Chapter 3

Experimental Procedure

The details of the fabrication process of the Mg-5.0Al-2.0Ca-0.3Mn (wt.%) (AXM520) alloy and nanocomposites are discussed in this chapter. In addition, the details of the experimental setups and relevant equations used to produce the experimental data and their methods of analysis are discussed.

3.1 Fabrication of alloy and nanocomposites

The AXM520 (Mg-5.0Al-2.0Ca-0.3Mn (wt.%)) alloy was manufactured from pure Mg (~99.9%) as well as Mg-30.0Ca (wt.%) and Al-10.0Mn (wt.%) master alloys (Oswal Minerals Limited, India). The AXM520 alloy-based nanocomposites (NCs) were produced by adding 0.5, 1.0, 2.0, and 3.0 (wt.%) SiC_{np} (average diameter 60 nm, Ultra Nanotech, India). The targeted and achieved compositions of the AXM520 alloy and NCs with their designations are summarised in Table 3.1.

Table 3.1 The sample designations and compositions of the alloy and nanocomposites.

Sample designation	Measured composition (wt.%)							Nanoparticles content (wt.%)
	Al	Ca	Mn	Fe	Ni	Cu	Mg	
AXM520	4.95	2.01	0.28	0.004	0.001	0.002	Balance	0
NC0.5SiC	5.01	1.99	0.27	0.006	0.001	0.001	Balance	0.5% SiC
NC1.0SiC	4.97	2.02	0.30	0.003	0.001	0.001	Balance	1.0% SiC
NC2.0SiC	5.03	1.97	0.28	0.005	0.002	0.003	Balance	2.0% SiC
NC3.0SiC	5.02	2.01	0.29	0.006	0.001	0.002	Balance	3.0% SiC

The alloy and NCs were prepared utilizing a squeeze-cast setup with a bottom pouring facility (Swamequip, India). In the beginning, the furnace of the casting setup was allowed to attain a temperature of 1023 K by resistance heating. After attaining the temperature, the Mg ingots were placed inside the graphite crucible located inside the furnace. Once the Mg ingots were melted, the calculated amounts of the preheated (473 K) Mg-Ca, Al-Mn master alloys, and

SiC_{np} were added to the Mg-melt. A mixture of the Ar and SF_6 gases in the ratio 99.5:0.5 (vol.%) was passed to the melt to prevent oxidation. The melt was stirred at 300 rpm for 5 min once the melt temperature reached 1023 K. The stirring process ensured the mixing of the added alloying elements and SiC_{np} with molten Mg. The liquid mixture was then allowed to settle at 1023 K for 1 min. The melt from the crucible was passed into a mild steel mould heated to 523 K. A vertically installed hydraulic ram squeezed the melt into the mould at 200 MPa. The melt solidified in about 60 s under 200 MPa. The final shape of the cast ingot was cylindrical, with a radius of 25 mm and 200 mm long. The compositions of all the materials were determined by an ICP-MS (Agilent Technologies, 7900).

3.2 Microstructural characterization of alloy and nanocomposites

3.2.1 X-ray Diffraction (XRD)

The phases present in the samples were investigated using XRD (PANalytical) employing CuK_α radiation (scan speed: 2 °/min). The X-ray diffraction data was then recorded in the 2θ range of 20 to 90 °.

3.2.2 Optical Microscopy (OM) and Scanning Electron Microscopy (SEM)

The microstructures of the as-cast alloy and NCs were studied using Optical Microscopy (OM) (LEICA DM2500M) and Field Emission Scanning Electron Microscopy (Carl Zeiss, Supra 40) furnished with an Energy-Dispersive X-ray Spectroscopy (EDS)(Oxford Instruments). The alloy and NCs were subjected to standard metallographic techniques. The samples were ground using 400, 800, 1000, 2000, and 2500 grit emery papers, followed by polishing with 1.5 and 0.5 μm diamond paste. The specimens were etched using a solution of 5 g picric acid, 100 ml ethanol, 20 ml H_2O, and 10 ml acetic acid. The Image-J software was employed on the SEM micrographs to estimate the fraction of the phases present.

3.2.3 Fractal analysis

The connectivity of the phase was assessed with the help of fractal analysis using SEM images. The SEM micrographs were converted into binary images, and then they were examined by an 'Image analysis algorithm'. The algorithm identified the largest connected mass (D_{max}) present in the image. Thereafter, the algorithm reconstructed the largest connected mass separately. The reconstructed image was then used to calculate the fractal dimension (D_f) using the pixel

counting method [35]. The total number of boxes required to cover the D_{max} was expressed as a function of edge length x (N(x)) as per Eq. 3.1.

$$N(x) = x^{-D_f} \quad \text{Equation 3.1}$$

3.2.4 Transmission Electron Microscopy (TEM) analysis

The Transmission Electron Microscopy (TEM) (FEI, Tecnai G2 20 TWIN) analysis was performed by taking a 3 mm disc from the as-cast ingot. Initially, the foils were mechanically thinned to 1 mm and then ion-milled (Gatan, Duo Mill 600) to make them electron-transparent.

3.3 Mechanical characterization of alloy and nanocomposites

3.3.1 Tensile and compressive tests

The tension and compression tests were conducted on the AXM520 alloy and NCs at ambient temperature under uniaxial loading. The specimens for both tests were prepared according to the ASTM-E8 and ASTM-E9 standards, respectively. The cast ingot was cut into small pieces and machined to the standard dimensions. A 50 kN Universal Testing Machine (UTM) (BISS, Electra 50) was employed to perform the tensile and compression tests. All the tests were performed using a constant strain rate, i.e., 8.334×10^{-5} s^{-1}. Three tests were performed at each parameter to evaluate the tensile and compressive properties.

3.3.2 Impression creep tests

The impression creep tests were carried out with a lever-based impression creep tester (SPRANK/3123/03/21, SPRANKTRONICS, India). The lever has an arm ratio of 1:10. One end of the lever was attached to a specimen holder, and the other end of the lever was connected to a loading cage. The indenter with the specimen holder was placed inside an electric resistance furnace. After that, the furnace was heated to a targeted temperature, and the entire arrangement inside the furnace was held at the temperature for 1 h to ensure thermal equilibrium. Then, the indentation process was started. A flat-end cylindrical tungsten carbide indenter of 1.0 mm diameter was employed for indentation. The specimens of $10\times10\times10$ mm^3 were used in the creep tests. The surfaces of the samples were cleaned using 1000 and 2000-grade emery papers before conducting the creep tests. The indentation depth was acquired using a sensor as a function of time. The selected ranges of temperature and stress for the impression creep tests were 390 to 490 MPa and 448 to 523 K, respectively.

3.3.3 Post-creep microstructural study

The microstructural changes and materials flow below the indentation of crept samples of the AXM520 alloy, and NCs were further examined. The indentations were bisected to obtain the flow patterns, as shown in Figure 3.1, and observed under SEM after standard polishing. The samples for Electron Backscatter Diffraction (EBSD) observation were electropolished (Lectropol-5, Struers) using a solution of 30% nitric acid and 70% methanol for 15 s with a voltage of 12 V. The EBSD data were acquired using an FE-SEM with a scanning step size of 1.5 µm.

3.4 Corrosion tests of alloy and nanocomposites

3.4.1 Hydrogen evolution and immersion tests

For hydrogen evolution tests, the samples of the AXM520 alloy and NCs were polished with 400, 800, 1000, 1500, and 2000 grades of emery papers, followed by cloth polishing using 1.0 and 0.5 µm diamond pastes. The samples were then exposed to a 3.5 (wt.%) aqueous NaCl solution at a pH of 7.0. An area of 15×15 mm^2 of the respective specimen was exposed to the solution for 60 h at 25 ± 2 ºC. The evolved hydrogen was collected using the water displacement technique in a measuring cylinder. Three samples of each variant were tested under identical conditions to check the reproducibility of the tests. The corrosion rates (mm/yr) of the alloy and NCs were calculated from the hydrogen evolution rate (ΔV_H) (ml/cm^2) for the exposed duration (t) (h) using the density (ρ) (1.74 g/cm^3) as per the following equation [44].

$$\text{Corrosion rate (mm/yr)} = \frac{94.608 \times \Delta V_H}{\rho \times t} \qquad \text{Equation 3.2}$$

The values of weight loss of the AXM520 alloy and NCs specimens (area 15×15 mm^2) were also recorded after immersion in NaCl solution for 60 h. The corrosion rates of the alloy and NCs were calculated using the following equation:

$$\text{Corrosion rate (mm/yr)} = \frac{87600 \times \Delta w}{\rho \times A \times \text{t}} \qquad \text{Equation 3.3}$$

where A (cm^2) is the exposed area of the specimen, and Δw is the weight loss (in g) measured after the removal of the corrosion products.

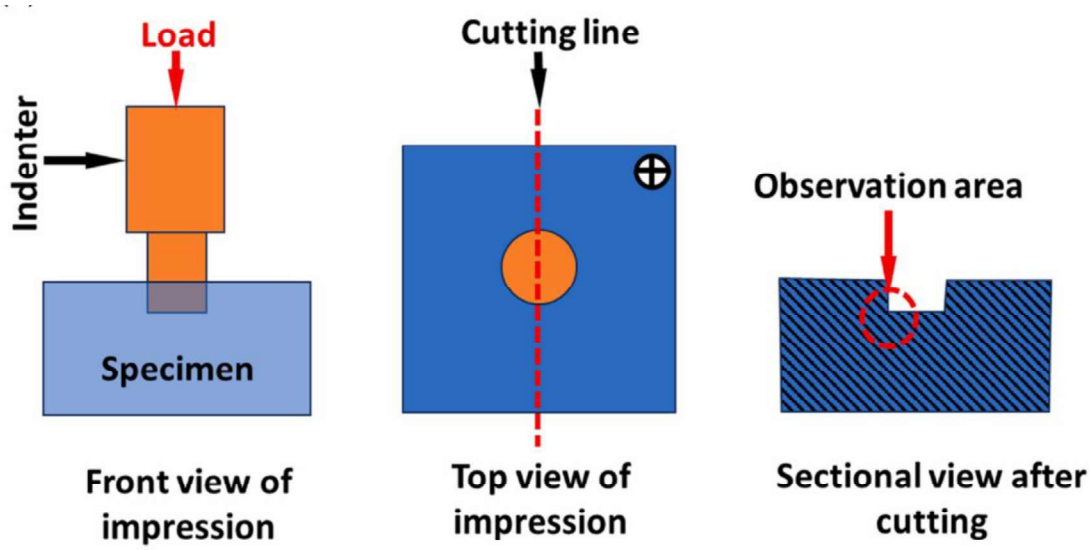

Figure 3.1 Schematic portraying the region of microstructural analysis below indentation after creep test.

3.4.2 Electrochemical corrosion tests

The electrochemical corrosion tests of the alloy and NCs were performed by employing an electrochemical workstation (Corrtest, CS350). The tests were done using a conventional three-electrode system. The alloy and NCs were used as a working electrode. A platinum net and Ag/AgCl with 3 mol KCl solution were used as a counter electrode and reference electrode, respectively. The entire enclosure was then filled with 3.5 (wt.%) aqueous NaCl solution, and a 10 cm^2 sample area was exposed to the solution. After that, the alloy and NCs' open circuit potential (OCP) was measured for 3600 s to ensure the stable E_{OCP} before conducting other electrochemical corrosion tests. Then, the electrochemical impedance spectroscopy (EIS) was performed, followed by a potentiodynamic polarization test. The EIS of each sample was measured from 100 kHz to 0.01 Hz, with ± 10 mV with respect to OCP. The potentiodynamic polarization test was conducted at OCP - 300 to OCP + 400 mV and the potential was varied at 0.01 mV/s.

3.4.3 Measurement of volta potential

The volta potential difference between the primary α-Mg and secondary $(Mg,Al)_2Ca$ (C36) phases of AXM520 and NC3.0SiC was measured using a Scanning Kelvin Probe Force Microscopy (SKPFM) (NT-MDT Service and Logistics Ltd., NTEGRA Prima). Before the experiment, the samples were polished, as mentioned earlier, and then cleaned using ethanol. The measurement was performed in a controlled atmosphere of 25 ± 2 ºC. A Pt-coated Si tip with 20 ± 10 nm was employed to map the surface profile and potential difference. The surface profile was measured using the tapping mode, while the potential signal was measured by raising the cantilever at a height of 50 nm.

3.4.4 Analysis of corrosion products

The morphology of the corroded film deposited on the alloy and NCs was captured by an SEM (Carl Zeiss Microscopy Ltd., EVO-Scanning Electron Microscopy MA15/18) with an EDS facility (Oxford Instruments Nanoanalysis, 51N1000 - EDS System). The corroded film's XRD diffraction pattern was recorded using Cu-K_α radiation (PANalytical) with a scanning speed of 5 º/min. Further, the corroded film's Fourier Transform Infrared Spectroscopy (FTIR) (Thermo Electron Scientific Instruments LLC, Nicolet iS5) was recorded in attenuated total reflectance mode. The FTIR spectra were recorded in the range of 550 to 4000 cm^{-1}. The corrosion product's X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, K-Alpha) was

also performed using an Al-K_α X-ray source. The 3D profilometry and SEM observation of the corroded surfaces were performed after removing the corrosion products using a 100 ml aqueous solution of 20 and 10 g of CrO_3 and $AgNO_3$, respectively.

3.5 Heat treatment of alloy and nanocomposites

The samples of 10×10×10 mm^3 were cut from the cast ingot. The specified samples were then homogenized in a tube furnace at a temperature of 773 K for 8 hr in Ar atmosphere and, subsequently, water quenched. The homogenized samples were artificially aged in a muffle furnace at a temperature of 523 K.

3.6 Designations of aged alloy and nanocomposites

The alloy is designated as AXM520HT, and the nanocomposites containing 1.0 and 2.0 (wt.%) of SiC_{np} are designated as NC1.0SiCHT and NC2.0SiCHT, respectively.

3.7 Hardness measurement

The aged samples were then taken out from the muffle furnace at a regular intervals of 30 min to measure their hardness using a Vickers hardness tester (Vertex Engineers & Associates, HV-50A). The applied load and dual time were 1 kgf and 10 sec, respectively.