# Electrochemical Studies of Magnesium - The Effect of Addition of Aluminium

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Electrochemical investigations were carried out on pure Mg and various Mg-Al binary alloys in 0.5 M NaCl with a view to understand the effect of aluminium addition to magnesium. The studies indicated a shift in the steady state open circuit potential towards positive values upto 3% aluminium addition. The potential of pure Mg was found to be more negative than Mg-Al alloys even during anodic polarisation upto a current density of 50 mA/cm². The impedance studies indicated a decrease in polarisation resistance ($R_p$), with aluminium addition. Anode efficiency was found to increase with aluminium addition; however, beyond 3% Al, it was found to decrease. Anode efficiency was also found to depend very much on current density. At very low current density (at about 5 mA/cm²), the difference in anode efficiency between pure Mg and Mg-Al alloys were found to be marginal.

Magnesium is extensively used for many applications - in the construction of aircrafts, rockets, missiles, motor vehicles, machinery & tools, for alloying with aluminium, reduction of oxides of metals, cathodic protection of steel structures and as a battery anode material [1]. For a battery anode material, the desirable characteristics are :

(i) large negative electrode potential,
(ii) high energy density,
(iii) high anode efficiency,
(iv) good polarisation characteristics,
(v) low open circuit corrosion,
(vi) uniformity of anode consumption etc.

Compared to zinc, magnesium is a very attractive anode material because of its higher negative electrode potential, higher energy density, more abundance etc. [2]. One factor which limits its wide use as an anode is its anomalous behaviour. Anodic behaviour of Mg differs from that of other anode materials like Zn, Cd, Pb in many respects:

(i) Though the standard reduction potential of Mg calculated from thermodynamic data is -2.375 V [3], it is never achieved in practice; the experimental value is about 1 volt more positive with respect to the theoretical value.

(ii) Mg exhibits an anomolous behaviour called *negative difference effect* [4]; during anodic polarisation of Mg, the cathodic reaction is stimulated in



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some way leading to the increased local corrosion/hydrogen evolution. Hence, the rate of anode consumption is very much greater than that predicted by Faraday's law; this leads to low anode efficiency.

(iii) Mg anode exibits delayed action [5] during initial period of discharge.

Numerous attempts have been made for the possible replacement of zinc and construct practical batteries with Mg anodes in aqueous, organic and fused salt electrolytes. However, only a few types of Mg batteries are available commercially [6].

For most of the applications, including battery applications, Mg is used in the form of an alloy. Earliest commercially used alloying elements were aluminium, zinc and manganese. These alloys were initially developed for structural applications. Aluminium and zinc were added to improve the mechanical and physical properties [7]. Mg alloys like AZ 31 (3% Al, 1% Zn) and AZ 61 (6% Al, 1% Zn) are in use at present for battery applications even though the electrode potential of pure Mg is about 100 mV higher than the above alloys [8]. The benefit of Zn addition for battery application is doubtful [9]. Al is reported to facilitate the formation of granular sludge. Many alloys of Mg containing Hg, Th, Pb have been tried in batteries which exhibit higher electrode potential, but their corrosion rate is reported to be much higher than that of pure Mg [8]. Many studies are reported on pure Mg and Mg-Al alloys [10-14], but a systematic investigation on the effect of Al addition on various aspects of electrochemical behaviour of Mg is not available in the literature.

## EXPERIMENTAL

*Alloy Preparation* : Various Mg-Al alloys containing 1% to 12% Al were prepared by melting Mg of 99.9% purity (supplied by National Metallurgical Laboratory, India) and high purity Al (E-Merck) in a graphite crucible using an electric pot furnace and casting into sheets. The alloys prepared were analysed to check the composition.

*Electrode Preparation* : The Mg-Al alloys and pure Mg were machined, connected to a copper wire and mounted in resin such that 1 $cm^2$ of sample is exposed. The samples were polished with different grades of emery and polishing grade alumina powder till a clean mirror finish surface was obtained.

*Electrochemical Cell* : Experiments were carried out in a three electrode glass cell. Freshly polished Mg was the working electrode, saturated Ag/AgCl electrode was the reference and platinum was the counter electrode. The counter electrode was separated from the working electrode by a fritted glass. The electrochemical studies were carried out in solution of AnalaR grade NaCl in double distilled water. The temperature of the cell was maintained at 25°C using a Haake thermostat. Experiments were conducted without stirring or deaeration.

Four types of electrochemical experiments were conducted: i) open circuit potential (OCP) studies as a function of time, ii) potentiodynamic anodic polarisation, iii) electrochemical impedance spectroscopy and iv) anode efficiency. Measurements were carried out using model 273 potentiostat/galvanostat of EG & G make and interfacing it with IBM computer. OCP - time studies were started immediately on immersion. All the other experiments were started 30 minutes after immersion of the sample in the electrolyte. Polarisation studies were carried out at a scan rate of 1 mV/ sec. For impedance studies, a Schlumberger frequency response analyser was used. Anode efficiency was determined by impressing various current densities, ranging from 5 to 200 mA/cm$^2$ for a period of two hours.

## RESULTS AND DISCUSSION

### Open Circuit Potential *vs* Time Studies

The variation of open circuit potential of pure Mg and Mg-Al alloys with reference to Ag/AgCl in 0.5 M NaCl as a function of time is shown in Fig. 1. It can be seen from the figure that OCP starts at a negative value, increases to less negative value with time and attains a steady value after about 10 minutes of immersion. The variation of potential with time may be due to the growth/ damage of the film on Mg. The shift of potential to less negative value may be due to damage of the film by aggressive chloride ions. A steady state potential is obtained when the formation of the film and destruction of the film lead to an equilibrium condition. The steady state potential of Mg and Mg-Al alloys is given in Table 1. The steady state potential is found to be highest in the case of pure Mg. On addition of Al, potential shifts to more positive values and this

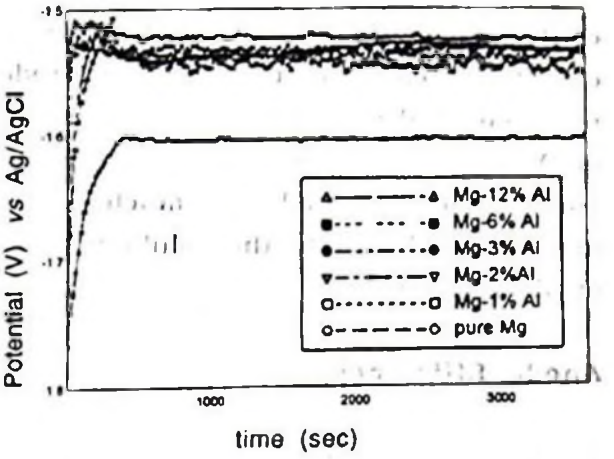



Fig. 1 : OCP *VS* time data for Mg and its alloys Medium 0.5 M NaCl

**Table 1**

**Steady State Open Circuit Potential of Pure Magnesium and its Alloys**

Medium 0.5 M NaCl at 25°

| Alloy Composition | E *vs* Ag/AgCl (sat) Volts |
|---|---|
| Pure Mg | -1.605 |
| Mg-1%Al | -1.551 |
| Mg-3%Al | -1.530 |
| Mg-6%Al | -1.530 |
| Mg-12%Al | -1.529 |

continues upto 3% Al. This shift is expected because of the lower electrode potential of Al compared to Mg. Addition of Al above 3% does not change the steady state potential very much. This may be attributed to the solubility limit of Al in Mg [15].

**Anode Efficiency**

Table 2 gives the results of anode efficiency for pure Mg and various Mg-Al binary alloys in 0.5 M NaCl for various current densities ranging from 5 mA/cm² to 200 mA/cm². Anode efficiency is found to be below 70% for all the samples. This is because of the wastage of Mg by local corrosion and also due to the *negative difference effect*. Anode efficiency values are found to decrease with increase in current density from 5 mA/cm² to 10 mA/cm² and then the value is found to increase upto a current density of 100 mA/cm². Further increase in current density results in decrease in efficiency for all samples except pure Mg and Mg-1% Al alloy.

At very low current density, the surface film on Mg may be able to repair itself resulting in good anode efficiency but as the current density becomes higher (say 10 mA/cm²) the surface film may be completely damaged. But further increase in anode efficiency above 10 mA/cm² may be due to lesser probability of hydrogen evolution at a more anodically polarised Mg surface. The decrease in anodic efficiency at very high current density may be attributed to the *chunk effect* reported by many authors [12]. The table also indicates the effect of Al addition. The anode efficiency increases on Al addition and reaches a maximum at 3% Al at all current densities and it decreases on further addition of Al. The decrease in anode efficiency in alloys with higher than 3% Al may be due to the presence of cathodic phases like $Mg_{17}Al_{12}$ in these alloys [12] which may contribute to

**Table 2**

**Anode Efficiency of Mg and Its Alloys**

Medium 0.5 M NaCl; Temp 25° Current density Varying from 5 - 200 mA/cm²

| Alloy Composition | Anode efficiency (%) at different current densities | | | | | |
|---|---|---|---|---|---|---|
| **Current Density (mA/cm²)** | **5** | **10** | **20** | **50** | **100** | **200** |
| Pure Mg | 63.6 | 56.7 | 57.5 | 59.0 | 60.3 | 60.8 |
| Mg-1%Al | 65.6 | 57.6 | 59.1 | 60.3 | 63.5 | 64.2 |
| Mg-3%Al | 66.4 | 62.4 | 66.0 | 67.3 | 68.8 | 66.0 |
| Mg-6%Al | 58.8 | 58.3 | 60.0 | 64.4 | 66.8 | 66.0 |
| Mg-12%Al | 57.5 | 57.0 | 58.2 | 61.4 | 63.2 | 60.8 |

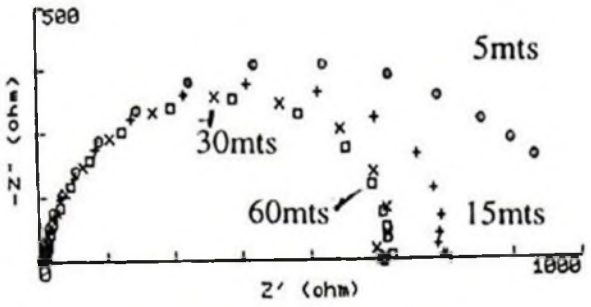



**Fig. 2 : Impedance Diagram at different times.** Specimen Mg; Medium 0.5 M NaCl

enhanced hydrogen evolution.

### Impedance Studies

The impedance spectra in Nyquist format of pure Mg in 0.5 M. NaCl at different periods of immersion is shown in Fig. 2. It indicates that the polarisation resistance ($R_p$) decreases during the initial periods of immersion and after about 30 minutes, it attains almost a stable value. The decrease in Rp with time may be due to the decrease in film thickness or breakdown of the passive film on Mg by the chloride ions. The value of $R_p$ becomes steady after 30 minutes; this may be due to the attainment of an equilibrium between film damage and repair. *The Nyquist plot for pure Mg and various Mg-Al alloys in 0.5 M NaCl after about 1/2 hr immersion time is shown in Fig. 3.* $R_p$ value is found to decrease with the addition of Al; this

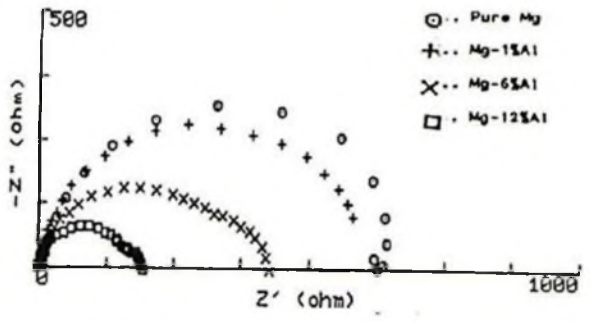



Fig.3 Impedance diagram for pure Mg and Mg-Al alloys in 0.5M Nacl after imersion time of 30 minutes

may be attributed to the formation of a porous film. An additional semicircle seen in the Nyquist plot for alloys with higher Al content may be due to solubility limit of Al in Mg or due to the presence of $Mg_{17}Al_{12}$ phases in these alloys.

### Polarisation Studies

The polarisation curves for pure Mg and Mg-Al alloys are shown in Fig. 4. It can be seen that cathodic polarisation is more pronounced than anodic polarisation indicating that the corrosion of Mg and Mg-Al alloys occurs under cathodic control. The potential of pure Mg is found to be higher than that for the alloys even at a current density of 50 mA/cm². Addition of 1% Al shifts the polarisation curve towards more positive values and further addition of Al shifts the curves towards negative potential. The values of corrosion current density ($i_{corr}$) determined by the extrapolation of Tafel slopes are given in the Table 3.

## CONCLUSION

1. The steady state open circuit potential of pure Mg is found to be higher than Mg-Al alloys in 0.5 M NaCl. A shift

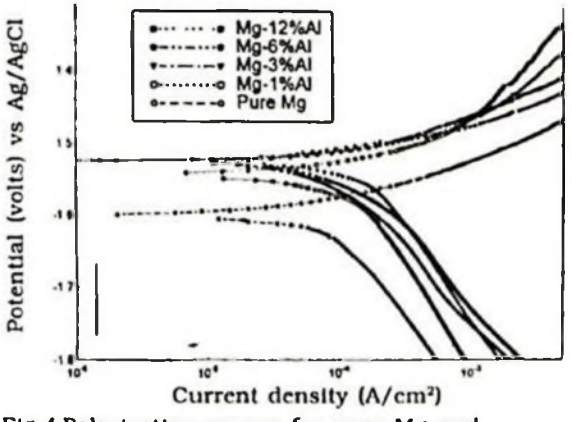



Fig.4 Polarisation curves for pure Mg and Mg-Al alloys in 0.5M Nacl

**Table 3**

**Corrosion Current Density of Mg and its Alloys**

Medium 0.5 M NaCl; Temp 25°C

| Alloy Composition | Corrosion Current ($\mu A/cm^2$) |
|---|---|
| Pure Mg | 81 |
| Mg-1%Al | 141 |
| Mg-3%Al | 162 |
| Mg-6%Al | 102 |
| Mg-12%Al | 135 |

in open circuit potential towards positive values is observed upto 3% Al. Further addition of Al is found to have no effect on potential. The potential of pure Mg is found to be higher than Mg-Al alloys during anodic polarisation upto a current density of 50 $mA/cm^2$.

2. The anode efficiency of Mg is found to increase by Al addition. The maximum anode efficiency is observed in alloys with 3% Al at all current densities.

3. The anode efficiency studies indicated a decrease in efficiency on increasing the current density from 5 to 10 $mA/cm^2$ and an increase in efficiency is observed on increasing the current density to 100 $mA/cm^2$. A decrease in anode efficiency is observed at 200 $mA/cm^2$ for most of the alloys.

4. The impedance studies indicated a decrease in polarisation resistance with the addition of Al. Nyquist plot for Mg alloys containing 3% Al and above indicated an additional semicircle.

5. The corrosion current densities for pure Mg is found to be lower than Mg-Al alloys in 0.5 M NaCl. Also the corrosion of Mg and Mg-Al alloys is found to occur under cathodic control.

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