3.1 MATERIALS

3.1.1 Metals and Master Alloys

The base alloy selected for the present study was AZ91 magnesium alloy. It was prepared by melting together the following metals.

1. Pure Magnesium ingots
2. Pure Aluminum ingots
3. Pure Zinc flaks
4. Al-10% Mn master alloy

The required alloying elements like Si, Sb and Sr were added in the form of master alloys to have effective recovery of elements. The following master alloys were used to prepare the required alloy systems.

1. Al-20% Si master alloy (for Si additions)
2. Al-10% Sb master alloy (for Sb additions)
3. Al-10Sr master alloy (for Sr additions)

3.1.2 Melting and Refining Flux

The flux ‘Magrex-60’ supplied by FOSICO industries was used for covering and refining the molten metal during melting. MgCl, MgF, MgO, etc. are the major composition of the flux. Fine sulfur powder was used for dusting around the melt jet to remove the oxygen so as to avoid oxidization during pouring of molten metal into the mould.

3.1.3 Mould

Cast iron mould shown in Figure 3.1 was used throughout the experiments. Initially, there was no pouring basin attachment with the sprue, which led to a restriction in pouring speed as higher pouring speed led to the spilling of molten metal into the floor. Moreover, since the fluidity of magnesium is less compared to
3.2 MELTING AND POURING

3.2.1 Cleaning of Materials

In order to remove the oxides sticking on the wall and bottom of the crucible from the previous melting the crucible was filled with water and kept for one day for oxides to get dissolved. Then it was cleaned with MS wire brush. All the steel tools used for melting and pouring purpose like skimmer, starrier etc and metal ingots were cleaned by metal wire brush. Metal ingots were then, cleaned with acetone. All the tools and metal ingots were preheated before use. The properly cleaned mould was given a graphite coat and preheated to 250°C in a heating oven for 1 h just before the casting.

3.2.2 Melting

The melting arrangement for magnesium alloys is presented in Figure 3.2. Resistance box furnace was used for melting. The preheated flux was sprinkled in the bottom and side of the cleaned crucible and kept inside the furnace. After the crucible reached the red hot condition, the preheated ingots were charged in to the crucible. Initially part of the total magnesium ingots were charged. After melting of charged ingots completed, the remaining ingots were then immersed into the molten metal. This kind of charging practice of metal ingots avoids the excessive oxidation during melting. Crucible was covered with furnace lid to minimize the air contact with the molten metal. Flux was sprinkled over the metal throughout the melting. Before addition of alloying elements, the top layer of oxides was completely removed and fresh layer of flux applied. The required amounts of master alloys were weighed and wrapped in aluminum foil and were slowly immersed into the melt. After additions, the melt was gently stirred for dissolution of the added elements. Again the top oxide layer was removed and fresh layer of flux was applied. The melt was held for 10 min to ensure the complete dissolution of elements in to the melt.
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3.2.3 Refining

After the complete melting of the metals in the crucible, the refining of melt was carried out at a temperature of \( \approx 720^\circ C \). Initially, the top layer (oxide layer) of the melt was removed and the melt was rigorously stirred for 2-3 min. Flux was applied during stirring. This stirring helps to mix the added flux with the melt uniformly. After thorough mixing, the top surface of molten melt was removed and a fresh layer of flux was applied. Then the melt was held for 10-15 min without distributing, which enabled the added flux to react with oxides inclusions present in the melt and become heavier and settled down in the bottom of the crucible.

3.2.4 Pouring and Casting

After the refining and settling process was over, the molten metal was poured into the preheated moulds. During pouring much care was taken to avoid the breakage of the top flux protective layer. The pouring was carried out gently without any jerk in the melt, since excessive jerk disturbs the settled oxide inclusions in the bottom. The flux layer near the lip of the crucible was pulled back gently by using a skimmer for smooth flow of molten metal. Sulfur powder dusting was carried out to remove the oxygen around the melt jet. Three fourth of the melt in the crucible was poured into the preheated mould. The remaining metal was poured separately as scrap. Figure 3.3 shows a photograph of one such casting. Figure 3.4 shows a schematic diagram of casting and indicating the locations from where sample for different testing were taken.
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Figure 3.3: Photograph of the magnesium alloy castings

Figure 3.4: Schematic diagram showing the magnesium alloy casting and sample locations
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3.3 ALLOYS PREPARED AND CHEMICAL ANALYSES

Using above described casting procedure, different alloys were presented prepared for the present study and given in Figure 3.5. To find out the actual elemental compositions in the alloys prepared, chemical analysis were carried out. Chemical analysis of most of the elements in the prepared alloys was carried out using conventional wet analysis technique based on the procedures given in the ASTM standards (Table 3.1). However, some of the alloy compositions were found out using inductively coupled plasma spectrometer (ICP Plasmascan, model LABTAM 8410). The major elements like Al, Zn, Mn, etc. in all the prepared castings were carried out; however, only few alloys, which were selected for the corrosion studies were subjected for the impurities (Fe, Cu, Ni) analyzes. The analyzed alloy compositions are presented in the Table 3.2.

![Flow chart showing various alloys prepared for the present study](image)

Figure 3.5: Flow chart showing various alloys prepared for the present study

<p>| Table 3.1: Testing procedures used for wet analysis to find out various elements |
|---------------------------------|--------------------------------|
| <strong>Elements</strong>                  | <strong>Test method</strong>               |
| Aluminum                      | ASTM E 35, Sec 13-17          |
| Silicon                       | ASTM E 35, Sec 88-92          |
| Antimony                      | Vogel's quantitative inorganic analysis Part F, Chapter XVIII, 13, Page no 73 |
| Strontium                     | Vogel's textbook of quantitative chemical analysis, 5th edition, chapter 11.42, page no. 468 |</p>
<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
<th>Si</th>
<th>Sb</th>
<th>Sr</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ91</td>
<td>9.3</td>
<td>0.8</td>
<td>0.18</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.025</td>
<td>0.0035</td>
<td>0.0048</td>
</tr>
<tr>
<td>AZ91 + 0.2% Si</td>
<td>9.5</td>
<td>0.65</td>
<td>0.2</td>
<td>0.22</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AZ91 + 0.5% Si</td>
<td>8.7</td>
<td>0.72</td>
<td>0.22</td>
<td>0.47</td>
<td>--</td>
<td>--</td>
<td>0.010</td>
<td>0.00204</td>
<td>0.0045</td>
</tr>
<tr>
<td>AZ91 + 0.2% Sb</td>
<td>8.35</td>
<td>0.6</td>
<td>0.15</td>
<td>--</td>
<td>0.16</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AZ91 + 0.5% Sb</td>
<td>8.9</td>
<td>1</td>
<td>0.1</td>
<td>--</td>
<td>0.58</td>
<td>--</td>
<td>0.015</td>
<td>0.0046</td>
<td>0.0039</td>
</tr>
<tr>
<td>AZ91 + 0.7% Sb</td>
<td>8.7</td>
<td>0.5</td>
<td>0.28</td>
<td>--</td>
<td>0.85</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AZ91 + 0.2% Sr</td>
<td>8.74</td>
<td>0.62</td>
<td>0.21</td>
<td>--</td>
<td>--</td>
<td>0.16</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AZ91 + 0.5% Sr</td>
<td>8.92</td>
<td>0.71</td>
<td>0.2</td>
<td>--</td>
<td>--</td>
<td>0.42</td>
<td>0.018</td>
<td>0.0051</td>
<td>0.0032</td>
</tr>
<tr>
<td>AZ91 + 0.7% Sr</td>
<td>9.1</td>
<td>0.6</td>
<td>0.17</td>
<td>--</td>
<td>--</td>
<td>0.73</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AZ91 + 0.2% + 0.2% Sb</td>
<td>8.3</td>
<td>0.84</td>
<td>0.31</td>
<td>0.26</td>
<td>0.16</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AZ91 + 0.5% + 0.2% Sb</td>
<td>9.3</td>
<td>0.63</td>
<td>0.02</td>
<td>0.52</td>
<td>0.19</td>
<td>--</td>
<td>0.038</td>
<td>0.005</td>
<td>0.0049</td>
</tr>
<tr>
<td>AZ91 + 0.2% Si + 0.1% Sr</td>
<td>9.15</td>
<td>0.68</td>
<td>0.18</td>
<td>0.22</td>
<td>--</td>
<td>0.14</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AZ91 + 0.5% + 0.1% Sr</td>
<td>8.78</td>
<td>0.92</td>
<td>0.28</td>
<td>0.42</td>
<td>--</td>
<td>0.126</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
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3.4 HEAT TREATMENT

3.4.1 Sample Preparation

To avoid the variation in microstructure and properties along the thickness of the casting and maintain the uniformity in microstructure, all the samples were taken from the wall side of the castings. Cylindrical pieces of 15mm Φ X 10mm height were machined out from the castings as shown in Figure 3.4. The surface of the sample, which was nearer to the wall surface of the castings was selected for further characterization (microstructure and hardness measurement).

3.4.2 Solution Treatment

Solution heat treatment was carried out in a muffle furnace. Machined samples to be heat treated were placed in a mild steel tray in such way that no piece touches others. A sand bed prepared using carbon char coal and dry sand with a volume ratio of 20:80 was placed in the furnace. This helped to evacuate oxygen present in the furnace during heat treatment. To have a continuous protection, the sand bed was replaced in the time interval of every 5 h. This procedure was found satisfactory to avoid the oxidation of magnesium samples during the heat treatment. The samples were solution heat treated for 48 h followed by water quenching at room temperature without much delay and kept in desiccators for subsequent ageing treatment.

3.4.3 Ageing Treatment

The solution treated samples were aged at 200°C for 100 h in a heat treatment oven to study the ageing behavior. Since the ageing temperature was less than 350°C (the temperature, at which magnesium starts to oxidize), ageing was carried out in an open atmosphere. Samples were taken out from the furnace at regular interval and air cooled to room temperature for hardness measurements.

3.4.4 Hardness

INTENDEC hardness machine was used for brinell hardness measurement of as cast and heat treated samples. The samples faces were leveled on both sides. One side of the specimen, on which hardness was measured was polished up to 600 fine
emery paper to remove the oxide and other scales in order to see the edges of the indentation mark clearly. 2.5 mm ball was used to make indentation. Load was fixed at 66.5 Kg with a dwell time of 30 sec. On an average 5 indentations were made and average value is reported.

3.5 MICROSTRUCTURAL OBSERVATION
3.5.1 Sample Preparation

3.5.1.1 Polishing

Initially the samples (15mm Φ X 10mm height cylindrical sample) were polished using different grade of emery papers of progressively fine grades of 80, 220, 400 and 600 grits. During paper polishing water was used as a cleaning agent. After completing the paper polishing, the samples were polished in a rotating disc of proprietary cloth (Selvyte cloth) charged with a diamond paste of 6, 3 and 0.25 μm particle size in sequence. Filtered kerosene was used as lubricant during cloth polishing. Samples were gently pressed against the rotation wheel. Since magnesium is a soft material much care was taken during polishing to avoid sketches and excessive surface contamination. Cleaning the samples with water (even with distilled water) found inefficient to remove surface contaminants of the polished samples. So, after the final polishing over, the surface of the samples was cleaned using ultrasonic cleaner in ethanol.

3.5.1.2 Chemical etching

Different kind of etchants were tried to get a clear microstructure. After various trails, picric acid based etchant was found to be an efficient one, which clearly revealed the microconstituents of magnesium alloys. The chemical composition of the etchant used in the present study is given below.

Picric acid – 6 grams
Acetic acid – 5 ml
Ethanol – 100ml
Distilled water – 10 ml
The etching time was found to be optimum with 2-3 seconds. Much care was taken during etching to avoid over etching otherwise, which would spoil the surface of the samples.

3.5.2 Optical Microscope

Microstructural specimens (after polishing and etching) were observed under a Leitz-Metalloplan optical microscope. Photographs were taken at different location with various magnifications.

3.5.3 Image Analysis

Quantitative analysis of the microstructure was carried out using a Leica 2001 Image Analyzer in conjunction with the optical microscope. Size of various intermetallics and grain size of various castings were measured by linear intercept method. The fields of observations were selected randomly at different locations of the sample. The size of Chinese script Mg2Si intermetallic phase was measured manually since its shape is complicated. In each case, at least ten fields were analyzed from a single specimen and the average value is reported.

3.5.4 Scanning Electron Microscope (SEM)

To identify the type of precipitates in various castings and to study the micro-mechanisms of fracture during tensile and creep, samples were cleaned in ethanol using an ultrasonic vibrator and the surface were examined in a JEOL, JSM 35C Scanning Electron Microscope operating at an accelerating voltage of 15-30 KeV. Same optical microstructural samples were used for SEM studies. The composition of various phases and intermetallics were analyzed using Energy Dispersive Spectroscope (EDS) attached with SEM. An average of ten EDS measurement was used to approximate the composition of phases. For fracture studies, 5 mm height samples cut near from the fractured surface were used. Most SEM images were taken using secondary electron (SE) although some images have been acquired form back scattered electrons (BSE).
3.6 X-RAY DIFFRACTION (XRD)

The various microstructural constitutes of castings were identified using XRD. 15 mm Φ and 3mm thick samples were cut from the castings and the surface scales were removed by rough polishing. XRD spectrums were obtained using Phillips PW 1710 Powder Diffractometer with Cu-Kα radiation.

3.7 MECHANICAL PROPERTIES

3.7.1 Tensile Testing

Room as well as high temperature (150°C) tensile testing was carried out using computer controlled INSTRON 8801 Universal Testing Machine. Ultimate tensile strength, yield strength and elongation were obtained directly from the computer interfaced with the machine. For room temperature test extensometer was used to get the % elongation during testing whereas for high temperature test, the ductility was measured manually after the test. Samples for tensile testing were prepared according to ASTM E8 Standard. Figure 3.6 shows the schematic diagram of a tensile specimen. For high temperature testing, the samples were heated in an oven attached with the INSTRON machine and kept for 15 min after the required temperature (150°C) reached to ensure the homogenization of temperature throughout the sample.

![Figure 3.6: Schematic diagram of a tensile specimen (ASTM E8 Standard)](image)

3.7.2 Creep Testing

Creep testing was carryout using 3 ton ‘MAYES’ creep testing machine with a lever ratio of 15:1 (Figure 3.7). Standard creep test samples (Figure 3.8) were machined out from the castings according to ASTM 138 standards. The displacement during creep was measured using two LVDTs mounted on the extensometer attached
on the gauge length (GL) of the test specimen. The required load was calculated according to the specimen diameter and lever ratio. The sample was heated using a three zone coil furnace. Specimen temperature was controlled with in $\pm 2^\circ$ C of the set point temperature using a Eurotherm make three zone temperature controller. Two thermocouples were attached, one near the top ridge and another near the bottom ridge of the test specimen, to ensure uniform temperature throughout the GL. (ref. Figure 3.8). The testing temperature was obtained around 1h and 30 min was given for the stabilization of temperature. Both the displacement and temperature was monitored and recorded at regular intervals (30 min) automatically through a Yokogawa make data logger.

![Photograph showing the creep testing machine](image)

Figure 3.7: Photograph showing the creep testing machine

Cold run was carried out to check the sample alignment with the loading axis, during which the loading and unloading was done in an increment of 5 kg up to 80 % of the elastic limit. The incremental displacement during loading and unloading steps were plotted to check for equal displacement during loading and unloading. In case of any difference occurred (more than 10%), the alignment of the test sample was adjusted.
Figure 3.8: Schematic diagram showing standard creep testing specimen

Figure 3.9: Typical hot run graph showing elastic and plastic strain region

Once the temperature of the specimen was stabilized the hot run was carried out. During hot run, loads were applied in a small possible increment to get a required final load on pan. The total loading was carried out within 5 min. The LVDT readings were noted down immediately after every stage of loading and the displacement data were plotted against the corresponding loads. Figure 3.9 shows a typical hot run graph from which elastic and plastic strain was calculated. The elastic strain thus obtained was deducted from the total incremental strain recorded during
creep testing to obtain exact creep strain. Immediately after the completion of loading, strain readings were taken for 30 min in the time interval of 1 min to have more data points for getting smooth primary stage creep curve, where the creep rate changes very fast. From the displacement data obtained from data logger, strain was calculated and plotted against time.

3.8 CORROSION TESTING

3.8.1 Sample Preparation

15mm Φ X 10mm height specimens were cut from the castings and then polished up to 600 grit SiC emery paper on all sides prior to mounting in an epoxy resin using a brass rod for electrical connection for electrochemical corrosion test. This procedure avoided the formation of bubbles and crevices at the specimen/epoxy interface, which could have affected the electrochemical measurements.

3.8.2 Polarization Test

The electrochemical tests were carried out using potentiodynamic anodic polarization method in ASTM D 1384 solution. The ASTM D 1384 solution contain 148 mg l⁻¹ of Na₂SO₄, 138 mg l⁻¹ of NaHCO₃ and 165 mg l⁻¹ NaCl (pH=8.3). All the corrosion test experiments were carried out at room temperature using 1 liter, five neck ASTM electrochemical cell consisting of three electrodes; working electrode, reference electrode (Ag/AgCl-Sat) and counter electrodes (Pt). The typical polarization cell arrangement for conducting all the electrochemical experiments is shown in Figure 3.10. Solartron 1287 Electrochemical Interface was in the polarization experiments. During electrochemical corrosion test, the electrode potential was anodically scanned at a scan rate of 10 mV/min from a potential of –1400 mV. All the electrode potential was measured against Ag/AgCl (in saturated KCl) reference electrode.

3.8.3 Electrochemical Impedance Studies

Electrochemical impedance spectroscopy (EIS) measurements were carried out using Solartron 1255 Frequency Response Analyzer (FRA) and Solartron 1287 Electrochemical Interface. The experiments were carried out in the frequency range
from 0.01 Hz to 100 kHz by superimposing an AC voltage of 10 mV amplitude at different potential. Data were presented as Nyquist and Bode plots. The Zplot/Zview software version 2.6 (Scribner Associates; Charlottesville, USA) was used for data acquisition and fitting of impedance spectra. The EIS results were interpreted using an “equivalent circuit” based on the electro physical model to ascribe a sub-electrochemical interface. The circuit description consist of an arrangement of \([R_s \ (C_{DL} \ || \ R_P)]\) elements, where \(R_s\) is the solution resistance, \(C_{DL}\) is the double layer capacitance in parallel connection with \(R_P\), which is the polarization resistance at the interface (Figure 3.11). The selection of this circuit was a compromise between a reasonable fitting of the experimental values and a minimum of components in the equivalent circuit. The characteristic parameters of these elements values are then obtained directly by fitting the experimental impedance curves, it was apparent that this approach provide reasonably accurate values of the circuit parameters between the impedance data obtained experimentally and those calculated from the circuit parameters. The reproducibility of the data obtained with repeated measurements on a series of electrodes was within ± 5% for each measured impedance point.

![Figure 3.10: Typical polarization cell for conducting all the electrochemical experiments](image-url)


3.8.4 Immersion Test

For carrying out the constant immersion testing, samples of size 15mm Φ X 10mm height were polished with 80, 220, 400 and 600 grit emery papers and then polished with 0.25μm diamond paste and cleaned with acetone. The cleaned samples were weighed and exposed to a solution of 3.5% NaCl in a beaker for 100 h. After the immersion test, the samples were cleaned in a solution of 200g/l CrO₃ + 19 g/l AgNO₃ at room temperature for 10 min to remove the corrosion products. Finally, it was again washed with distilled water and weighted. The weight loss was calculated from the different between the initial and final weights. From weight loss, corrosion rate was calculated using the formula given below:

\[
\text{mpy (miles per year)} = \frac{534W}{DAT}
\]

where,

- \(W\) – Weight loss during immersion in grams
- \(D\) – Density of the sample in g/cc
- \(A\) – Surface area of the sample exposed to the corrosive media in square inch
- \(T\) – Immersion time in hours.