

Comparative Study of the Corrosion Behavior of Magnesium AZ31B Alloy and Mg in 3.5 wt% NaCl Solution

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Abstract: AZ31B Mg alloy offers promising features for the weight reduction of the large size automotive parts in order to reduce the fuel consumption and reduce the carbon dioxide emission in the environment. It having a good corrosion resistance in the air, but in humid condition and in the presence of chlorine ion reduces its corrosion performance. Due to which the use of Mg alloys in the external automotive applications. A deep understanding of the corrosion behavior of the alloy is necessary to improve its corrosion performance. The present work is carried out to understand the corrosion behaviour of Mg alloy AZ31B. The 3.5 wt% NaCl solution is used as the medium. Weight analysis and potentiodynamic polarisation testing method are used to measure the corrosion rate. In weight loss analysis weight of the sample is measured after every 24 hours. The surface morphology of the corroded surface analyzed using scanning electron microscopy. A comparison has been also done between the pure Mg and Mg AZ31B alloy. Hardness of the base metal and alloy has been compared using Brinell hardness test.

Key Words: Magnesium AZ31B alloy, Optical microscopy, Potentiodynamic polarisation testing, scanning electron microscopy, Hardness, Weight loss

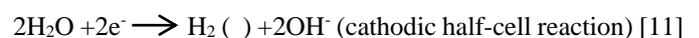
1. Introduction

Magnesium is the one of the lightest material. Mg having a density of 1.74 gm/cm³. So this feature makes magnesium as one of the best material which can be used in automobile industries [1]. In automobile industries the components are designed to reduce the weight of the structure, so that fuel consumption can be reduced. Reduction in fuel consumption makes the automobile more economic and it also reduces the emission of harmful gases in the environment. Magnesium can be used to reduce the weight of components, but there is one of the measure problem associated with the magnesium which is its corrosive nature. The corrosion resistance of the Mg is very poor, which is the biggest obstacle to use Mg in automobile industries. To overcome this problem scientist has become with Magnesium alloys. Alloying elements are added to improve the corrosive properties and mechanical properties of the Mg. The material scientist has developed an AZ series of magnesium alloy. In this series A stands for aluminium and stands for zinc. This series contain about 2 to 10 percent of aluminium and around 1 percent zinc and manganese (Mn) is also one of the important alloying element [1]. Examples are AZ31, AZ91, AZ80, AZ63, AZ92 etc. these Mg alloys having good corrosion properties as compared to their base metal. Further surface

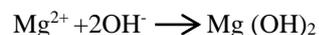
treatment of these alloy leads to more better corrosion resistance and make these alloy more preferable to use in automobile and other applications. There are many factor that influence the corrosion properties of the Mg alloys for example the environment in which alloy component has been working. In an environment which contains chloride solution the corrosion behaviour of the alloy mainly depends upon the pH of that medium and what amount chlorine ion concentration is there. In this case oxygen having not any considerable effect on the corrosion of the Mg alloys [2]. The corrosion of the Mg alloys in a chloride solution initiate like small pits. These pits arises at the sites of scratches or rough surface of the alloy [6]. The mechanism of the pitting of the Mg alloy is different from the mechanism of pit formation in the steel. In the steel autocatalytic pitting take place. But in Mg alloy there is formation of corrosion product Mg (OH)₂, this corrosion product form over the pits and retard further dissolution of Mg from the pits [7]. Following reactions occurred when Mg alloys are immersed in NaCl solution [8].



The hydroxyl (OH⁻) are produced by using the cathodic half-cell reaction.



The produced Mg²⁺ ions are consumed by precipitation of crystalline Mg (OH)₂ platelets.



The alloying element aluminium has a great influence on the corrosion behaviour of Mg alloys in chloride solution [4]. Mn formed iron containing compound that settle out and can be removed out before the solidification of the Mg alloy. And the compound Al-Mn-Fe which remain in the alloy having low cathodic activity as compared to pure iron [5]. Zn is added to the magnesium to further improve its mechanical properties due to solid solution strengthening [3]. The present study focuses on the comparative study of corrosion behaviour of Mg AZ31B alloy and pure Mg in 3.5 Wt% NaCl solution. Comparison is done by using weight loss method, Potentiodynamic polarisation test and scanning electron microscopy (SEM) of the corroded surface.

2. Experimental Methods

A. Material

In the experiment we have used AZ31B Mg alloy specimen which has been imported from china. The Chemical composition of the material is given in the Table-1.

Table-1
Chemical Composition

Alloying element	Al	Zn	Mn	Mg	Si	Cu	Ni	Fe
Weight %	3.1	0.87	0.3	95.69	0.03	0.002	0.005	0.005

B. Static Immersion Testing

Weight loss method is a quantitative method to determine the corrosion rate. A specimen is prepared by polishing the surface by using emery paper. The surface area and initial weight of the sample is calculated. A 3.5 Wt% NaCl solution is prepared by adding 35 gm of NaCl salt in 1 litre of distilled water. The pH of the solution was 6.9. Then this solution is poured in two beaker of 200 ml. In one beaker Mg AZ31B alloy sample was immersed and in the second beaker pure Mg. weight loss of each sample is measured after every 24 hours and weight loss was measured. The corrosion rate in mm/year calculated using the relation given in eq. (1).

$$CR = \frac{87.6 \times W}{DAT} \text{ mm / y} \quad (1)$$

Where, W= weight loss in mg. D= density of material in g/cm³, A= surface area in cm², T= time in hours.

C. Electrochemical Testing

The electrochemical testing was done by using an Auto Lab corrosion measurement system, CH-600D series, and U.S. motel installed with CH instrument beta software potentiostat interfaced to Pentium-3 compatible system. Flat cell was used for potention dynamic polarisation testing. Three electrodes are there, working electrode which is our sample material, the auxiliary electrode which was of platinum, reference electrode was of Ag. The three electrode are dipped inside 3.5 Wt% NaCl solution. Test is carried out at a scanning rate of 0.01 V/s, after the steady state potential was developed. The exposed area was 0.0496 cm². corrosion rate is measured using relation given in eq. (2).

$$CR(\text{mm / yr}) = \frac{3270 \times M \times i_{corr}}{\rho \times Z} \quad (2)$$

D. Surface Morphology

The surface morphology of the corroded surfaces of the sample AZ31B was characterized by scanning electro microscopic test. JEOL jbm 0390LV model was used for SEM. The SEM test of the sample was done after 24 hours, 48 hours, 96 hours and 192 hours.

E. Hardness Test

Brinell hardness test of the AZ31B Mg alloy and Mg has been done. A steel ball indenter of 10mm diameter was used and a load of 500 Kgf is applied on the specimen for sufficient time. Indentation was done on three different points. The diameter of the indentation is observed by using an optical eye piece.

3. Experimental Results

A. Static Immersion Test

Corrosion rate of Mg AZ31B alloy and pure Mg is observed with respect to exposer time using static immersion test. The result is shown in Table-2, and the comparison of corrosion rate (mm/year) of AZ31B and Mg is shown by using a graph (Fig. 1) between corrosion rate and exposer time. By analysing graph it has been seen that the corrosion rate of Mg is much higher than the corrosion rate of AZ31B alloy. The trend has been seen that corrosion rate of Mg and AZ31B alloy increases continuously for 120 hours and after that it start decreasing. In case of Mg corrosion rate again start increasing after 240 hours and for AZ31B alloy it starts increasing after 264 hours. The corrosion rate in case of az31B alloy was about 5 mm/year, while in a case of Mg it was around 7mm/year. So effect of alloying elements can be seen by comparing the corrosion rates of both the samples.

Table-2
Corrosion rate of Mg AZ31B alloy and pure Mg.

Time (hours)	Weight loss (mg) AZ31B Mg alloy	Corrosion rate (mm/year) AZ31B Mg alloy	Weight loss (mg) pure Mg	Corrosion rate (mm/year) Pure Mg
24	31.9	5.3533	41.85	7.0231
48	65.5	5.4959	85.23	7.1514
72	99.2	5.5491	129.45	7.2412
96	133.7	5.6092	175.11	7.3465
120	167	5.6050	219.42	7.3644
144	196.8	5.5043	254.8	7.1265
168	225.7	5.4108	296.7	7.1130
192	254.1	5.3302	338.62	7.1032
216	281.9	5.2563	378.51	7.0577
240	309.5	5.1939	415.65	6.9752
264	337.4	5.1473	462.13	7.0502
288	370.6	5.1827	506.74	7.0865
312	402.2	5.1919	550.43	7.1054
336	434.1	5.2035	593.08	7.1091

As we immersed the specimen in 3.5wt% NaCl solution spontaneous dissolution of the exposed surface was observed owing to the high reactivity of Mg with a standard potential of -2.37 VSHE, after few seconds the emission of gas bubble starts rising from the surface of the specimen, these gas bubble was of hydrogen and dissolution of the material start from the surface of specimen. Dark spots start appearing on the surface of the specimen and formation small pits starts. As the exposer time increases the size of pits start increased, as the pits

emerged with each other. The surface morphology of the sample will be discussed in the later section.

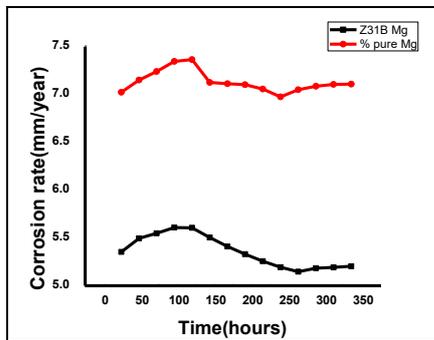
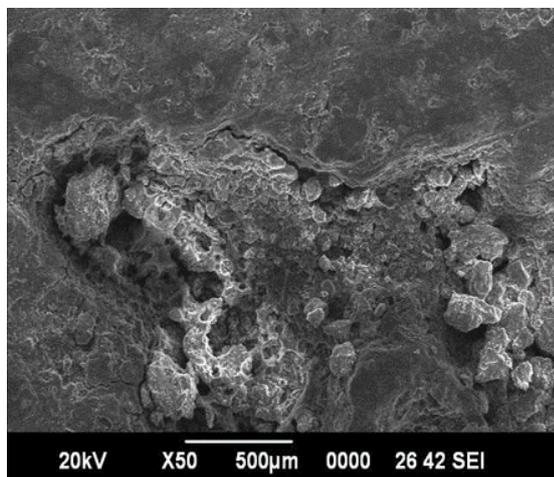


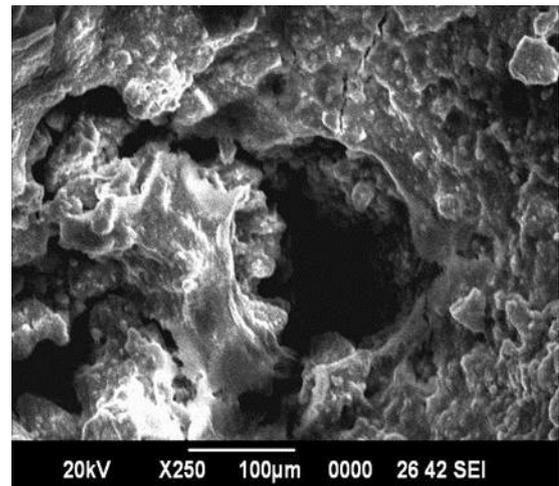
Fig. 1. Corrosion rate vs. Time graph for Mg AZ31B alloy and Mg.

B. Surface Morphology

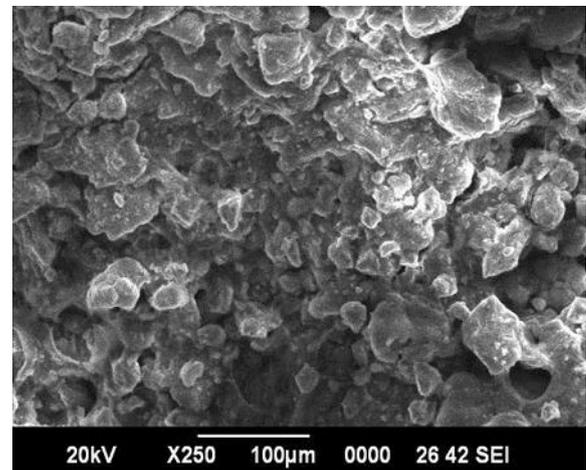
Scanning electron microscopy of the AZ31B Mg alloy has been done after 24 hours, 48 hours, 96 hours, 192 hours, shown in Fig. 2 respectively. It has been seen that initially small pits formed (shown in Fig. 2(a)) due to the dissolution of magnesium, pit diameter varied differently. These pits grow competitively with some of the pits merging others (shown in Fig. 2(b)). As the immersion time increases we have observed that the corrosion rate start decreasing. And when SEM of the same sample has been done it has been seen that a layer of corrosion product deposited over the pits. Shown in Fig. 2(c). The corrosion product was the $Mg(OH)_2$. Due to the formation of corrosion product a passive film is formed over the pits which decreases the corrosion rate and resist the corrosion to propagate deeper in the pits. As the exposure time of specimen in solution increases the concentration of chloride ion (Cl^-) increases and this breaks the passive film layer of $Mg(OH)_2$ and again the corrosion rate of the alloy starts increasing (Fig. 2(d)). When the specimen was carried out of the solution and its corrosion product is removed it has been seen that the surface of the specimen is full of irregularities and a comparison between the specimen before corrosion and after the corrosion can be seen in the Fig. 3.



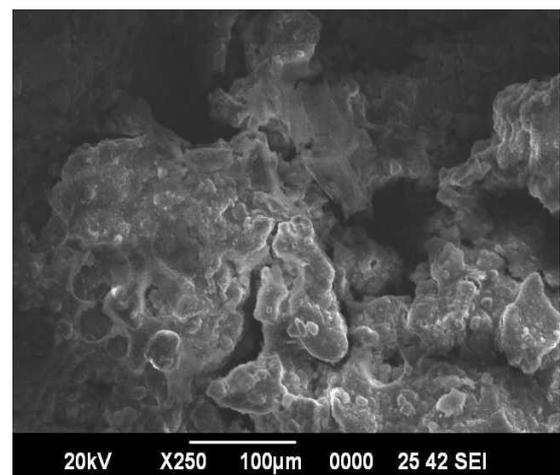
(a)



(b)



(c)



(d)

Fig. 2. (a) After 24 hours (b) 48 hours (c) 96 hours (d) 192 hours

C. Electrochemical Test

After doing electrochemical testing of Mg AZ31B alloy and Mg Tafel plot was obtained shown in Fig. 4. respectively. The Tafel plot is between potential and $\log(I_{corr})$, where I_{corr} is

corrosion current density and it has been taken in logarithmic scale because order of fluctuation of corrosion current density is very high, so by using logarithmic scale it will become linear. It has been found that corrosion current for Mg is higher than the corrosion current of the AZ31B Mg alloy. Table-3, shows the value of corrosion current density, anodic slope value, cathodic slope value, polarisation resistance and corrosion rate (mm/year). The corrosion rate of the Mg is more than the corrosion of the AZ31B Mg alloy. From this it has been clear that due to alloying Mg with other elements, there is increase in the corrosion resistance.



(a)



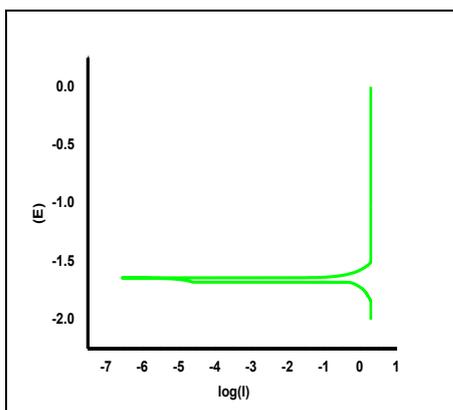
(b)

Fig. 3. Appearance of exposed samples before and after immersion of 336 Hrs.in 3.5% NaCl solution.

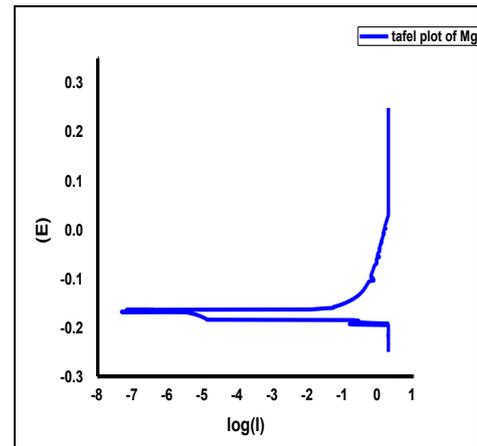
Table-3

Data obtained from electrochemical test

Sample	Linear polarisation Resistance	$I_{corr.}$ (10^{-4} A/cm ²)	b_a (V dec ⁻¹)	b_c (V dec ⁻¹)	Corrosion rate (mm/year)
AZ31b	0.38075	2.301453	3.468	3.250	5.1311
Mg	1.40971	3.8898	0	3.851	8.8228



(a)



(b)

Fig. 4. (a) Tafel plot for Mg AZ31B alloy (b) Tafel plot for Mg.

D. Hardness Test

Brinell hardness test was done for Mg and Mg AZ31B alloy. The data of the hardness test shown in Table-4. It has been seen that Brinell hardness number for the AZ31B is around 54 and for Mg is around 39. The hardness of the Mg AZ31B alloy increased due to alloying element Al and Zn. Addition of Al in the Mg matrix leads to solid solution strengthening of the alloy and precipitation hardening also occur there when at room temperature Al is precipitated around grain boundaries. It increase strength and hardness of the alloy. Zn also leads to solid solution strengthening. So alloy AZ31B having improved hardness than pure Mg.

Table-4
Hardness test calculation

S.No.	Sample	Diameter (mm)			Average diameter(mm)	Hardness (B.H.N)
		D ₁	D ₂	D ₃	D _{avg.}	
1	AZ31b	3.5	3.5	3.2	3.4	53.43
2	Mg	3.9	4.1	3.9	3.96	38.93

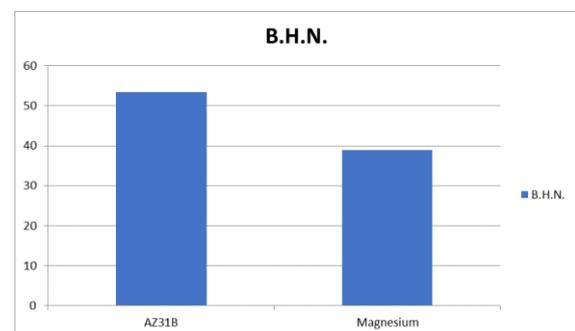


Fig. 5. Graph for hardness comparison of Mg and AZ31B alloy

4. Conclusion

Mg AZ31B alloy having a good corrosion resistance than the pure magnesium. Corrosion in the alloy is initiated and propagated through the most defective sites such as scratches and grinding marks. The intergranular corrosion is severe in the material. As in few small pits start forming and after some time

expand over the bulk surface. After few seconds, when the sample is immersed in the NaCl solution hydrogen gas evolved and dissolution of material starts, which leads to the formation of pits. Size of the pits increases as the pits propagate and merge with other pits. $MgOH_2$ pellets formed as corrosion product which reduces the deep corrosion of the alloy. By using scanning electron microscopy it can be clearly seen the formation of pits, formation of cracks due to corrosion and formation of the corrosion product layer on the surface. From the potentiodynamic polarization it is cleared that corrosion rate of AZ31B alloy is less than the base metal Mg. The corrosion resistance of AZ31B increases due to the addition of Mn, as manganese form Fe containing compound and which are removed before the solidification of the Mg. The hardness of the AZ31B alloy is B.H.N.53.43 which is more than the base metal having hardness B.H.N. 38.93. The hardness of AZ31B alloy is improved due to the presence of Al and Zn, due to the solid solution strengthening. The alloying element improves

the corrosive properties of the magnesium and also increase the mechanical properties of material.

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