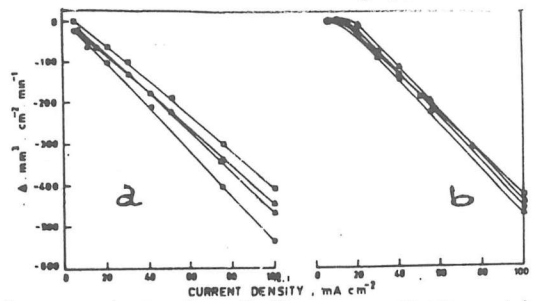


Fig.3 Plot of △ vs. c.d. for ZnMg in a) $MgCl_2$, b) $Mg(ClO_4)_2$

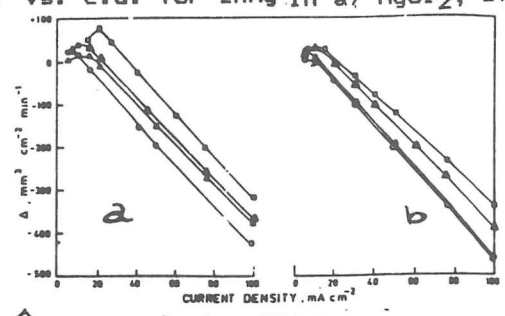


Fig.4 Plot of △ vs. c.d. for CECRI Mg in a) NaCl, b) $NaClO_4$

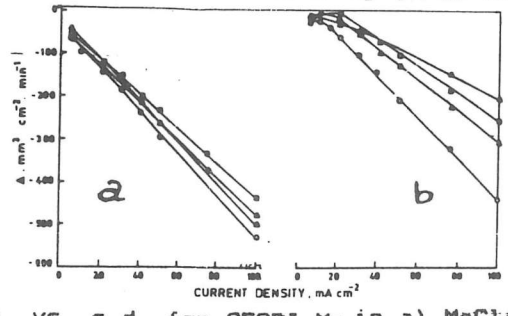


Fig.5 Plot of △ vs. c.d. for CECRI Mg in a) $MgCl_2$, b) $Mg(ClO_4)_2$

a positive difference effect is observed which then becomes zero and finally at high current densities a complete negative difference effect has been observed. 'CECRI Mg' in $MgCl_2$ and $Mg(ClO_4)_2$ shows only negative difference effect at all current densities and concentrations similar to 'ZnMg' as seen from Fig.5. Figs 6 and 7 show the variation of difference effect with current density for 'SpMg' in NaCl, $NaClO_4$, $MgCl_2$ and $Mg(ClO_4)_2$ solutions respectively. This grade also follows the same trend as other electrodes in NaCl and $NaClO_4$ with positive difference effect at low current density which switches over, to negative difference effect with increase in current density through zero. But in $MgCl_2$ and $Mg(ClO_4)_2$ positive difference effect is altogether absent and shows only negative difference effect.

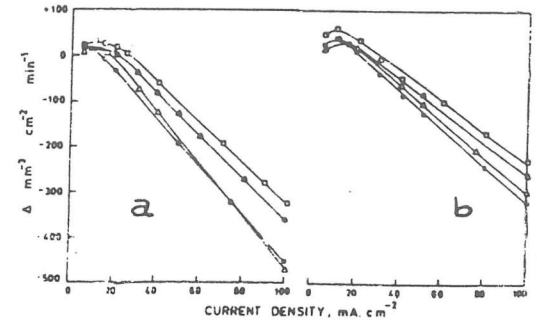


Fig.6 Plot of △ vs. c.d. for SpMg in a) NaCl, b) $NaClO_4$

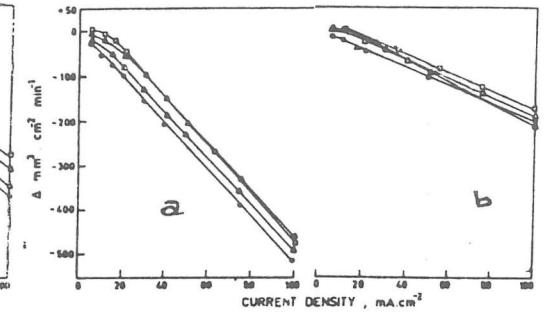


Fig.7 Plot of △ vs. c.d. for SpMg in a) $MgCl_2$, b) $Mg(ClO_4)_2$

Legends of figures 2 – 7

-o- 0.05 M, -△- 0.10 M, -▲- 0.20 M, -□- 0.50 M

A close scrutiny of all systems represented by figures 2 to 7 reveals the fact that among the systems under study 'Sp Mg' in $Mg(ClO_4)_2$ exhibits the minimum difference effect. All the three grades at low current densities and concentrations show positive difference effect in NaCl and $NaClO_4$ only. This may be explained as follows. When no current is passed the volume of hydrogen (Vo) is evolved only from the anode resulting from chemical dissolution. But when the same electrode is polarised anodically the self dissolution is reduced initially, inhibiting the dissoluion of Mg and consequent evolution of hydrogen resulting in a low value of Vt. Hence Vo becomes larger than Vt giving a positive value to difference effect. This has been attributed to some interference with the supply of electrons to local cathodes, hindering the formation of hydrogen. This may be due to the formation of oxide/hydroxide films [9] masking the surface and reducing the effective anodic areas and anodic dissolution, thereby decreasing the amount of hydrogen from chemical attack giving comparatively smaller Vt, resulting in a positive difference effect. As the current density increases, deformation of the surface films takes place exposing small areas for attack and increasing the value of Vt which results in a zero difference effect. This indicates an ideal behaviour, in which no difference effect exists at all, which means that the system behaves ideally in complete agreement with Faraday's law. The negative difference effect exhibited by all grades of magnesium at high current densities may be due to the rupture of surface films

exposing more and more active areas to corrosive media [10], causing rapid dissolution and hydrogen evolution making Vt >> Vo resulting in a negative difference effect, whose extent increases with increase in the current density.

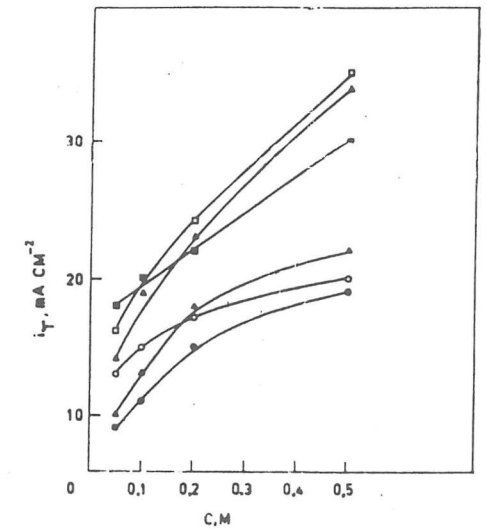


FIG: 8 VARIATION OF i_T WITH CONCENTRATION
FOR ZnMg -o- IN NaCl, -•- IN $NaClO_4$
FOR CECRI Mg -•- IN NaCl, -o- IN $NaClO_4$
FOR SP Mg -o- IN NaCl -•- IN $NaClO_4$

The present study confirms the vital role of current density on the anodic dissolution of Mg in these solutions. It enables to locate and fix a current density at which the positive difference effect changes to negative difference effect. The current density at which the transition occurs is termed as the 'Transition current density' denoted by the symbol 'i_T'. This parameter can henceforth be defined as the current density at which a transition from positive difference effect to negative difference effect or vice versa occurs. The transition is governed by the nature of

electrode material, electrolyte and their composition. Fig.8 clearly brings out the dependence of the new parameter on the characteristics of the system and its surroundings. It is seen that 'i_T' is different for different grades of metal in a particular medium and is also found to increase with increase in concentration. It may be viewed that apart from nature and concentration of the electrolyte, purity of the anode material rather than the low level of impurities exerts more influence on the magnitude of this new parameter. For a particular concentration of an electrolyte 'i_T' is found to be least for 'ZnMg' followed by 'CECRI Mg' and finally 'SpMg' in the increasing order of their magnesium content. Hence it can be concluded that as the purity of the anode material increases the value of 'i_T' also increases. Impurities may be many and their effects on hydrogen evolution may also be complex, hence an explanation on the basis of the purity of the anode has been forwarded. As the magnesium content in the anode material increases, the anodic polarisation decreases and the current density required for the transition also increases. Therefore as the purity increases, the transition occurs at high current densities.

A comparison of 'i_T' values in both NaCl and $NaClO_4$ shows that the value is higher in NaCl than in $NaClO_4$ under identical conditions. This is due to more aggressiveness of NaCl over $NaClO_4$ which gives a larger Vo making 'i_T' more positive than $NaClO_4$. Hence the transition also occurs at high current densities, providing a higher value to 'i_T'.

The absence of a transition in $MgCl_2$ and $Mg(ClO_4)_2$ may be due to the less corrosive nature of these electrolytes towards magnesium as well as common ion effect which retards the self dissolution markedly keeping Vo very low, so as to make 'i_T' always negative under all conditions. This may also be due to spalling or disintegration of tiny metal particles from the surface especially at higher current densities, which separately react with the medium to liberate hydrogen.

CONCLUSION

On the basis of the above observations the following conclusions have been made.

1. Both anions and cations play significant roles in the electrochemical dissolution of magnesium.
2. Magnesium and its alloys mostly exhibit a negative difference effect in different electrolytes and their anomalous behaviour may be attributed to this fact.
3. It is possible to propose a new parameter called 'Transition current density' (i_T) at which transition from positive difference effect to negative difference effect or vice versa takes place.
4. This parameter 'i_T' is found to depend on the nature of the electrolyte and the anode material.

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