Investigation of Electro-chemical performance of AZ31 Magnesium alloy – CaSiO$_3$ Metal Matrix Composites in different environments

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Abstract:
The electrochemical behaviour of AZ31 magnesium alloy as matrix made as metal matrix composites (MMC) by adding the reinforcement with various weight percentages of Calcium Silicate (CaSiO$_3$) powder was investigated under the influence of 3.5 percent Sodium Chloride (NaCl) and Simulated Body Fluid (SBF) environments using electrochemical workstation. After experimentation, the results exhibit that the pure magnesium alloy sample with 0% calcium silicate exhibits the corrosion rate higher value (40.562mmpy) compared to the other samples when 4% of calcium silicate is added as additive which exhibits the lower corrosion rate (25.510mmpy). Similarly, the polarisation resistance is also calculated for the samples and the average value of polarisation resistance for the pure magnesium sample is 153.813mA and the other for other samples it lies in between 140.5 mA to 185.72mA respectively. By experimentation it concludes that addition of reinforcement with various weight percentages plays a significant role in the reduction of corrosion rate of AZ31 magnesium alloy rather than using it in a pure form.

Key Words: AZ31 Magnesium Alloy, Simulated Body Fluid, Electrochemical Behaviour, MMC, NaCl

1. Introduction: Magnesium is the sixth abundant element available in earth from different sources like Magnesite, dolomite, carnallite and sea water, and similarly it is fourth abundant cation in human body. Magnesium has an exclusive and inherent corrosion behaviour and kinetics properties compared to other metals. The degradation of metals generally occurs by three well known reasons like wear, corrosion and fracture. When pure magnesium is exposed to environments like oxygen or water, its surface undergoes chemical reaction by forming an oxide surface film. With its inherent limitations including vulnerability to corrosion resistance, low creep resistance, many research works was focussed on coatings of magnesium to control corrosion rate and addition of reinforcements, fabrication process using conventional methods like casting, forming, process and other fabrication methods like stir casting process, advanced manufacturing methods like additive manufacturing, Wire Arc Additive Manufacturing (WAAM) where deposition of metal is done in layer by layer form. Adding of other elements as additives to pure magnesium alloys series like AZ31, AZ91,AZ91D,AZ92 etc also effects the corrosion rate [1]. Conventional corrosion test methods require vast time and specific environment conditions, where the corrosion test is analysed by both mass and volume loss methods. By technology development, new techniques are introduced to presage the corrosion rate of metal in defined environment which are familiar as electrochemical techniques that consumes less time and cost. These electro-chemical techniques offer an easy study of kinetics of corrosion which is an added advantage and mostly preferred in many labs at present. Corrosion of metals is mainly occurred due to an irreversible oxidation and reduction
reactions due to the influence of oxidizing agent. The electrochemical reaction which is a chemical process where the charge transport occurs at the interface of metallic conductor (electrode) and ionic conductor(electrolyte). By adding different additives as reinforcement in pure magnesium alloy to make them as metal matrix composites will also influence its improvement of specific strength, stiffness, damping behaviour, wear rate, creep and fatigue properties compared by conventional magnesium alloy. The microstructure and mechanical properties like tensile strength, yield strength, ductility, hardness is also improved by adding reinforcement particles [2]. The AZ31 magnesium alloy of commercial grade exhibits much corrosion rate which is main drawback to use the alloy for different applications. The corrosion rate of these alloys is predicted in different environments like various percentages of NaCl , KOH, H₂SO₄,KCl, Simulated Body Fluid etc. The pH value of these environments is to be considered while working with different solutions, because by chemical reactions layer is formed on the surface of metals can be observed which acts as protecting layer against corrosion and also material reaction with environment also initiates and enhances the corrosion rate of metal in particular environment[3].

Surface improvements like coatings with other materials can be done which are preferred in various applications where the coatings are done by different process like hot spray process, electroplating, sol-gel coatings, synthetic coatings, other natural and artificial polymer coatings which influences the corrosion resistance of magnesium alloy. Addition of elements like Al, Mn, Ca, Zn, and other rare earth elements shows better results related to corrosion resistance, wear resistance and mechanical properties etc., the silicon carbide particles added as reinforcement with magnesium alloy enhances the corrosion resistance with the improvement of volume fractions. Calcium phosphate [4,5].

As these magnesium alloys are preferred as bioimplants which are implanted for Orthopaedic, dental applications due to its low density, high strength to weight ratio and easy formability properties. But its biodegradability in some environments controls its usage in vast manner which has high grade demand in designing a controllable in vivo corrosion rate and also improvement in its mechanical properties at present which attracts many researchers in this field. The metal matrix composites from these magnesium alloys cover some percentage of its demand but not able to cover all fields like high temperature conditions [6].

The in vivo corrosion is predicted by experimental analysis for different materials using the apparatus like potentiostat where alloys , commercial available materials like Al, MS, Copper, SS and other coupons fabricated by different process also can be done by these polarisation techniques like Tafel curves, and impedance spectroscopy analysis, cyclic voltammetry analysis etc with the help of electrochemical workstation under the influence of various environments [7,8]. The prediction the electro-chemical behaviour and tribo-corrosion behaviour of coupons deposited with advanced technologies of additive manufacturing like LENS technology, or WAAM process, where samples are deposited by selected process parameters in a controlled atmosphere to restrict the oxidation of samples from surrounding environment which alters the results related to mechanical, microstructural, and electro-chemical behaviour depend upon process parameters and properties of selected material to fabricate the sample and also selected fabrication process . [9,10,12,14-17]

The biocorrosion behaviour is generally predicted by using Potentiostat / Galvanostat equipment in defined environments as simulated body fluid (SBF), Hank’s solution, etc where the immersion of coupon or exposure of coupon surface area in the media will exhibit the related corrosion rate. The ratio of surface volume to surface area of coupon will effect the corrosion rate of metal in different solutions [11]. The post processing technique like heat treatment also effect the properties of coupons made of magnesium alloys, austenitic steels, Co-Cr-W alloys, Co-Cr-Mo alloys, Aluminium alloys etc which are utilised for different applications in various fields. [18-23].

Beyond metals, polymers, ceramics, the fibre material also plays a role which acts as a substrate material in copper coated bio-implantable wide network antennas. These antenna acts as a detecting device and to detect the object by networks [24].

2. Materials and Equipment:
2.1 Specimen Preparation:
AZ31 Magnesium alloy samples are first fabricated by stir casting process by adding various weight percentages of calcium silicate CaSiO$_3$ which are mentioned in Table-2. In AZ31 magnesium alloy, the Aluminum content is at maximum of 3% and Zinc as 1% and the miscellaneous elements contributes at a maximum of 0.40% and the balance is Magnesium. Here in the present work, the samples are fabricated by addition of calcium silicate from 0%, 2%, 4%, 6% and 8% by altering the magnesium percentage in the alloy, without altering the other elements, Aluminum and Zinc. A general pure AZ31 magnesium alloy chemical composition is mentioned in Table-1. The compositions of calcium silicate added to prepare the specimens and the composition details are mentioned in Table-2. The specimen samples are shown in Fig-1, the samples are S-1 to S-5 from left to right.

| Sl. No | Sample Number | Magnesium Percentage | Calcium Silicate Percentage | Aluminium Percentage | Zinc Percentage | Total Percentage of Other Elements | Total Percentage |
|-------|---------------|----------------------|-----------------------------|----------------------|----------------|-----------------------------------|-----------------|
| 1.    | S-1           | 95.6                 | 0                           | 3                    | 1              | 0.4                               | 100             |
| 2.    | S-2           | 93.6                 | 2                           |                      |                |                                   |                 |
| 3.    | S-3           | 91.6                 | 4                           |                      |                |                                   |                 |
| 4.    | S-4           | 89.6                 | 6                           |                      |                |                                   |                 |
| 5.    | S-5           | 87.6                 | 8                           |                      |                |                                   |                 |

From the Table-2, the S-1 sample is a pure magnesium sample with 0% Calcium Silicate added as additive. Similarly, S-2 is added with 2% of Calcium Silicate, S-3 is added by 4%, S-4 has 6% and lastly S-5 is added with 8% Calcium Silicate which are fabricated using Stir casting process.

2.2 Electrolytes:
The media or electrolyte always plays a critical role when the metal coupon is surrounded by a media which initiates the corrosion degradation of metal by chemical process occurred between metal and media. Materials always will be in contact with anyone of the media either a dry atmosphere or a liquid solution.
In the present work, various electrolytes are selected to evaluate the corrosion rate of AZ31 Magnesium Alloy which are Simulated Body Fluid (SBF), Distilled Water, 3.5 percent NaCl Solution.

2.2.1 **Simulated Body Fluid (SBF):** The body fluid with an ion concentration which has nearer composition of human blood plasma with similar human body temperature conditions which is Simulated Body Fluid. The various ions present in SBF are listed in Table-3. The SBF is useful to predict the in-vivo bone bio-activity of material and examination of formation of apatite formation on material by the influence of SBF.

### Table-3 Ions present in Simulated Body Fluid

| Sl. No | Chemical Name     | Abbreviation | Percentage in mmol/L |
|-------|-------------------|--------------|----------------------|
| 1.    | Sodium Chloride   | NaCl         | 136.8                |
| 2.    | Sodium Bicarbonate| NaHCO₃       | 4.2                  |
| 3.    | Potassium Chloride| KCl          | 3.0                  |
| 4.    | Potassium Phosphate| K₂HPO₄   | 1.0                  |
| 5.    | Magnesium Chloride| MgCl₂       | 1.5                  |
| 6.    | Calcium Chloride  | CaCl₂        | 2.5                  |
| 7.    | Sodium Sulphate   | Na₂SO₄       | 0.5                  |
| 8.    | Sodium Nitride    | Na₃N         | 3.08                 |

2.2.2 **NaCl Solution:** Sodium chloride solution with 3.5% M is used to predict the corrosion rate of AZ31 magnesium alloy, where the NaCl solution is prepared by adding 35gms of pure Sodium Chloride form double time distilled water of 1 litre.

2.3 **Equipment:**

2.3.1 **Electrochemical Workstation:** The instant corrosion rate prediction is done using an electrochemical workstation (Make: Biologic SAS, France, Model No: SP-300) which is shown in Fig-2 attached with a flat corrosion cell. A flat corrosion cell shown in Fig-3 is filled with electrolyte of approximately 270ml. Specimen and Electrodes (Working Electrode, WE; Counter electrode, CE; and Reference Electrode, RE) are fixed in corrosion cell and the terminals are connected to electrochemical workstation. The specified terminal colours attached to electrodes are Blue colour to Reference Electrode (RE) which is made of platinum, the White colour terminal is connected to Counter Electrode (CE) which is a Ag/AgI₂ and the red colour terminal is connected to Working Electrode(WE) which is the specimen(here, AZ31 Magnesium Alloy). The terminal connections to electrodes are shown in Fig-4. EC-Lab software (supplied by Biologic SAS, France) is used to predict the corrosion of magnesium samples fabricated by stir casting process added with various compositions of Calcium Silicate (CaSiO₃). This software provides a facility to predict Corrosion Rate (CR), polarisation resistance (PR), Cyclic Voltammetry (CV), Potentio-static Impedance Spectroscopy (PEIS) and many more.
3. Methodology:
The NaCl Solution is prepared by adding 35 grams of Sodium Chloride powder to double filtered distilled water of 1 litre, where the weight of NaCl powder is measured with weighing balance (MAKE: OHUS, JAPAN) which has 0.0001g accuracy. A quantity of 270ml of NaCl solution, three electrodes (platinum, Ag/ AgI2, Specimen) are placed in specified places and made the flat corrosion cell ready, and the whole setup of cell is attached to terminals of electrochemical workstation (Potentiostat / Galvanostat) which are shown in Fig-4. In the present work, corrosion rate in mmpy and polarisation resistance in ohms are predicted for the magnesium samples under the influence of both 3.5% NaCl and Simulated Body Fluid environments.
The interface of Tafel plot is shown in Fig-5 and the interface of polarisation resistance is shown in Fig-6.

3.1 Tafel Plot Curve:
In the interface of Tafel plot curve, Rest for \( t_R \) indicates the fixation of time in hours, minutes and seconds, by default it shows 30min of time for \( t_R \), which means the recording of potential stays in rest for 30minutes of time. The Scan Ewe with \( dE/dt \) should be mv/sec , otherwise the scan rate of experiment will become slow and takes time to complete, if it is in mV/sec implies that per every second 10 milliVolts (mV) of potential is applied as the external source. This Tafel plot consists oxidation and reduction process which shows as positive and negative regions or anodic and cathodic regions. The beta (\( \beta \)) coefficients for both anodic and cathodic regions are denoted by \( \beta_a \) and \( \beta_c \) which is the slopes of Tafel curve. A typical Tafel plot curve is shown in Fig-7 and the flow chart of Tafel curve is shown in Fig-8.
3.2 Polarisation Resistance:
It is defined as the slope of the potential-current density for a free corrosion potential indicated by Eq. 1. It is also used to find the corrosion rate and beta coefficients of Tafel plot curve.

\[ R_p = \frac{\Delta E}{\Delta I}, \Delta E \to 0 \quad (1) \]

In this the polarisation resistance is determined by only three or four potential steps, where in general the four step method is used to exhibits maximum accuracy. The general \( R_p \) procedure is indicated in flow chart shown in Fig-9 and the four step process is shown in Fig-10 and three step is mentioned in Fig-11.

4. Results and Discussions:
4.1 Curves in 3.5% NaCl Solution
4.1.1 Tafel Curves
Fig. 12 Tafel Plot Curves of All Samples in 3.5% NaCl Solution

4.1.2 Polarisation Resistance:

Fig. 13 Polarisation Resistance Curve of all sample in NaCl Solution

4.2 Curves in Simulated Body Fluid Solution
4.2.1 Tafel Plot Curves:
4.2.2 Polarisation Resistance Curves

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**Table 4** Polarisation resistance Values in SBF fluid

| Sl. No | Specimen Number | $R_p$ anodic Value | $R_p$ Cathodic Value | $R_p$ Average Value | $I_{corr}$ Value |
|--------|------------------|--------------------|----------------------|---------------------|------------------|

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Fig-14 Tafel Plot Curves of All Samples in SBF solution

Fig-15 Polarisation Resistance Curves of all samples in SBF Fluid
1. S-1   159.1  148.53  153.81  -0.056.669
2. S-2   162.5  141.56  152.03  -0.053.125
3. S-3   160.8  150.09  155.44  -0.062.258
4. S-4   155.7  163.36  159.53  -0.083.255
5. S-5   148.9  175.47  162.18  -0.096.892

Table 5 - Tafel Curve Values in SBF Fluid

| Sl. No | Sample Number | Corrosion Potential $E_{corr}$ Value (mV) | Corrosion current Density $I_{corr}$ Value (µA) | Tafel Slopes | Corrosion Rate (in millimetres per year) (mmpy) | Corrosion Rate (in mils per year) (mpy) |
|--------|----------------|--------------------------------------------|-----------------------------------------------|--------------|-----------------------------------------------|------------------------------------------|
| 1.     | S-1            | -1641.326                                  | 283.753                                       | 265.9         | 245.9                                         | 40.562                                   | 1486.236                                 |
| 2.     | S-2            | -1702.501                                  | 482.886                                       | 317.0         | 328.9                                         | 31.569                                   | 1102.354                                 |
| 3.     | S-3            | -1669.949                                  | 360.874                                       | 324.2         | 310.8                                         | 25.510                                   | 895.365                                  |
| 4.     | S-4            | -1701.036                                  | 416.036                                       | 310.8         | 315.8                                         | 29.881                                   | 1059.368                                 |
| 5.     | S-5            | -1703.622                                  | 431.555                                       | 299.2         | 314.8                                         | 35.654                                   | 1384.495                                 |

Conclusions:
After completion of experiment, the following conclusions are drawn

❖ The sample(S-1) exhibits less value of beta anodic and beta cathodic where these are the slopes of anodic and cathodic values of Tafel curve.
❖ The sharp point in the curve is actually the point where the current reverses polarity as the reaction changes from cathodic to anodic.
❖ The log values in current are provided which are used to plot the Tafel plot curve because of wide of input current values.
❖ The Sample S-2 Exhibits more $I_{corr}$ value than other samples, where this $I_{corr}$ value is needed to calculate the corrosion rate of metal in mm/py or in mpy.
❖ The corrosion rate of sample S-1 which is a pure AZ31 magnesium alloy sample exhibits more corrosion rate than other samples.
❖ In general the cathodic process the metal receives more electrons from electrodes or from other source in electrolyte by the supply of external current which initiates the release of electrons and shifts the potential of metal or slow down anodic process and speeds up the cathodic or vice-versa.
❖ The average $R_p$ value is more for sample S-5 than other samples.

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