CHAPTER 3

EXPERIMENTAL WORK

The experimental work used in the current research is included in this chapter. It includes an experimental work plan, details of developed fluxes, alloys, and experimental set-up. This research work is divided into five parts.

Part I: Develop the magnesium melting fluxes and identify the best among them

Part II: Effect of addition of various manganese sources on magnesium metal

Part III: Effect of temperature on solubility of manganese in magnesium

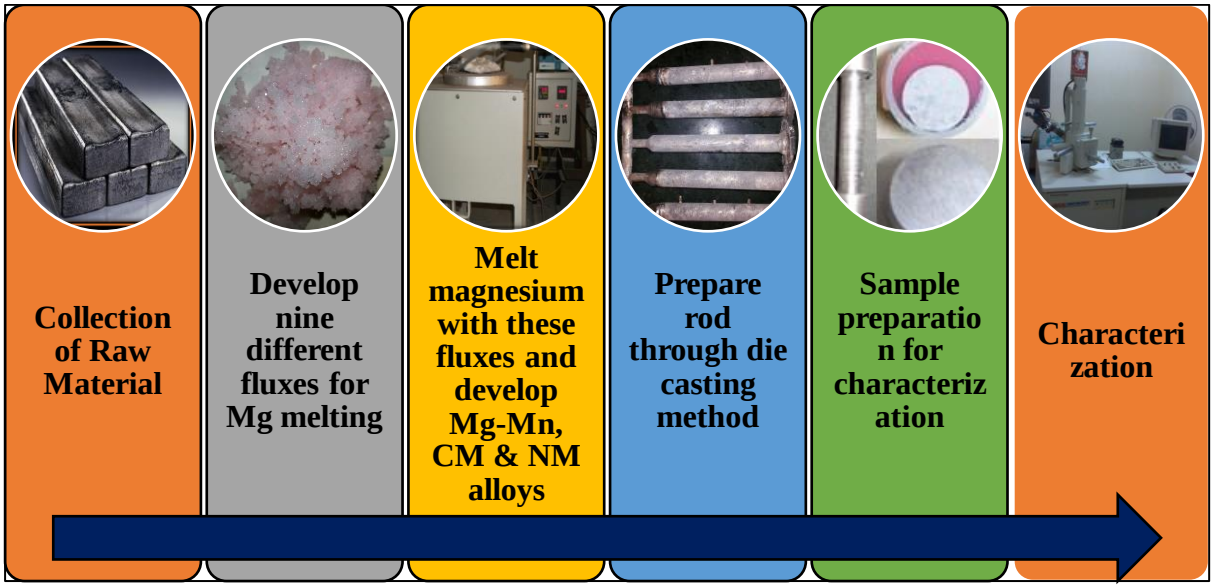
Part IV: Develop and study the Mg-Cu and Mg-Cu-Mn (CM) alloys

Part V: Develop and study the Mg-Ni and Mg-Ni-Mn (NM) alloys

Here, all the steps and practises followed in these five parts are covered. At the end, tests to examine microstructure, mechanical properties and corrosion rate are covered.

3.1 Overall Flowchart of Experimental work

Overall experimental work carried out in this research is shown figure 3.1.



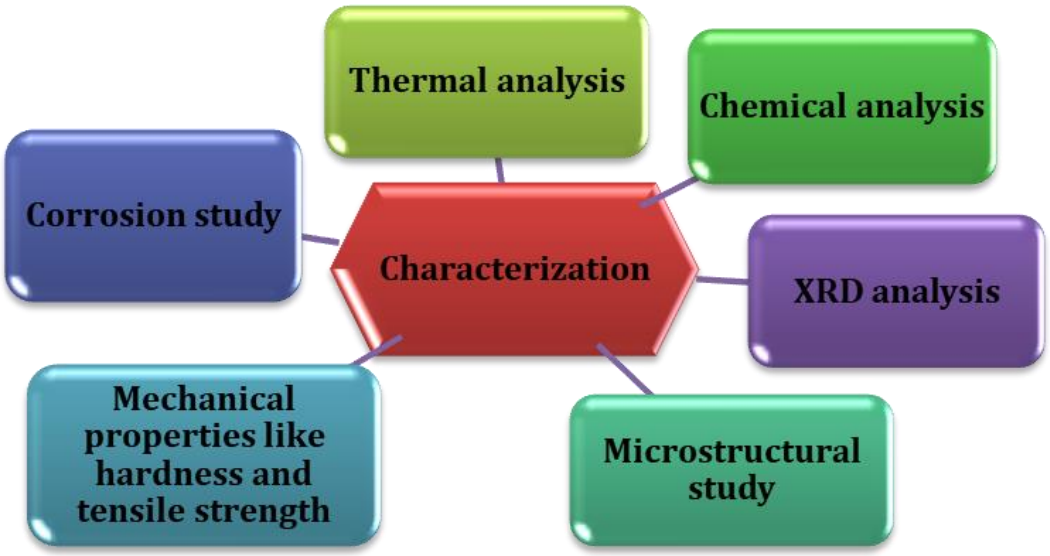


Figure 3.1 Overall flowchart of experimental work

3.2 Procurement of Raw Materials and Practical Work

Raw materials required for this research work are as follow.

1. Commercially pure magnesium, manganese, copper, nickel
2. Degassing tablet
3. Various chlorides, fluorides and oxides

Commercially pure magnesium and degassing tablet was purchased from C. K. Enterprise, Vadodara. Commercially pure manganese, copper and nickel were procured from Aadhya Engineering, Vadodara. Various AR grade chlorides, fluorides and oxides used for flux preparation were purchased from S. D. Fine Laboratory, Vadodara.

Melting practices were carried out at our department premises and at personal space. Chemical analysis, microstructure observation, tensile testing and corrosion study was done at department itself. Optical microscopy and hardness test was carried out at TCR Advanced Engineering, Vadodara.

3.3 Experimental Setup

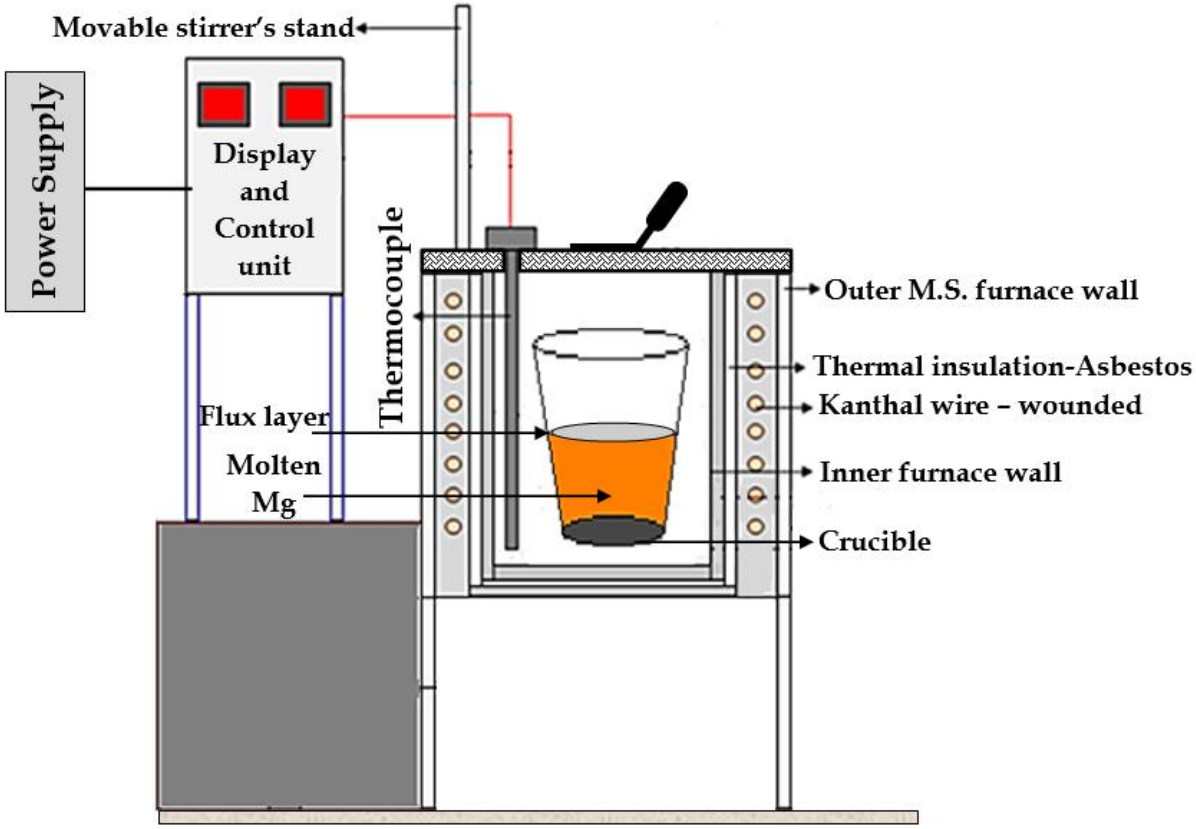


Figure 3.2 Schematic diagram of experimental setup

Electrical resistance melting furnace was used for melting of magnesium. This furnace consists of the following:

1) Melting zone:

It is basically a square cross-sectioned zone with an outside wall made of M.S. and an inner wall made of S.S. with a hole on the bottom side. A number of heating coils are positioned between the outer and inner walls to provide resistive heating for melting. Kanthal wire is used to make the heating coils.

2) Crucible:

The raw materials for the heating furnace are kept in a Graphite crucible. After melting, with the help of a toggle, the molten mixture is poured into a metallic die.

3) Thermocouple:

A thermocouple of the Chromel-Aluminum type has been placed in the melting zone to measure the melt's temperature and display it in degrees Celsius on the temperature display panel.

4) Temperature controller:

The thermocouple and heating coil are both connected to the temperature controller. The automatic system controls the temperature and maintains it within the predetermined range.

5) Metallic die:

Die is made up of grey cast iron. It consists of two halves. The liquid metal poured this die to get a rod shape casting by solidification process. The dimensions of the die are shown in figure 3.3.

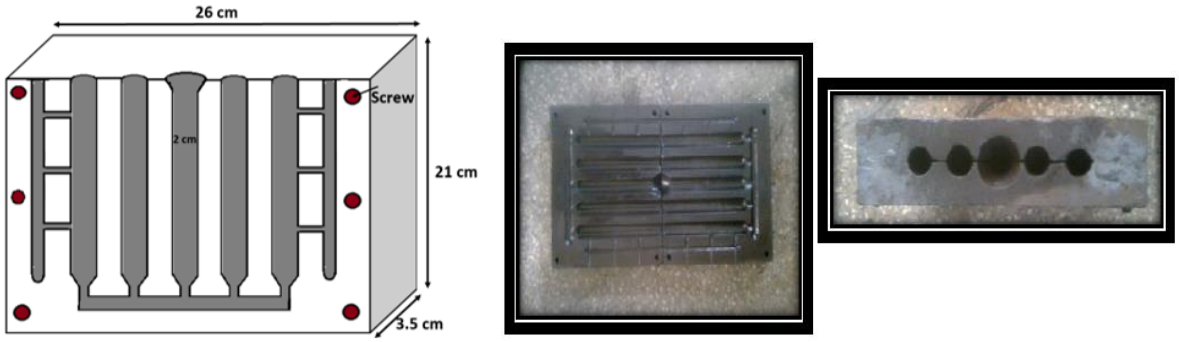


Figure 3.3 Metallic die

6) Auxiliary Equipments:

1. **Regular and electronic Weighing Scale:** Weighing balance were used to measure the amount of raw materials such as Mg, Mn, Cu, Ni and chlorides, fluorides and oxides.
2. **M.S. rod:** M.S. rod was used for manual stirring of melt.
3. **Glows:** Used to protect hands during operations.
4. **Toggle:** Toggle was used to handle hotter equipment's for safety point of view. Molten metal was poured into the die by griping the crucible by toggle.
5. **Burner:** Burner was used to preheat die.
6. **Skimmer:** Skimmer was used to clean the dross from the upper layer of molten metal.
7. **Drossing Pan:** Upper layer of the fluxes were removed from the molten metal before pouring. Drossing pan was used to hold this dross.
8. **Hammer:** Hammer was used to assembled the die, eject the solid metal from die.
9. **Hacksaw blade:** Used for cut the samples in different sizes.

3.4 Experimental Procedure

Experiments were performed in five parts. Detailed procedural steps of each part is discussed here.

3.4.1 Part I: Develop the magnesium melting fluxes and identify the best among them

❋ **Experimental Steps of Flux Preparation**

1) Collect chlorides, fluorides and oxides in powder form.
2) Preheat all chemicals at 100 °C temperature in oven.
3) Take a weight of chlorides, fluorides and oxides as per shown in table 3.1.
4) All chemicals were hand-mixed by a glass rod for up to 5 minutes to get uniform distribution.

Chemical and equipments and apparatus used in this preparation are shown in figure 3.4.

Table 3.1 Composition of Fluxes with an individual melting point [45, 114, 119–122]

Sr. No.	Flux No.	Composition (%)	Melting Point (°C)	Sr. No.	Flux No.	Composition (%)	Melting Point (°C)
1	Flux 1 (320)	76 $MnCl_2$ 13 CaF_2 11 MgO	650 1382 2642	6	Flux 6	45.5 $MgCl_2$ 40 KCl 4 NaCl 4 $CaCl_2$ 5 CaF_2 1.5 MgO	712 770 800 782 1382 2642
2	Flux 2 (220)	57 KCl 28 $CaCl_2$ 12.5 $BaCl_2$ 2.5 CaF_2	770 782 959.8 1382	7	Flux 7	38.5 $MgCl_2$ 36 KCl 4 NaCl 4 $CaCl_2$ 16 CaF_2 1.5 MgO	712 770 800 782 1382 2642
3	Flux 3	44.5 $MgCl_2$ 38 KCl 8 $BaCl_2$ 4 NaCl 4 $CaCl_2$ 1.5 MgO	712 770 959.8 800 782 2642	8	Flux 8	45.5 $MgCl_2$ 45 KCl 4 NaCl 4 $CaCl_2$ 1.5 MgO	712 770 800 782 2642
4	Flux 4 (230)	55 KCl 34 $MgCl_2$ 9 $BaCl_2$ 2 CaF_2	770 712 959.8 1382				
5	Flux 5 (310)	20 KCl 50 $MgCl_2$ 15 CaF_2 15 MgO	770 712 1382 2642	9	Flux 9 (250)	23 KCl 72 $MnCl_2$ 2.5 $BaCl_2$ 2.5 CaF_2	770 650 959.8 1382

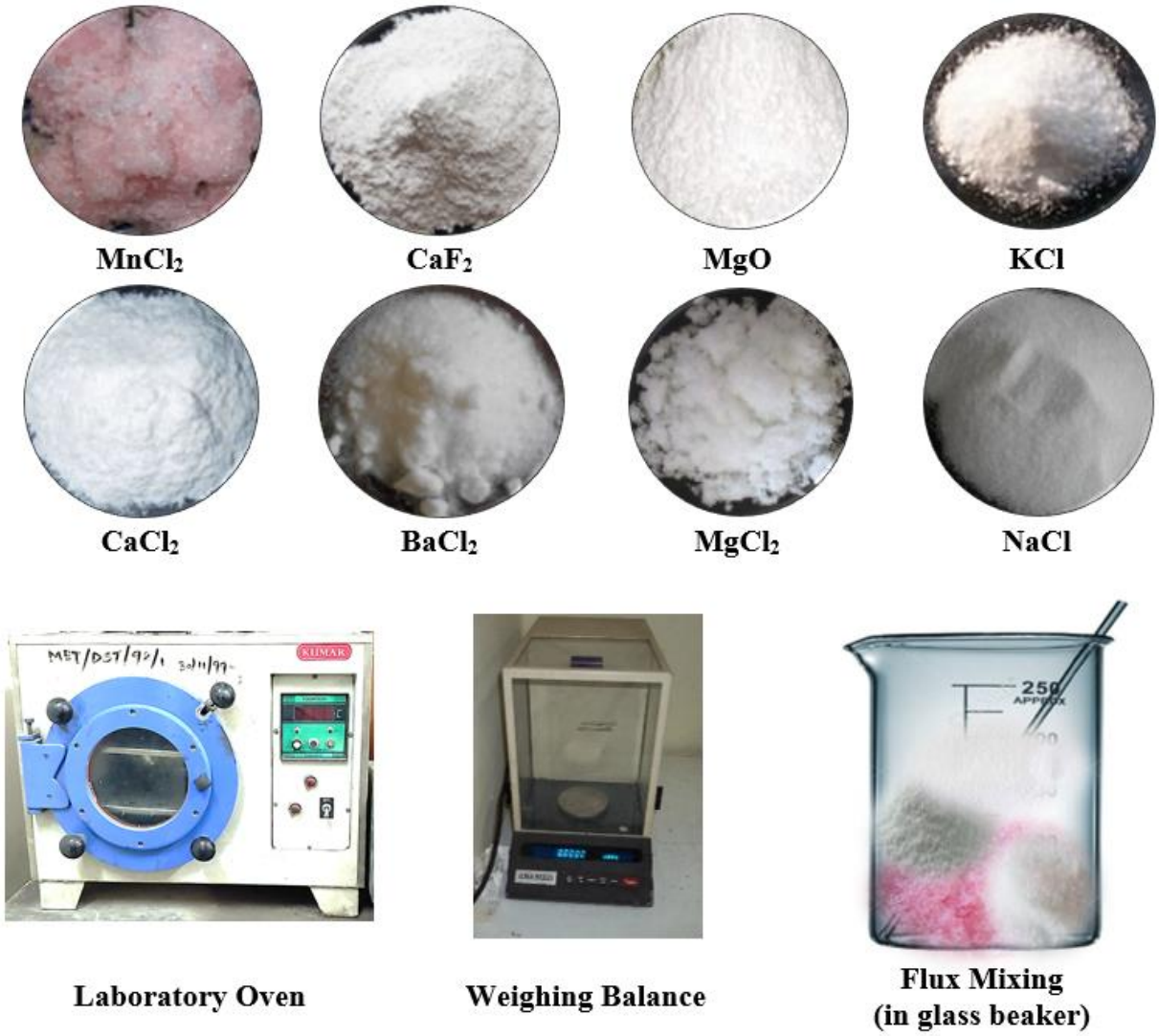


Figure 3.4 Chemicals, Equipments and apparatus used in flux preparation

❋ **Experimental Steps to Prepare Surface Layer of Flux on Magnesium**

1) A magnesium piece of 3 × 3 cm was cut from the magnesium ingot and weigh it.
2) Flux amount was calculated from magnesium's weight (5 % of Mg weight).
3) The sample was kept in a small crucible and the top surface of this magnesium piece was covered with prepared flux.
4) Heat the samples up to 640°C in an electric resistance furnace. (Just before the melting of Mg metal.)
5) The heated flux layer of the magnesium piece was analyzed by visual and scanning electron microscopy after cooling to room temperature.
6) The same process is followed for all nine samples.
7) Steps followed in this experiment are shown in figure 3.5.

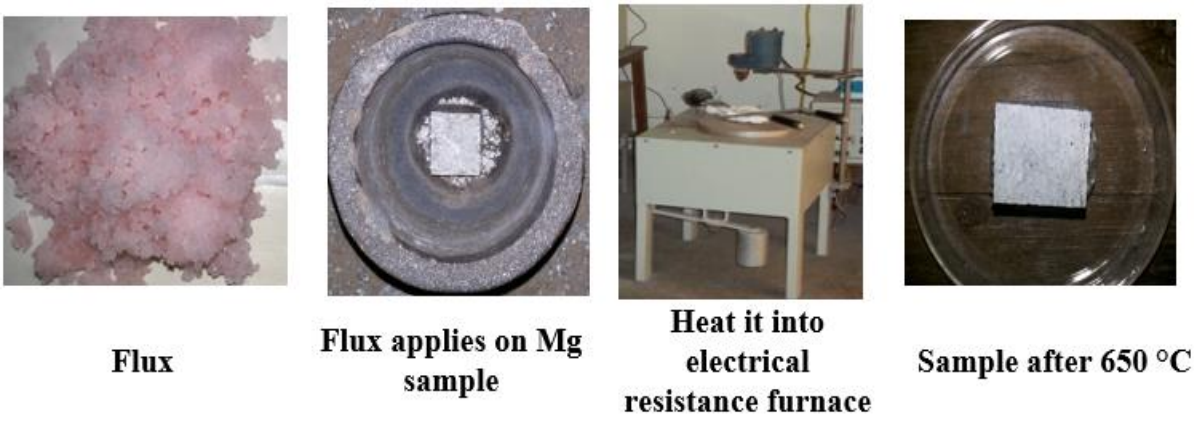


Figure 3.5 Steps for surface layer of flus on magnesium

❋ **Experimental Steps for Magnesium Casting**

1) Prepare flux 1 using composition mentioned in table 3.1.
2) Cut the magnesium ingot into pieces and measure the weight in weighing balance. (548-gram weight taken)
3) Total 27.40-gram preheated flux put below and above magnesium sample.
4) The flux covered magnesium sample kept in graphite crucible.
5) Put this crucible inside the electrical resistance heating furnace.
6) Set 720 °C temperature in the furnace.
7) After melting, add the degassing tablet in molten metal to remove gases.
8) The flux layer on the molten magnesium surface was removed by skimmer.
9) Preheat metallic mold (Cast Iron)
10) After manual stirring, the prepared liquid melt poured into a preheated metallic mold (Cast Iron) in rod shape at 720 °C.
11) All nine types of fluxes were prepared by the same casting process.
12) Experimental setup and final casting are shown in figure 3.6.

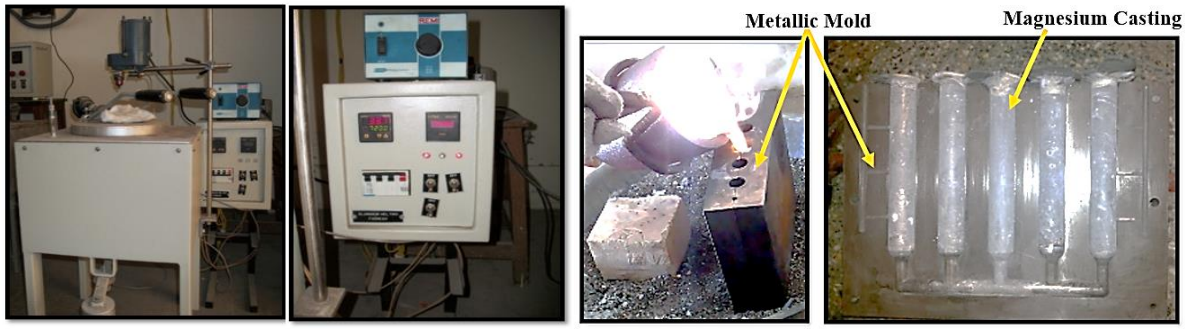
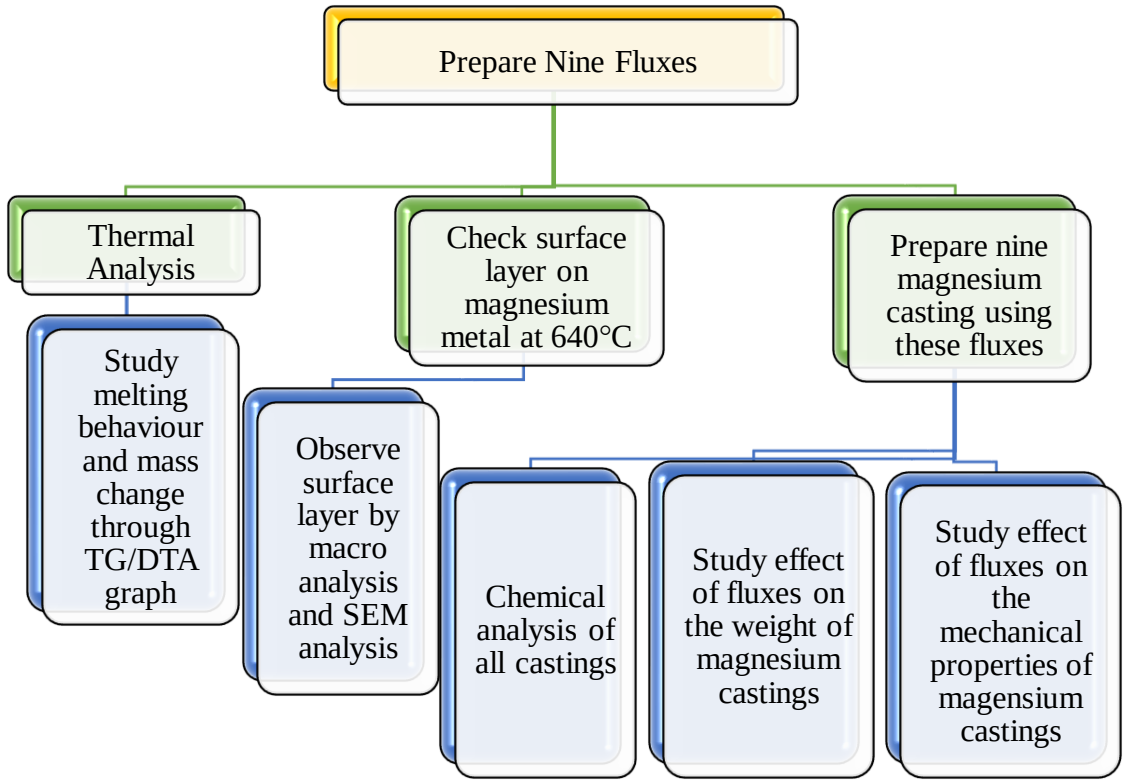


Figure 3.6 Experimental setup and final casting

Flowchart of Experimental Work & Characterization



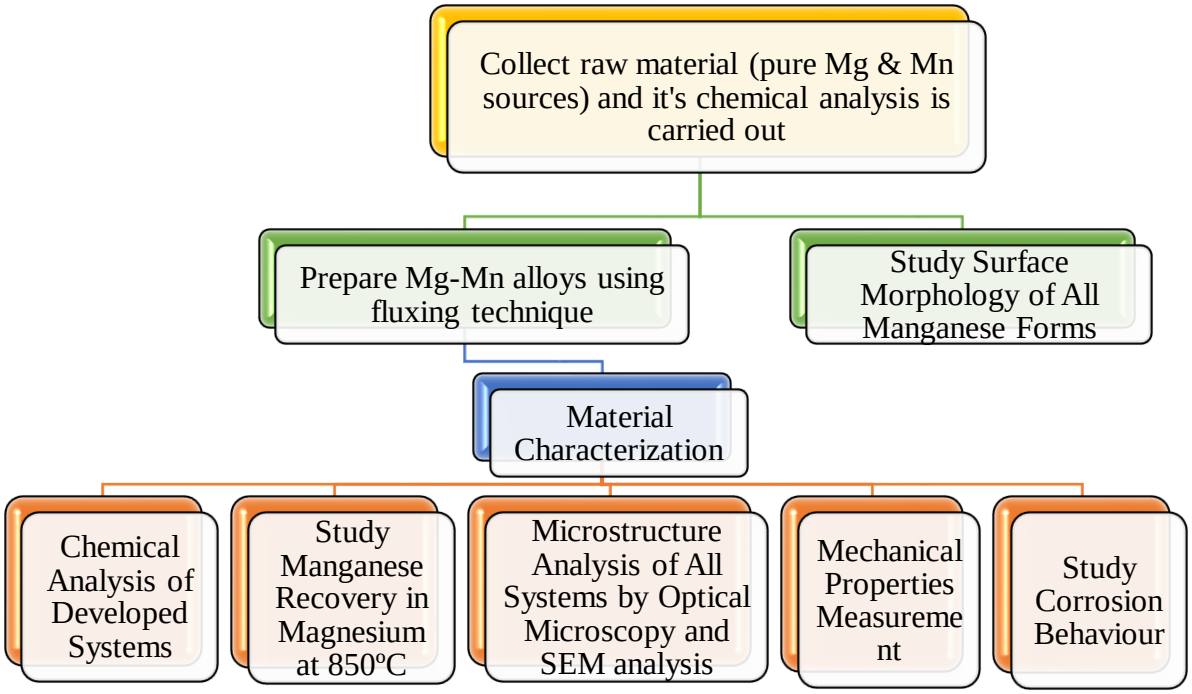
3.4.2 Part II: Effect of addition of various manganese sources on magnesium metal

Experimental Steps of Casting:

1) Prepare flux 9 using composition mentioned in table 3.1.
2) Cut the magnesium ingot into pieces and weigh it.
3) Preheated flux and manganese coarse powder kept in bottom and upper surface of the magnesium sample.
4) The magnesium sample kept in graphite crucible.
5) Put this crucible inside the electrical resistance heating furnace.
6) Set 850 °C temperature in the furnace.
7) After melting, add the degassing tablet in molten metal to remove gases.
8) The flux layer on the molten magnesium surface was removed by skimmer.
9) Preheat the metallic mold (Cast Iron).
10) After manual stirring, the prepared liquid melt poured into a preheated metallic mold (Cast Iron) in rod shape at 850 °C.
11) Mg-$MnCl_2$ powder, Mg-MnO_2 powder, Mg-Mn fine powder and Mg-Mn flakes (electrolytic) systems were also prepared by the same casting process.
12) Experimental steps followed in this part is shown in figure 3.7.

Figure 3.7 Experimental steps of Mg-Mn flakes system

- **Flowchart of Experimental Work & Characterization:**

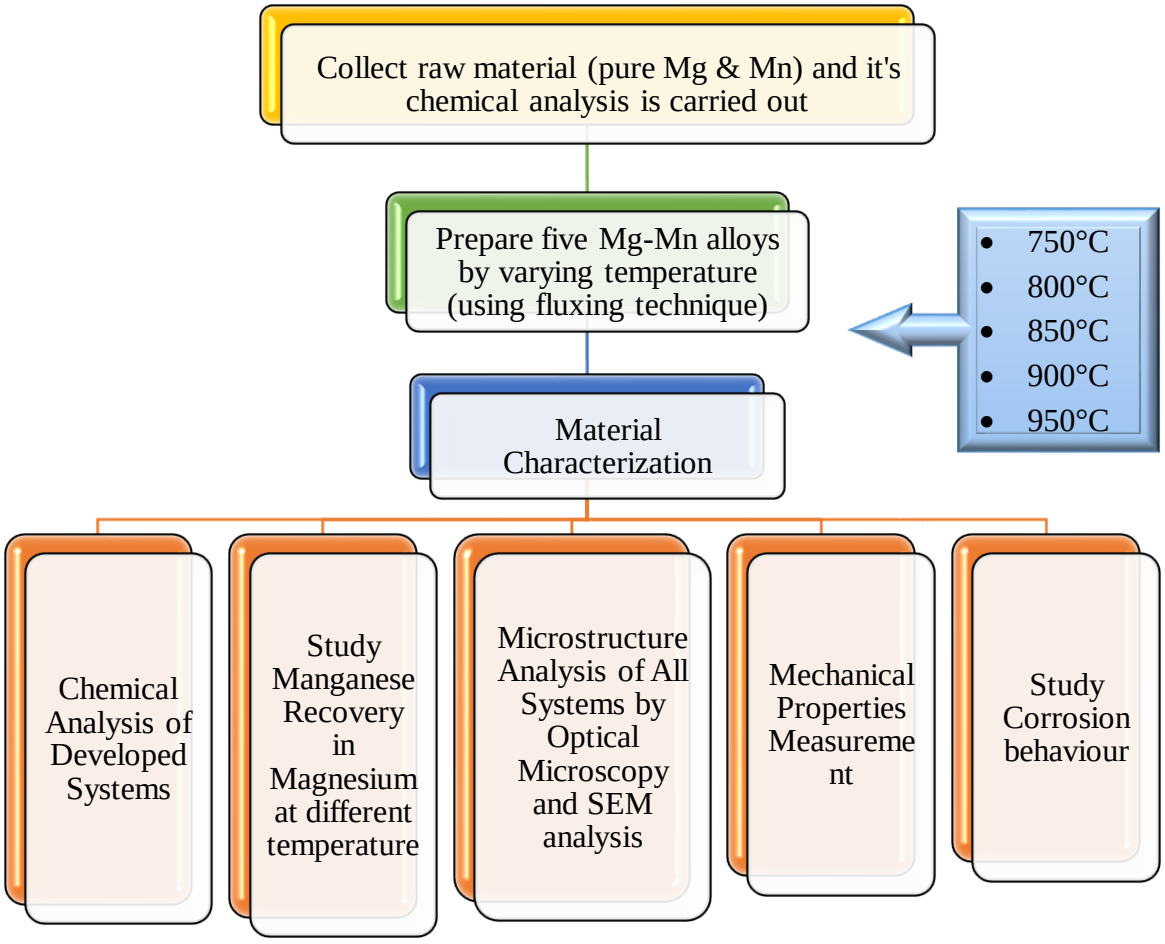


3.4.3 Part III: Effect of temperature on solubility of manganese in magnesium

- **Experimental Steps of Casting:**

1) Experimental steps discussed in section 3.4.2 and figure 3.7, are same followed for development of Mg-Mn flakes systems.
2) Only the melting temperature is different. In this part, molten magnesium is held at different temperatures i.e., 750°C, 800°C, 850°C, 900°C, 950°C for 1 hour.
3) The melt was stirred for 3-4 minutes and after complete degassing and defluxing, it was poured at respective temperatures into a preheated permanent gray cast iron die.

- **Flowchart of Experimental Work & Characterization:**



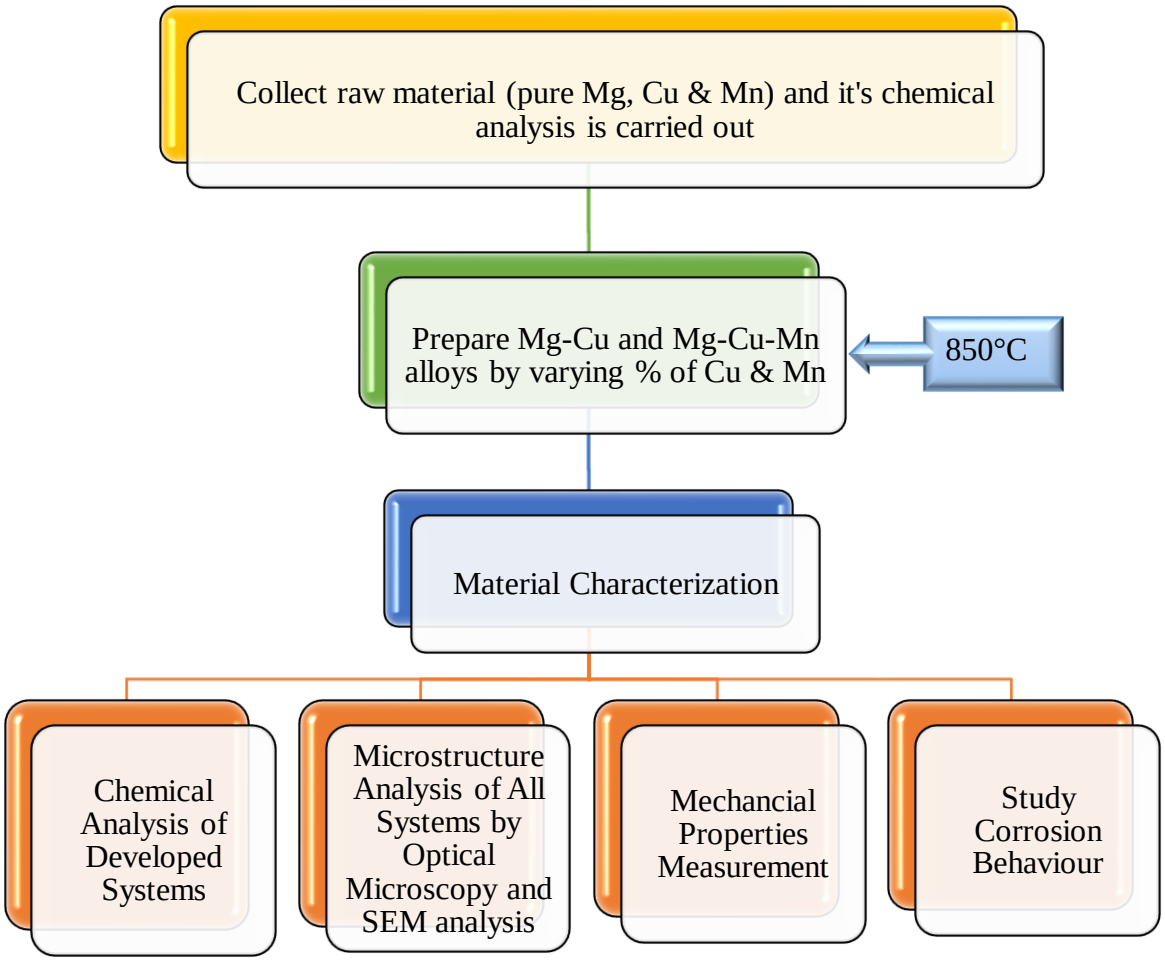
3.4.4 Part IV: Develop and study the Mg-Cu and Mg-Cu-Mn (CM) alloys

Experimental Steps of Casting:

1) Prepare flux 9 using composition mentioned in table 3.1.
2) Cut the magnesium ingot into pieces and weigh it.
3) Flux (preheated) and copper kept in bottom and upper surface of the magnesium sample.
4) The magnesium sample kept in graphite crucible.
5) Put this crucible inside the electrical resistance heating furnace.
6) Set 850 °C temperature in the furnace.
7) The melt was held at this temperature for 1 hour.
8) After melting, add the degassing tablet in molten metal to remove gases.
9) The flux layer on the molten magnesium surface was removed by skimmer.
10) Preheat the metallic mold (Cast Iron).
11) After manual stirring, the prepared liquid melt poured into a preheated metallic mold (Cast Iron) in rod shape.
12) All Mg-Cu and Mg-Cu-Mn alloys were prepared by the same casting process.
13) Materials used in this process are shown in figure 3.8. Setup and auxiliary materials used in this part are same as shown figure 3.7.

Figure 3.8 Materials used to develop Mg-Cu and Mg-Cu-Mn alloys

Flowchart of Experimental Work & Characterization:



3.4.5 Part V: Develop and study the Mg-Ni and Mg-Ni-Mn (NM) alloys

Experimental Steps of Casting:

1) Experimental steps discussed in section 3.4.4 and figure 3.7, are same followed for development of Mg-Ni and Mg-Ni-Mn alloys.
2) In this part, Nickel and Nickel-Manganese are added.
3) After manual stirring, the prepared liquid melt poured into a preheated metallic mold (Cast Iron) in rod shape at 850 °C.
4) All NM alloys were prepared by the same casting process.
5) Materials used in this process are shown in figure 3.9. Setup and auxiliary materials used in this part are same as shown figure 3.7.

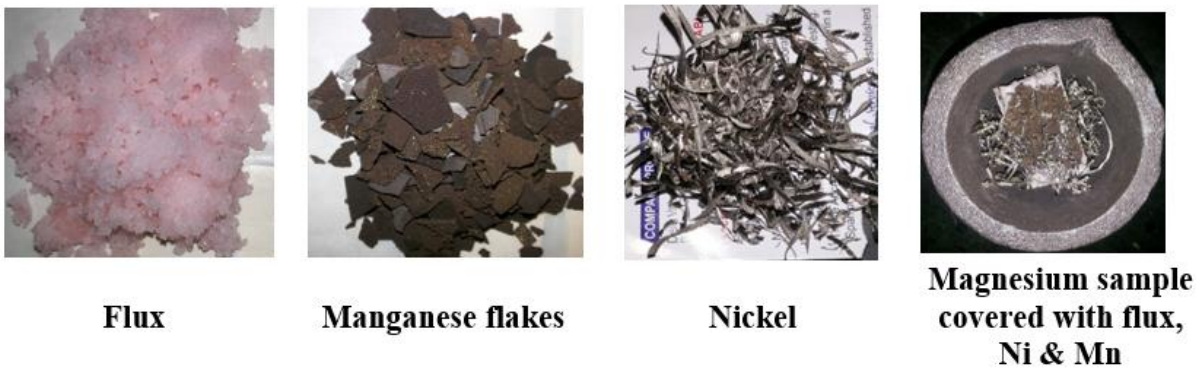
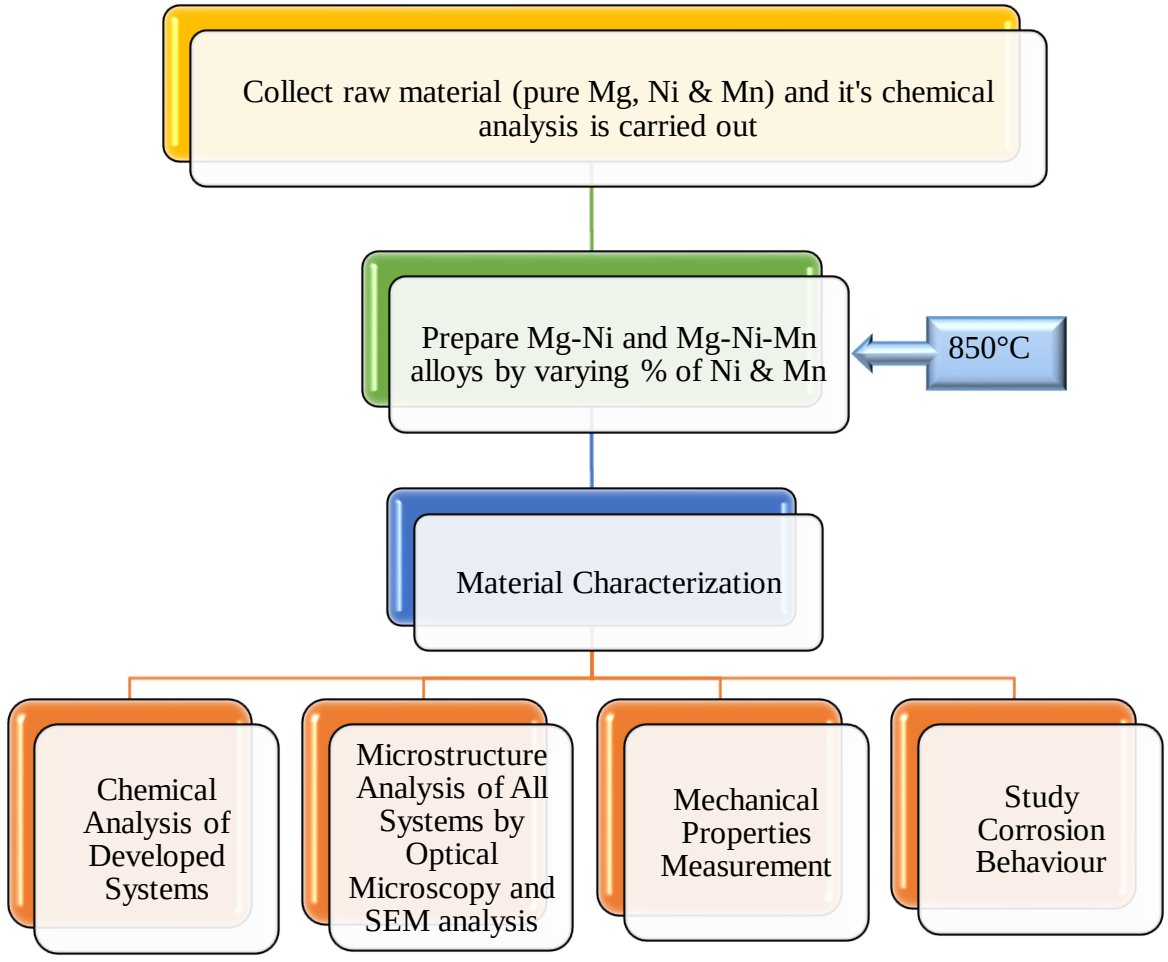


Figure 3.9 Materials used to develop Mg-Ni and Mg-Ni-Mn alloys

- **Flowchart of Experimental Work & Characterization:**



3.5 Thermogravimetric/Differential Thermal Analysis

To understand the behavior of all nine fluxes during heating, from room temperature to till melting state, TG/DTA analysis was carried out. TG/DTA study indicates decomposition sequences, mass change and melting sequences of fluxes individually. The thermal analysis

was carried out by NTEZSCH STA 449 F3 thermal analyser system which is shown in figure 3.10. Samples were analyzed from 23ºC to a maximum of 700ºC (973K) with a constant heating rate of 10ºK/min for each nine fluxes. Around 7-11 mg sample was taken for every analysis. Alpha alumina was used as reference material. Samples were tested in a nitrogen atmosphere as per standard procedure. The idea is to test all fluxes in air but due to presence of chlorides, oxides, or fluorides, it is not advisable to run the fluxes samples in the air. The results were analyzed for all the samples as per the thermal events exhibited by the samples.

Figure 3.10 Thermal analyser

3.6 Metallography Process

Basic steps for sample preparation include;

1) Sampling:

To accurately represent the alloy's overall properties, the specimen should be chosen from the suitable region. In sampling, proper location of the sample were selected.

2) Cutting:

The finished product is in rod shape after casting. Therefore, cutting is essential for characterising it. The necessary size samples were cut using an automatic hacksaw cutting machine. Approximate specimen size for microscopic analysis are 15 mm diameter and 10 mm height.

3) Grinding:

Grinding repairs surface damage caused by sectioning.

a) Rough Grinding:

Getting a suitably smooth surface on the specimen is the first step that must be taken. Either a moderately coarse file or an emery belt powered by a motor are used for this.

b) Fine Grinding:

Series of abrasive papers (from coarsen fine) were used in grinding. There are several grades of paper, with 500, 1000, 1500, 2000, and 2500 grains of silicon carbide per square inch. We used wet grinding here. Kerosene is employed in this method of grinding because it flushes off the broken abrasive particles and maintains a cool surface for the specimen.

Figure 3.11 Grinding and Polishing steps

4) Polishing:

The objective of polishing is to make the surface flat and to fully removed scratches. A highly polished surface is created by removing the minor scratches that were added during the previous grinding procedure. On laps or polishing wheels, it is carried out. These wheels are often made of brass, bronze, or stainless steel and covered with polishing cloth of the proper quality. Soft materials should be polished at a low speed. Al_2O_3 powder mixed with distilled water and this solution is applied on the cloth of polishing wheel. After polishing, a scratch-free mirror-like surface is achieved.

3.7 Microstructure Observation

3.7.1 Optical Microscopy

The primary tool for phase identification is optical microscope. A picture is enlarged by the optical microscope by passing a light beam across the sample. First, the sample needs to be ground with sandpaper of various grain sizes. The sample must next be polished until it has a scratch-free, mirror-like appearance. The preparation of samples requires careful expertise because, without it, the optical microscope is useless.

Metallographic samples were prepared by mounting them in cold setting resin. They were etched with a 2% Nital solution for 20 seconds and then microstructure was characterized by Olympus optical microscope GX51. Photograph of Olympus microscope is shown in figure 3.12.

Figure 3.12 Specimen and Olympus optical microscope GX51

3.7.2 Electron Microscopy (SEM)

The sample was prepared by normal polishing techniques and transversally sectioned for microstructural examination. Using a scanning electron microscope, the specimen's microstructure was examined. The study of the surface topography of solid materials is its main application. In comparison to optical or transmission electron microscopy, it allows for a depth of field that is much higher. SEM has a resolution of 3 nm, which is two orders of magnitude less than TEM's.

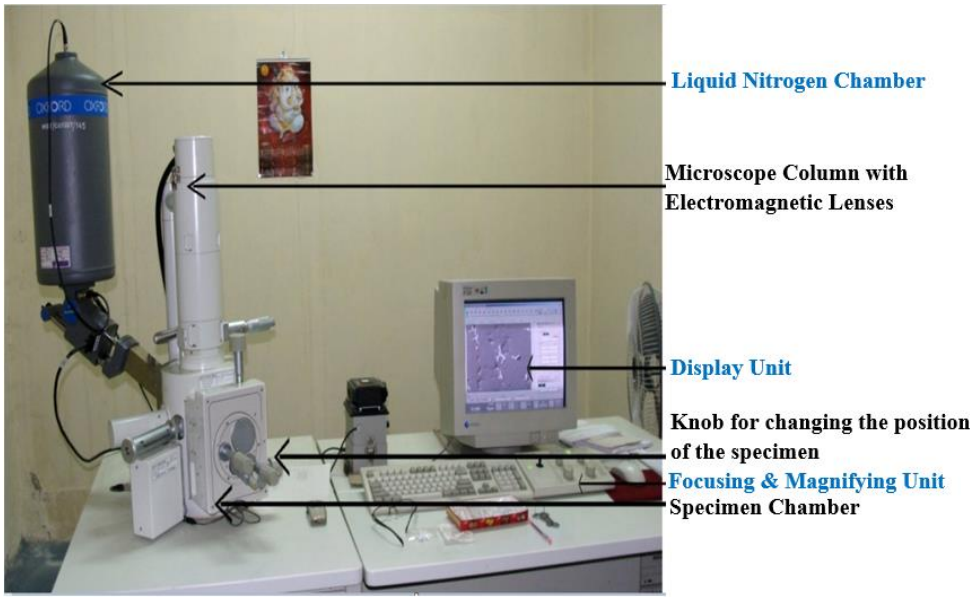


Figure 3.13 Scanning Electron Microscope (JEOL JSM-5610LV) with EDS

Microstructure observation of all samples were done by JEOL Scanning Electron Microscope (JSM-5610 LV). Photograph of SEM is shown in figure 3.13.

❋ **Chemical Analysis:**

The chemical composition of developed alloys was determined by Energy Dispersive Spectroscopy which is connected with scanning electron microscope. The accuracy of the instrument is 99.99 wt.%.

3.8 XRD Analysis

A computer-controlled X-ray Powder Diffractometer is called X'pert Pro. X-ray tube, incident and diffracted beam optical components, the Goniometer, which consists of the platform that supports and moves the sample, and the detector make up a majority of its components. The Bragg-Brentano parafocusing geometry is used by X'Pert Pro. The machine generates a diffraction pattern of the sample loaded in the sample stage with the support of the operating programme "X'Pert Data Collector". A collection of powder diffraction data (PDF files) for various types of materials is available from the International Centre for Diffraction Data (ICDD), a non-profit scientific organisation devoted to gathering, editing, publishing, and disseminating powder diffraction data for the identification of crystalline materials.

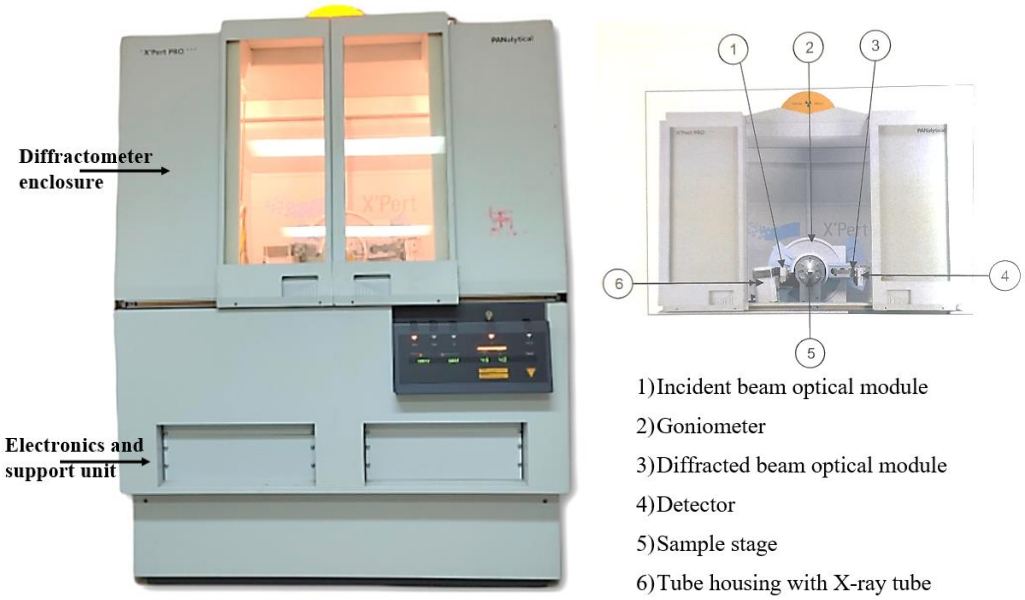


Figure 3.14 X-ray diffraction system

An X-Ray diffractometer (X'pert Pro-Pan analytical) shown in figure 3.14, was used to determine the phase constituents. The X-ray diffraction was performed using CuKα radiation with experimental parameters of 40 mA, 45 kV, scanning velocity of 10 °/min, and scanning angle from 10° to 90°.

3.9 Mechanical Testing

The following tests were performed on the specimens prepared.

3.9.1 Hardness Testing

A technique for assessing a material's hardness or resistance to penetration is micro hardness testing. Diamond pyramid indenter is the main part of the micro-hardness test apparatus. The hardness of all developed alloys was measured using FIE Micro Vickers hardness tester at 100 grams load (figure 3.15). The load was applied for 10 seconds and then released. Measure the Indentation (length of the two diagonal) of the indenter. Measure the Vicker's hardness using equation 3.1. The averages of three measurements were reported for each system.

$$Vickers\ Hardness\ (HV) = 1.854 \times \frac{F}{d^2} \qquad \text{(Equation 3.1)}$$

where,

F = applied load (kg)

d^2 = the area of the indentation (mm^2)

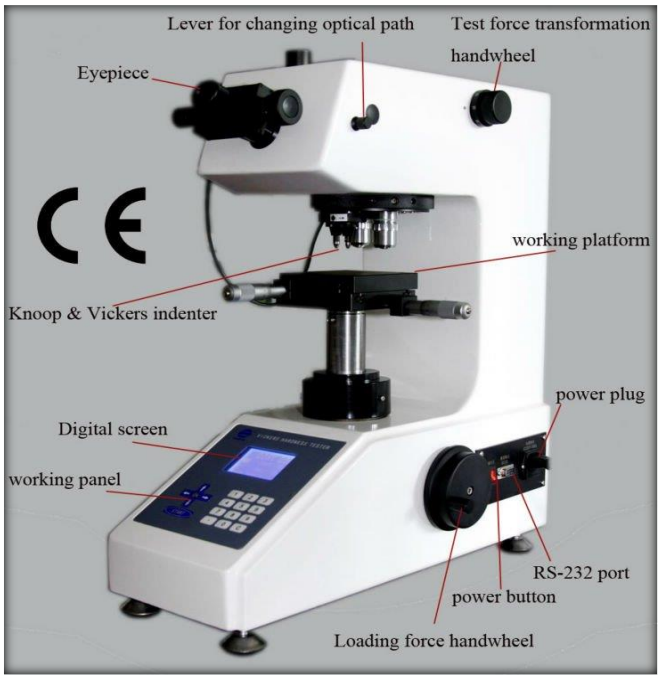


Figure 3.15 Micro-Hardness test machine

3.9.2 Tensile Testing

The Monsanto-20 tensile testing equipment was used to measure tensile strength, % elongation and % reduction area. The use of this equipment is intended specifically to precisely control the strain rate being applied to the tensile specimen.

1) **Standard Size of specimen:** 7.8 mm to 8.1mm O.D., 42mm total length, 26 mm gauge length, 5.0 mm gauge diameter, 1mm radius of fillet.

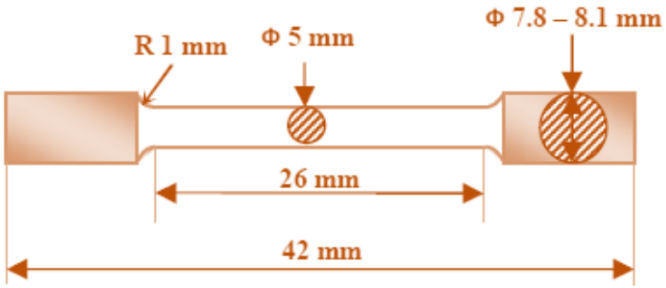


Figure 3.16 Line diagram of tensile test specimen

2) **Available load limit settings:** 20kN/2000kgf - Red, 2000N/200kgf - White, 200N/20kgf - Blue. We fixed it at red.
3) **Strain-Rate:** The cross-head speed was set to 0.5 millimeters per minute.

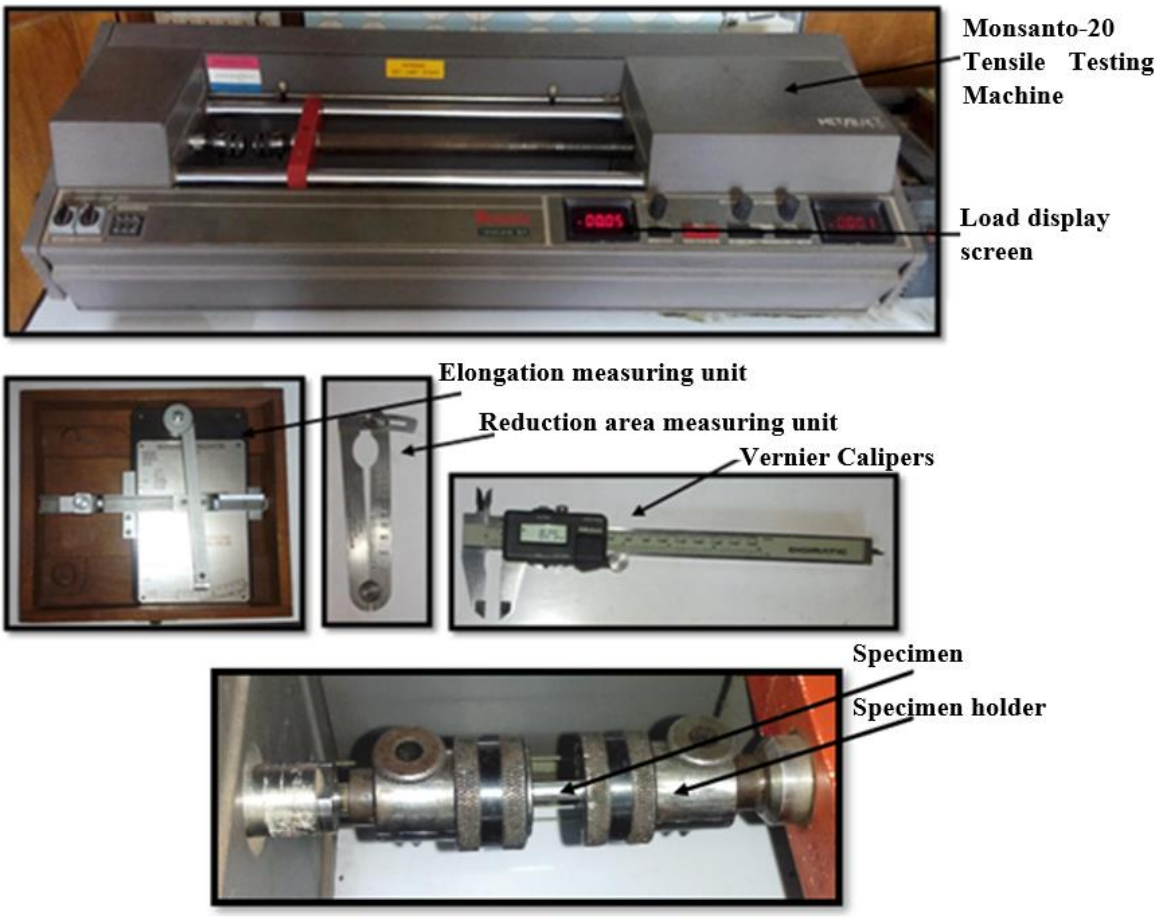


Figure 3.17 Monsanto-20 tensile testing equipment & its related accessories

Figure 3.17 shows image of tensile testing machine. It is especially made for testing at low strain rates.

❋ **Precautions:**

1) The specimen should not be misaligned in the specimen holder.
2) Avoid using higher strain rates.
3) It is important to take precautions to ensure that the specimen breaks from the centre rather than the sides. This can be done by removing any porosities that may have developed during the casting process, avoiding any non-uniformity in the specimen's cross-section, and using a CNC machine to prepare the sample.

3.10 Density Measurement

Density of magnesium and its alloys is measured by two methods.

1) Water displacement method [128]

In this method 100 ml Flask is used. First samples are weighed in weighing balance. Then pour 60 ml water in flask and note volume $V_{initial}$. After that till the flask and put the weighed sample in flask and measure volume V_{final}.

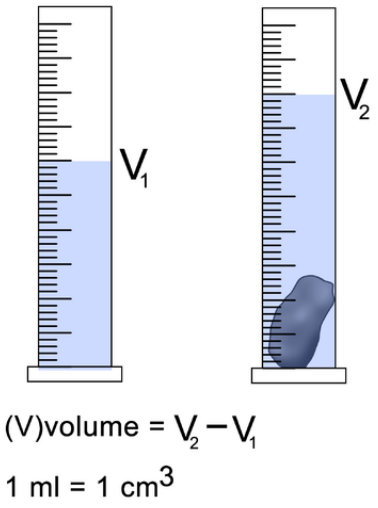


Figure 3.18 Density measurements by water displacement method

Density is measured with the help of equation,

$$Density\ (D) = \frac{M}{V} \qquad \text{(Equation 3.2)}$$

Where, $V = V_{final} - V_{initial}$ (cc)

V_{final}= Final reading on scale (Flask)

$V_{initial}$ = Initial reading on scale (Flask)

M = Mass (in gm)

D = Density (g/cc)

2) Geometry Method

In this method, volume of the sample was measured by its dimensions. Using equation 3.3, density was calculated.

$$Density = \frac{M}{V} = \frac{M}{\frac{\pi}{4}d^2 l} = \frac{M4}{\pi d^2 l} \quad \text{(Equation 3.3)}$$

Where, M = Mass (in gm)

d = diameter of the cylindrical sample (cm)

l = length of the sample (cm)

3.11 Corrosion Rate Determination

An immersion test (ASTM G31-71) was used to measure the corrosion rates of all alloys. [129] All samples were measured before testing for length (l), width (w), thickness (t), and weight (Wi). At room temperature, pure magnesium and Mg-Mn alloys samples were immersed in 3.5 wt.% NaCl solution for 24 hours and 48 hours. CM alloys were immersed in the same solution for 6 and 12 hours, whereas NM alloys were immersed for 1.5 and 2 hours. The samples were collected after the dipping time was completed and were dipped for one minute in CrO_3, $AgNO_3$, Ba $(NO_3)_2$, and reagent water solution. [130] After being dried in hot air, the specimens were weighed again. Figure 3.19 shows image of immersion test samples and materials.

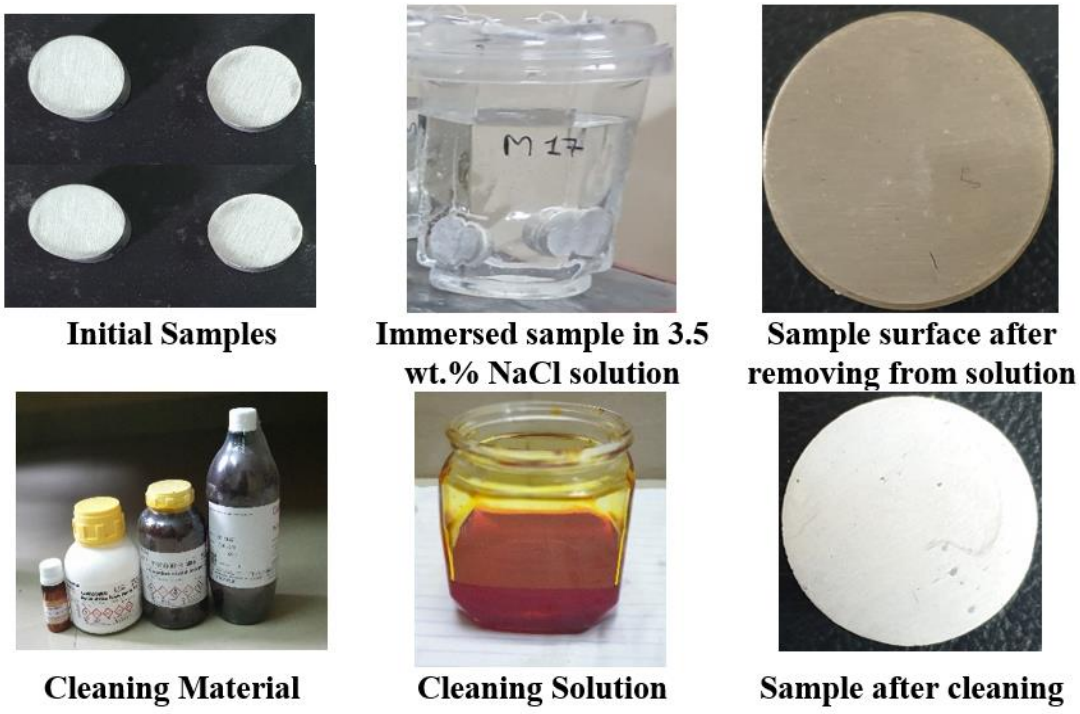


Figure 3.19 Immersion test samples and materials

The corrosion rate of all developed alloys was calculated by equation 3.4. [131]

$$mpy = \frac{534\,W}{D\,A\,T} \qquad \text{(Equation 3.4)}$$

where,

W: weight loss (mg)

D: density of sample (g/cc)

A: Area of specimen exposed to corrosion (inch2)

T: Time of exposure (hours)