CHAPTER 4

MATERIAL AND EXPERIMENTAL INVESTIGATIONS

4.1 INTRODUCTION

This chapter deals with the details of various experimental procedures and processes involved in this study. In the first phase the properties of pure magnesium and Titanium dioxide particles are discussed. The second phase presents with the various stages involved in production the composite specimens and micro structural studies of the prepared composite specimens. The third phase discusses in detail about the procedures involved in conducting the experimental investigations to study the physical properties like hardness, density mechanical properties like tensile strength, compression strength, and yield strength, percentage of elongation, impact strength, wear and frictional behaviour and electro chemical behaviour of different composites specimens. The metallographic investigations were carried out by XRD, EDAX, and Scanning Electron Microscope (SEM) to study the influence of Titanium dioxide particles on wear mechanisms.

4.2 MATERIALS USED

4.2.1 Magnesium

Magnesium is the lightest commercial metal among the metals available for structural applications. It is a silvery-white alkaline earth metal and one third lighter than Aluminium. As per the literature review, it stands in eighth most abundant material in the world. It usually presents in the natural minerals like dolomite and magnesite. The sea is the main source that contains trillions of tonnes of magnesium and provides 850,000 tonnes per year. It is prepared by reducing magnesium oxide with silicon or by the electrolysis of molten magnesium chloride. It has the superior quality of lowest density and highest machinability in engineering materials. The
properties of the magnesium can be improved by alloying addition with titanium, aluminium, zinc, copper, nickel, tin and thorium. The magnesium alloys are divided into cast alloys and wrought alloys. The magnesium cast alloys have the properties similar to those of cast alloys of aluminium. But in comparison with strength to weight ratio, magnesium castings are superior to the aluminium alloys. The wrought magnesium alloys possess limited ductility due to their HCP crystal structure. Above 220°C temperature the alloys could be readily hot worked. The structural shapes of magnesium alloys are frequently formed by extrusion or forging. Magnesium alloys have comparatively high strength to weight ratio. Machinability of magnesium alloys is the best of any commercial metal available in the world. This material is best suited where lightness is the principal consideration.

The Magnesium powder or form of ribbon is heated to certain temperature that ignites or burns with an intense of white light and releases large amount of heat. It also burns in pure nitrogen and pure carbon dioxide. Magnesium reacts with cold water very slowly. It forms a thin protective coating of magnesium carbonate when it is get in touch with moist air. The fire produced by magnesium is not extinguished by water, since water reacts with hot magnesium and releases hydrogen which can cause the fire to burn more ferociously. The effective way to stop the burning fire is by using chemical extinguisher and covering with sand. The properties of the material are listed in Table 4.1. Magnesium may be prepared from electrolysis of fused magnesium chloride, most repeatedly obtained from sea water. It can be used as reducing agent in the preparation of Uranium and other metals that are purified from their forms of salts.
Table 4.1 Properties of Magnesium

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Material</th>
<th>Magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phase</td>
<td>Solid</td>
</tr>
<tr>
<td>2</td>
<td>Melting point</td>
<td>650 °C [923 K]</td>
</tr>
<tr>
<td>3</td>
<td>Boiling Point</td>
<td>1091 °C[1363 K]</td>
</tr>
<tr>
<td>4</td>
<td>Density</td>
<td>1.738 g/cm³</td>
</tr>
<tr>
<td>5</td>
<td>Heat of fusion</td>
<td>8.48 kJ/mol</td>
</tr>
<tr>
<td>6</td>
<td>Heat of vaporization</td>
<td>128 kJ/mol</td>
</tr>
</tbody>
</table>

Figure 4.1 Photograph of pure magnesium

4.2.2 Titanium dioxide

Titanium is present in most igneous rocks and their sediments and it is always found bonded with another element that does not occur in natural pure form. Pure titanium is a transition metal with a lustrous silver-white color and is resistant to corrosion including sea water and chlorine. Titanium has the highest strength to weight ratio of any metal. Even though titanium is used in many products, nearly 95% of the purified metal is used to make titanium dioxide (TiO₂). The corrosion resistance can be improved by forming a thin layer of titanium dioxide (TiO₂) on its surface that is extremely
difficult to penetrate for these materials. It is non-magnetic, biocompatible and is not good as to conduct the electricity and heat. The properties of Titanium are listed in Table 4.2. Many elements like Aluminium, Vanadium and nickel are alloyed with titanium to produce light weight alloys. Its resistance to cavitations and erosion makes it, is an essential structural metal for aerospace and automotive applications. Titanium dioxide ($\text{TiO}_2$) is a whitening pigment used in paints, foods, medicines and cosmetics. (Sameer Kumar et al 2016) reported that the reinforcement particles should be stronger than matrix material to get desired properties. When comparing the values of properties listed in Table 4.1 and Table 4.2. Titanium dioxide has some superior properties. It is found that strong enough to get the desired properties of composites.

**Table 4.2 Properties of Titanium**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Properties</th>
<th>Titanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phase</td>
<td>Solid</td>
</tr>
<tr>
<td>2</td>
<td>Melting point</td>
<td>$1668 ^\circ \text{C} \ [1941 \text{ K}]$</td>
</tr>
<tr>
<td>3</td>
<td>Boiling Point</td>
<td>$3287 \ ^\circ \text{C} [3560 \text{ K}]$</td>
</tr>
<tr>
<td>4</td>
<td>Density</td>
<td>$4.506 \text{ g/cm}^3$</td>
</tr>
<tr>
<td>5</td>
<td>Heat of fusion</td>
<td>$14.15 \text{ kJ/mol}$</td>
</tr>
<tr>
<td>6</td>
<td>Heat of vaporization</td>
<td>$425 \text{ kJ/mol}$</td>
</tr>
</tbody>
</table>

Titanium is the strong and corrosion resists metal. It has some superior properties like stiffness, toughness and light weight. From the sources, it is the ninth most abundant metal in the world. For the past few years, titanium has become an engineering material in its pure form as well as alloyed form. Titanium has two allotropy forms, one is HCP alpha phase and
other is BCC beta phase. The transformation from alpha to beta phase occurs at 885°C. (Pookmanee et al 2009) prepared the titanium dioxide by sol-gel method and explained that titanium dioxide is the useful material for semiconducting transition metal oxide which has unique characteristics like non-toxicity, resistance to photo chemical and chemical erosion. In solar cells and chemical sensors this material is found more applications.

Figure 4.2 (a-b) Photographs of Titanium dioxide

4.3 PREPARATION OF TEST SPECIMENS

4.3.1 Pre-treatment of Magnesium

The raw material of pure magnesium cut pieces were immersed in 10% sodium hydroxide solution at 90-100°C for 15 minutes and then washed with methanol. Then the pieces were dried immediately with the environment of air. The weighed quantities of pure magnesium were placed inside the furnace and it was melted.

4.3.2 Preparation of Titanium dioxide

Ilmenite ore is the main source of titanium dioxide. Rutile is the next most sources. Generally the titanium dioxide is manufactured by sulphate process (by the use of sulphuric acid) or chloride route. In the sulphate route the Ilmenite is dissolved in sulphuric acid. To remove any
unwanted material like iron. The material is heated in a calciner to evaporate the moisture like content before it is added in the melting furnace.

4.3.3 Melting and casting of test specimen

Table 4.3 Proportions of the prepared specimens

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Proportions</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure magnesium</td>
<td>Φ30 x 250 mm</td>
</tr>
<tr>
<td>2</td>
<td>Mg+ 2.5 % TiO₂</td>
<td>Φ30 x 250 mm</td>
</tr>
<tr>
<td>3</td>
<td>Mg+ 5 % TiO₂</td>
<td>Φ30 x 250 mm</td>
</tr>
<tr>
<td>4</td>
<td>Mg+ 7.5 % TiO₂</td>
<td>Φ30 x 250 mm</td>
</tr>
<tr>
<td>5</td>
<td>Mg+ 10 % TiO₂</td>
<td>Φ30 x 250 mm</td>
</tr>
</tbody>
</table>

Figure 4.3 Photograph of Stir casting setup
The vacuum stir casting method in stages is used to fabricate five samples. Table 4.3 represents the proportion of particles with matrix material. The experimental set up to produce the samples is presented in Figure 4.3. The schematic view of the stir casting setup is presented in Figure 4.4. In the stir casting process the reinforcing phases usually in powder form are distributed into the molten magnesium by means of mechanical stirring. The raw materials used in experiments are represented in Figures 4.1 and 4.2 (a-b). The effect of high strength can be achieved by homogenous distribution of secondary particles in the matrix by stirring process.

**Figure 4.4 Schematic view of Stir casting setup**

Otherwise uneven distribution can lead to premature failures in both reinforcement free and reinforcement rich areas. The main concerned with this process is segregation of reinforcement particles that is caused by surfacing or settling of the reinforcing particles during the melting and casting processes. Since the magnesium alloy is highly sensitive to oxidation, there is a possibility of entrapment of gases and other inclusions in the stir casting process. This will further increase the viscosity of the molten metal and
produce imperfections within the material. Thus the stirring process needs to be more astutely controlled for magnesium alloys than aluminum alloys in order to prevent the entrapment of unwanted gases and other inclusions. Since magnesium is a flammable material and easily gets oxidized in the presence of oxygen, a shielding gas is required to control the atmosphere inside the furnace. The protection of this environment from the oxygen is prevented by the use of Argon. Argon is used for thermal insulation in energy efficient windows that the element undergoes almost no chemical reactions. The outer atomic shell makes argon stable and resistant to bonding with other elements. It is mostly used as an inert shielding gas in welding and other high-temperature industrial processes where ordinarily unreactive substances become reactive. At room temperature, Argon is chemically inert under most conditions and low thermal conductivity thus forms no confirmed stable compounds.

Under an applied stress, slip of dislocations and initiation of micro crack can occur in these areas relatively easily, eventually resulting in failure of the material. In the areas of significant segregation or agglomeration of normally highly brittle hard particles, weak bonds are formed in the material which can lead to the reduced mechanical properties of composites. The stirrer is used in stir casting process to avoid segregation of reinforcing particles which is caused by the surfacing or settling of the reinforcement particles during the melting and casting processes. The final distribution of the particles in the solid depends on material properties and process parameters such as the wetting condition of the particles with the melt, strength of mixing, relative density, and solidification rate. The distribution of the particles in the molten matrix depends on the geometry of the mechanical stirrer, stir- ring parameters, placing of the mechanical stirrer in the melt, melting temperature, and the characteristics of the particles added. (Poddar et al 2009) reported that the clusters of particles, porosity and high oxidation were controlled by stirring temperature. In our research work the matrix material is heated to
above liquidus temperature and the allowed to cool in between the stage of semi solid. The particles are preheated and then mixed with matrix material. Then the combinations of composites are heated again to above melting temperature of matrix material. The control panel set up to indicate the various temperatures to control the process is as shown in Figure 4.5.

The melting and casting is performed in stages to avoid the gas layer around the surface. Normally Particles have a thin layer of gas absorbed on their surface, which impedes wetting between the particles and matrix metals. In comparison with conventional stirring, the mixing of the particles in the semi -solid state can more effectively break the gas layer because the high melt viscosity produces a more abrasive action on the particle surface. The produced final samples are shown in Figure 4.6. The first three samples represent the composites after machining and next two represent before machining stage.

![Figure 4.5 Control panel of Stir casting setup](image)
4.4 MICRO STRUCTURAL STUDIES

4.4.1 XRD Analysis.

X-ray powder diffraction (XRD) is a powerful rapid analytical technique essentially used for phase identification of available crystalline material and also provides information on unit cell dimensions. First the material to be analyzed is finely ground and homogenized. It is used to determine the average bulk composition. X-ray diffraction is now a widespread technique for the learning of crystal structures and atomic spacing. X-ray diffraction is based on the principle of constructive interference between the monochromatic X-rays and the crystalline samples. These X-rays are supplied by a cathode ray tube and then the rays are filtered to produce monochromatic radiation. Then the rays are collimated to concentrate and again directed towards the fabricated samples. The interaction of the incident rays with the specimens produce constructive interference as a diffracted ray if it satisfies the conditions of Bragg's Law \((n\lambda=2d \sin \theta)\).
Figure 4.7 X-Ray Diffraction equipment.

The relationship between the wavelengths of electromagnetic radiation to the angle of diffraction is defined by this law. It provides the information about the lattice spacing in a crystalline sample. Finally the diffracted X-rays are detected, processed and then counted. The random orientation of the given material to all diffraction directions is attained by scanning the sample with a range of 2θangles. The diffraction peaks are converted into d-spacings which permits the identification of each constituent material in the samples. Then the values are compared with standard reference patterns. The X-Ray diffractometer equipment is presented in Figure 4.7.

The XRD patterns of the specimens prepared by stir casting process are shown in Figures 4.8 and 4.9. The samples are polished with mirror like surfaces with an automatic polisher. The phase analysis was carried out with a speed of 3 degree/ minute with a range of 0-100 degrees. The sample is placed in sample holder with the assurance of upper surface is flat. The sample and detectors are allowed to rotate certain angles corresponding the intensities of diffracted X-rays are continuously monitored and recorded. When the material contains the lattice planes and appropriate d-spacings to diffract X-rays, a peak value in intensity can be measured at the value of θ.
Figure 4.8 XRD pattern of Mg-TiO$_2$ Sample 1

Figure 4.9 XRD pattern of Mg-TiO$_2$ Sample 2
Each peak value has two separate reflections $K\alpha_1$ and $K\alpha_2$. But the peak locations may overlap with $K\alpha_2$ and appears as hump on $K\alpha_1$ at small values of $2\theta$. At the higher values of $2\theta$ the separation will be larger. Generally the combined peaks can be treated as one. The diffraction peak at $2\lambda$ position is usually measured at 80% peak height as the center of the peak.

As the intensities agree with the theoretical values, the increase in the peak areas gives the information about the kinetics of the reaction process. It means that the composite was formed with in the systems. From the XRD pattern shown in Figures 4.8 and 4.9, the main diffraction peaks corresponding to the phases of Mg and Ti were detected. The results are normally presented as peak positions at $2\theta$ and X-ray counts (value of intensity) were given in the form of a table or an x-y plot. Intensity ($I$) is either referred as peak height or the area under the peak as integrated intensity. The relative intensity can also be recorded as the ratio of the peak intensity to that of the most intense peak for reference. It is expected that the powder particle size can affect the process. It is observed that smaller particles of the elemental powder are more beneficial in the reaction between Mg and Ti. It is evident that TiO$_2$ is formed completely and a large quantity of molten magnesium fully infiltrates through the aperture gap of the particulate. In present scenario X-ray powder diffraction is most extensively used for the identification of minerals, inorganic compounds and unknown crystalline materials. The studies in material science, geology and environmental science the determination of unknown solids are critical to the researchers. The XRD analysis can be applied to identification of fine grained minerals otherwise it is difficult to identify optically, characterization of crystalline materials, measurement of unit cell dimensions and determination of sample purity. XRD can also be used to determine crystal structures, modal amounts of minerals, characterization of thin samples, mismatching between substrate and films, measuring dislocation densities and make textural measurements like orientation of grains.
4.4.2 EDAX Analysis

Energy Dispersive Analysis of X rays (EDAX) is often referred as EDX or EDS is the technique with the use of X-rays for the identification of elemental composition and chemical characterization of materials. The main components involved in this equipment are the excitation source (electron beam or x-ray beam), X-ray detector, pulse processor and analyzer. The applications may include the product materials research, trouble shooting and deformation. This system can be attached to electron microscopy instruments like Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) instruments.

The excitation of electron beam is also used in scanning electron microscopes (SEM) and scanning transmission electron microscopes (STEM). X-ray fluorescence (XRF) spectrometers are using X-ray beam excitation. A detector is used to convert X-ray energy in terms of voltage signals. The output signals are sent to a pulse processor that measures the values of the signals. The processor sends the measured signals to the analyzer for data display and further analysis. The capability of image capture identifies the specimen of interest. The data generated by EDAX analysis is corresponding to the elements present in the samples as showing spectra peaks. The mapping of elements and interpretation of image analysis can also be done with this equipment. For the contamination analysis and the investigations related to industrial forensic science the EDX is an essential tool. The specific advantage of this technique is non-destructive. There is no need for the separate preparatory works for the samples under examination.

It relies on the principle of an interaction of X-ray excitation from a source and a fabricated sample. It follows the fundamental principle of chemical elements. It is assumed that each element in the material has a unique atomic structure. That structure of the given material allows a
unique set of peaks when it is interacted with electromagnetic emission spectrum.

The characterizations of sample materials, machined from extruded bars were polished and characterized for their microstructures. The samples are polished with mirror like surfaces with an automatic polisher. The Energy-dispersive X-ray spectroscopy is used to identify the constituents of chemical elements in the prepared composites. The machined samples from EDM were given to EDX analysis for identifying the presence of particles and their peak values. The phase analysis was carried out with a speed of 3 degree/minute with a range of 0-100 degrees. As the intensities agree with the theoretical values, the increase in the peak areas gives the information about the kinetics of the reaction process. The X-Ray diffraction data were taken with a Rigaku D/Max-B x-ray diffractometer with Bragg – Brentano para-focusing geometry, a diffracted beam monochromatic, and a conventional copper target x-ray tube set to 40 KV and 30 mA. The EDX images for the reinforcements (2.5%, 5% and 10%) with magnesium matrix were presented in the Figures 4.10, 4.11 and 4.12. It is evident that TiO$_2$ is formed completely and a large quantity of molten magnesium fully infiltrates through the aperture gap of the particulate. From the images it is clearly observed that the Mg, Ti and O elements were present in the prepared samples.
Figure 4.10  EDS pattern of Mg + 2.5% TiO$_2$

Figure 4.11  EDS pattern of Mg+5 %TiO$_2$
Figure 4.12  EDS pattern of Mg+10% TiO$_2$

EDS equipment is not only used to identify the presence of chemical elements in a sample but also estimate their relative abundance. The various factors are influencing the accuracy of this quantitative analysis. Certain elements will have overlapping peaks in X-ray emission (e.g., Ti K$_{\beta}$ and V K$_{\alpha}$, Mn K$_{\beta}$ and Fe K$_{\alpha}$). Sometimes the nature of the sample affects the accuracy of the measured composition. X-rays are generated by any atom in the sample that is sufficiently excited by the incoming beam. Certain isotropic x rays are available to detect and measure chemical composition. The accuracy and precision of analysis are depending on the energy of the X-ray, the amount of composition and density of material. There is a possibility of deviation in accurate estimation of the sample composition from the measured X-ray emission spectrum due to X-ray absorption effect. Hence it requires the application of quantitative correction procedures that also referred as matrix corrections.
4.4.3 SEM Analysis.

Figure 4.13 Photograph of Scanning Electron Microscope

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The typical instrument setup is represented in Figure 4.13. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, and (in environmental SEM) in wet conditions. Magnification in a SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times. Unlike optical and transmission electron microscopes, image magnification in the SEM is not a function of the power of the objective lens. SEMs may have condenser and objective lenses, but their function is to focus the beam to a spot, and not to image the specimen. Provided the electron gun can generate a beam with sufficiently small diameter, a SEM could in principle work entirely without condenser or objective lenses, although it might not be very versatile or achieve very high resolution. In a SEM, as in scanning probe microscopy, magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device.
Assuming that the display screen has a fixed size, higher magnification results from reducing the size of the raster on the specimen, and vice versa. Magnification is therefore controlled by the current supplied to the x, y scanning coils, or the voltage supplied to the x, y deflector plates, and not by objective lens power.

4.4.3.1 Components of SEM

The components involved in a typical SEM are electron source, Thermionic gun, electromagnetic lense, vacuum chamber, Field emission gun, sample chamber with stage, computer, detectors (secondary electron, backscatter, diffracted backscatter, X-ray) etc. In addition to the above, it requires a stable power supply, vibration-free space and vacuum and cooling system. It is necessary the instrument is to be placed in an area that isolates from ambient magnetic and electric fields.

4.4.3.2 Imaging in SEM

An electron gun generates a beam of energetic electrons that are focused onto a series of electromagnetic lenses. The lenses are wrapped with coils. The coils can be adjusted to focus the incident electron beam towards the sample. It causes the fluctuations in the voltage and altering the speed of electrons comes in contact with the specimen surface. The operator can adjust the magnification through the electron beam and suitable location of the part to be scanned with the use of computer. The solid sample is placed in vacuum chamber through the stage. The electron beam is focused onto the sample. The interface between the incident electrons on the surface of the sample is evaluated by the acceleration rate of incident electrons that carry significant amounts of kinetic energy. The surface energetic electrons are released by the application of incident electrons onto the sample. The interface yields the effective information like size and shape, texture and sample composition via scatter patterns.
Figure 4.14 Sample images of Scanning Electron Microscope

(a) Pure Mg sample  (b) Mg+5 %TiO₂ (c) Ti particle in Mg matrix
(d) Mg+2.5 %TiO₂ (e) Mg+ 5 %TiO₂ (f) Mg+7.5 %TiO₂
Figure 4.15  Sample images of Scanning Electron Microscope
(a) Mg powder form  (b) TiO$_2$ powder form  (c) Mg+2.5 %TiO$_2$
(d) Mg+5 %TiO$_2$  (e) Mg+7.5 %TiO$_2$  (f) Mg+10 %TiO$_2$

The scattered electrons are attracted by variety of detectors including secondary, backscatter, diffracted and X-rays detectors. The backscatter electrons are incidental electrons that reflect backwards. The images can provide composition data related to element and compound detection. The diffracted backscatter electrons resolve crystalline structures in addition to the orientation of minerals and micro-fabrics. The X-rays detector
emitted from beneath of the sample surface gave the element and mineral information. Usually the SEM produces black and white and three-dimensional images for further analysis.

4.4.3.3 Specimen preparation

Before going to SEM characterization, the prepared specimens were systematically degreased and then dried to get rid of any outgasing from organic contamination. The specimens were ground on 800 grit SiC paper and again cooled with water. In order to get metallographic finish the samples were polished to 1 µm diamond finish using ethanol as lubricant. After cleaned by the volatile solvent, the samples were blown dry using a compressed gas to ensure the dusts are removed from the surface.

4.4.3.4 Characterization

The Scanning Electron Microscope (SEM) uses powerful magnification tool that again utilizes focused beams of electrons to obtain information. Because of its advantages like high-resolution and three-dimensional images SEM is widely accepted. It provides topographical, compositional and morphological information that makes them priceless in a multiplicity of science and industry applications. In order to characterize the microstructure of Mg-TiO₂ composites, Scanning Electron Microscope is used. The interface of Mg and TiO₂ is examined through the SEM. The grain size with its boundary of pure magnesium specimen is presented in Figure 4.14 (a). From the microscopic point of view the bonding within the magnesium matrix is ensured with less porosity. The image reveals the presence of small amount of TiO₂ particles which is shown in Figure 4.14(b). It is noted that free interference of the components are strongly connected and precipitate obtained.
The interface looks in a fine comportment shows the good bonding between the ceramic and matrix. The Metallographic examinations of the composite materials after the fabrication of samples revealed the uniform distribution of the TiO$_2$ reinforcing particles in the magnesium matrix. The structure obtained from the observation ensures the perfect bonding between the matrix and particles of composites. The particle of TiO$_2$ in variation in sizes that is not soluble in magnesium matrix is presented in Figure 4.14 (c). The magnification of 1000 x shows that very little micro pores are present on the surface. The upper surface of the fabricated samples with an of magnification of 100µm are presented in Figure 4.14 (d-f). Figure 4.14 (d) represents the combination of Mg with 2.5% TiO$_2$ particles. Figure 4.14 (e) represents the combination of Mg with 5% TiO$_2$ particles. Figure 4.14 (f) represents the combination of Mg with 7.5% TiO$_2$ particles. With the aid of SEM images, the designer can found the morphology of the surfaces with different reinforcement condition.

The powder form of pure magnesium sample is presented in Figure 4.15 (a). The powder form of titanium dioxide sample is presented in Figure 4.15 (b). This type of images is more helpful to find the interspacing between the reinforcement particles, grain sizes and grain boundary between the particles. Figure 4.15 (c) represents the combination of Mg with 2.5% TiO$_2$ particles. In the interpretation small sizes of micropores are found. Figure 4.15 (d) represents the combination of Mg with 5% TiO$_2$ particles. The ribbon like structures was found in the image. The magnification 500x is used in images (c and d). Figure 4.15 (e) represents the combination of Mg with 7.5% TiO$_2$ particles. The particles with clear grain boundaries were found in this image. Figure 4.15 (f) represents the combination of Mg with 10% TiO$_2$ particles. The primary and eutectic phases were found in the SEM image. When comparing the images from 4.15 (c-f), the variation in the percentage of reinforcement particles can be easily determined.
4.5 TESTING OF MECHANICAL PROPERTIES

4.5.1 Density Test

One of the most important physical characteristic of matter is its density. All objects have density and that may increase or decrease as the result of actions taken on the object. The personal property of density is important for the mechanism of the universe and for our daily lives. It is quite simple to find the density of an object and see the outcome of density. The density or more accurately the term volumetric mass density of a substance can be represented as mass divided by its unit volume. Density may increase either with increasing mass or with reducing volume. For a pure substance or material the value of density has the same numerical value as its mass concentration. Since the composites are composed of two or more constituent materials the density may vary according to their percentage of contribution. It is obvious that different materials usually may have different densities. In addition to that the density may be relevant to buoyancy, packaging and purity.

In order to compare the densities across various systems of units, sometimes it can be replaced by the dimensionless quantity known as relative density or specific gravity. It can be expressed as the ratio of the density of the determined material to that of a standard material, usually water. Thus a relative density is less than one means that the substance can float in water. Often the density of extruded specimens was estimated with Archimedian principle. It states that when a body is fully or partially immersed in a fluid, there will be a chance for exertion of the upward buoyant force and its numerical quantity should be equal to the weight of the displaced fluid by that body. The direction of force always acts in the upward direction at the center of mass of the displaced fluid. Archimedes' principle is a basic law of physics and applicable to fluid mechanics. In practice this principle allows the buoyancy of an object under the above condition is to be calculated. The
downward force on the object is merely its weight. The upward or buoyant force on the object is that confirmed by Archimedes' principle. Thus the resultant upward force on the object is the difference between the buoyant force and its weight. The value of this resultant force is positive, the object rises and negative, the object sinks. If there is no positive or negative i.e zero, the object is neutrally buoyant. The actual density can be calculated by determining the specimen mass and volume, and basing on the apparent loss of weight after immersing the specimen in water. The prepared samples were first weighed in air. Then the samples were tied with a string then weighed in while hanging in water. Then the density is calculated by the following general formula (4.1).

Density of specimen

\[ \frac{\text{Wt. of sample in air} \times \text{density of water}}{\text{Wt. of sample in air} - \text{Wt. of sample in water}} \]  

(4.1)

The theoretical density of each composites were determined by comparing the sum of volume (weight divided by the respective density) of constituents and the volume of composite. The sample immersed in a fluid is as shown in Figure 4.16. The percentage of porosity is calculated by using the following equation (4.2).

\[ \text{% of porosity} = 1 - \frac{\text{measured density} \times 100}{\text{theoretical density}} \]  

(4.2)
Figure 4.16 photograph of sample immersion in water

Most of the applications in automobile industries especially in internal combustion engines require low dense materials for their intended operations. In other heavy applications such as bullets a high density is preferable for high impact forces. High density is also important where inertia is a consideration, for example in counterweights for rotating components. The density is important because in many different constructions there is a need for light enough to float (as the case of boats in marine applications) or easily be suspended in air (planes).

4.5.2 Hardness Test

Hardness is the mechanical property of the material that enables it to resist plastic deformation habitually by penetration. But also it refers to resistance to scratching, bending, abrasion or cutting. It provides resistance to indentation and could be determined by measuring the depth of indentation. Hardness testing is divided into two categories macro-hardness and micro-hardness. Macrophase covers testing with an applied load over 1 kg or about 10 Newton (N). Micro-hardness testing, with applied loads less than 10 N, is normally used for smaller samples, thin specimens, plated surfaces or thin films. Hardness is not a fundamental physical property but characteristic of a material. The measurement of hardness is not defined by the fundamental units like Length, Mass and Time. The relative hardness measurements are
used commonly now a day. But this method has certain limitations in practical use and do not provide exact numeric data or scales predominantly for modern day metals and materials. The standard method to attain a hardness value is based upon the indentation area or depth, applied force and time.

### 4.5.2.1 Macrohardness

Rockwell, Vickers, and Brinell, are three principal standard test methods to express the relationship between hardness and the size of the impression. Each of these methods is separated into a range of scales, defined by a combination of indenter geometry and applied load for practical and calibration reasons.

**Figure 4.17 Rockwell hardness tester**

The accurate hardness conversion between various methods and scales for a wide range of materials is a trivial task for the designers. The values of hardness of the materials are depending upon the consideration of homogeneity of specimen, shape of indenters, cold working properties as well as elastic properties and different loads causes the problem into more complication. The conversion tables and charts are prepared with approximate equivalents, particularly when converting to a method or scale which is actually impossible for the particular test material and thus cannot be confirmed.
The Rockwell hardness tester with ASTM E-18 standard is adopted to check the macro hardness of the fabricated composites. The Rockwell hardness setup to determine the macrohardness values is presented in Figure 4.17. The samples were machined up to the required size to conduct the experiments. It consists of application of load with indenting the test material by the use of diamond cone or hardened steel ball indenter. The ball indenter is pressed into the test material under a preliminary minor load usually 10 kgf. When it is reached into equilibrium, an indicating device moves based on the movements of the indenter and responds to changes in depth of penetration of the indenter is set to as a datum position. Then the preliminary minor load along with an additional major load is applied with resultant increase in penetration. If it comes to equilibrium then the additional major load is detached but the preliminary minor load is still maintained. The removal of the additional major load permits a partial recovery, thus reducing the depth of penetration. The calculations were made on the permanent increase in depth of penetration, resulting from the application and removal of the additional major load for the Rockwell hardness number. The macro hardness of polished cross-sections was determined on the Rockwell 15 T superficial scale using a 1/16 in. diameter steel ball indenter with a 15 kg major load, in accordance with the ASTM E18-92 standard. Five indentations were made on each of the transverse section of samples. The hardness values are estimated for both pure magnesium and fabricated composite materials reinforced with the TiO₂ phase particles. Finally the average hardness of each samples were calculated and plotted as a curve.

4.5.2.2 Microhardness

The two most common techniques used for measuring microhardness are Vickers and knoop hardness tests. The Vickers hardness with ASTM E-384 standard is selected to measure the micro hardness of the Mg -TiO₂ composites. This standard specifies a wide range of light loads using a
diamond indenter to make an indentation on the sample which is measured and converted to a hardness value. This method is very useful for testing various types of materials, but test samples should be highly polished to facilitate measuring the size of the impressions. A square pyramid shaped diamond is used for testing in the Vickers scale. The Vickers setup is presented in Figure 4.18. It uses an indenter probe that is displaced into a surface under an applied specific load. The indentation naturally has a defined dwell time. Like the traditional mechanical testing, the size or depth of indentation is measured to determine value of hardness. The Vickers test has the vast advantage of one hardness scale being used to test all materials. The indenter must be placed perpendicular to the test specimen. It is learnt that an error of even less than 2° from perpendicular will distort the indentation shape and introduce errors. A larger tilt angle may cause the specimen to move under the applied force. The mounted specimen is placed within this device and ensures that the plane of polish is automatically indexed perpendicular to the indenter. In order to ensure the reproducibility in the hardness test an automated test cycle of loading with the application for the desired time and unloading is used. During the testing the vibrations must be carefully controlled, because of the applied force decreases. Manual application and removal of the applied force for the micro hardness testing is not recommended due to the difficulties in controlling vibrations that causes the changes in indent size. In this test, the force is applied smoothly without impact and detained in contact for 15 seconds as dwell time. The force must be controlled specifically. After removal of the applied force, both diagonals are measured and the average is used to calculate the HV according to the loads of 500 gf.
The hardness value can be calculated by using the following mathematical expression.

\[HV = \frac{2000 L \sin\left(\frac{\alpha}{2}\right)}{d^2} = \frac{1854.4 L}{d^2}\]  \hspace{1cm} (4.3)

Where \(d\) is the mean diagonal length (\(\mu\)m), \(L\) is the load (gf) and \(\alpha\) is the face angle (136°).

In order to align with usable Brinell hardness numbers the angle of 136° between the opposite faces was preferable. The hardness calculation is purely based on the diagonals length and the problem is in identification of indent tips. It requires proper illumination, adjustment of the optics for best resolution and contrast, and careful focusing of the specimen. The micrometer lines have a limited thickness. Before the measurement, it should be ensuring that two filar lines just into contact and then zero the micrometer. The interior sides of the filar lines shall be adjusted so the indent tips just touch each line. The light source should provide sufficient even illumination for maximum contrast and resolution. The accuracy of the filar micrometer or other measuring device should be verified using a stage micrometer.
4.5.3 Tensile Test

The assessment of the mechanical behavior of the prepared samples under conditions of tension and compression is performed to provide basic material property data that is critical for component design and service requirements. The importance of tensile and compression strength values and the suitable standard methods for testing these properties are specified for the variation of particles in magnesium matrix. These mechanical property tests are characteristically performed using a universal mechanical testing instrument. A tensile test is a method for determining behavior of materials under axial tensile loading. The tensile testing equipment with tensile sample is presented in Figure 4.19. The tests are conducted by fixturing the specimen into the test apparatus and then applying a force to the specimen by separating the testing machine crossheads. The crosshead speed can be varied to control the rate of strain in the test specimen. Data from the test are used to determine tensile strength, yield strength, and modulus of elasticity. Measurement of the specimen dimensions after testing also provides reduction of area and elongation values to characterize the ductility of the material. Tensile tests can be performed on many materials, including metals, plastics, fibers, adhesives, and rubbers. Testing can be performed at sub-ambient and elevated temperatures. A test specimen is the most significant component of tensile testing for it defines the actual physical property of the material being tested. The specimen must conform to accurate physical dimensions and must be free of induced cold working or heat distortion. The selection of appropriate qualified laboratory personnel and perfectly calibrated tensile machines are important, since the ultimate test results are based on the quality and accuracy of the prepared test specimen. A precision milling machine with a highly skilled machinist and considerable hand finishing can achieve the required configurations of the test specimen. However, the slow milling cutter speeds because heavy chip loads and can induce severe internal distortion to the
machined edges. The amount of induced cold working or heat distortion could not be determined by visual inspection; hence test results frequently produce erratic and inaccurate tensile properties.

Figure 4.19 Tensile testing equipment

Static tensile tests of the fabricated composite materials were made with the ASTM Standard B557 -06 is followed at room temperature.

Figure 4.20 ASTM specimen standard for tensile test

The examined test pieces in the tensile test have a overall length of 65 mm and gauge length 15 mm. The ASTM standard cylindrical tensile specimen is shown in Figure 4.20. Two specimens from each combination are used to measure the values of the yield stress (YS) and ultimate tensile strength (UTS) by using standard universal testing machine.

Compressive strength or compression strength is the capacity to withstand the applied loads for the given material or structure. Unlike the
tensile strength test it tends to reduce size specifically length of the specimen.

4.5.4 Compression Test

A compression test is used to determine behavior of materials under crushing loads or compressive (push type) load. The given specimen is compressed by the application of loads and deformation at various loads is monitored. Usually the Compression tests are conducted by loading the test specimen between two plates, and then the force is applied to the specimen by moving the crossheads together. During the test, the specimen is compressed, and deformation versus the applied load is perfectly recorded. Compressive stress and strain are calculated and plotted as a stress-strain diagram. The compression test is used to determine elastic limit, proportional limit, yield point, yield strength, and (for some materials) compressive strength.

![Figure 4.21 Compression testing setup](image)

The measurement of the plastic flow behavior and ductile fracture limits of a material can be determined by axial compression testing as per the ASM hand book. In measuring the plastic flow behavior of a material requires homogenous compression test conditions, while measuring limits of ductile fracture took advantage of the barrel formation and controlled stress and strain conditions at the equator of the barreled surface when compression is carried
out with friction and variations of the strains during a compression test. The axial compression testing is also helpful for measurement of elastic and compressive fracture properties of brittle materials or low-ductility materials. In any case, the use of specimens having large L/D ratios should be avoided to prevent other modes of deformation like buckling and shearing. The compression testing set up is presented in Figure in 4.21.

4.5.5 Impact Test

An impact test is an energetic test conducted on a selected specimen(s) that is usually notched. The specimens are usually struck and broken by a single blow in a specifically designed machine. The impact strength is the ability of a material to absorb shock and impact energy without breaking. The impact strength is calculated as the ratio of impact absorption to test specimen cross-section. The aim of conducting this experiment is to measure the toughness or energy absorption capacity of the given materials or composites.

![Figure 4.22 (a) Impact testing machine (b) Test specimen](image)

Toughness is mainly dependent upon temperature and the shape of the test specimen. Generally an impact is a high force or shock applied over a short time period when two or more bodies collide. Such a force or acceleration usually has a greater effect than a lower force applied over a proportionally longer time period of time. The effect depends critically on the
relative velocity of the bodies to one another. The impact tester is presented in Figure 4.22(a). The size and notch dimensions are presented in Figure 4.22(b). The impact test is dependent on the size of the specimen and notch. The specimens with different composition of Mg-TiO$_2$ composites are placed horizontally like the simply supported beam. The notches are positioned accordingly to be hit by the pendulum arm. The pendulum is released from the rest position and energy absorbed by the material noted from the readings scale.

4.6 DRY SLIDING WEAR TEST

Dry sliding wear tests were conducted using a computerized pin-on-disc tester.

![Figure 4.23 Pin on Disc wear testing machine](image)

4.6.1 Objectives of wear test

The objectives of conducting dry sliding wear test with the use of pin on disc machine are

- To measure and analyze the wear characteristics of the fabricated specimens.
• To find the influencing parameters on the wear characteristics
• To optimize the wear output.
• To ascertain the validation of friction laws.

4.6.2 Equipment used for wear test

The pin on disc equipment and wear specimens are presented in Figure 4.23. The wear tests were carried out as per ASTM G-99. The machine consists of a single lever arm connected with a ball (pin) on disc. The standard size of the disc is Φ165 mm x 8mm thickness. The rotating disc is made up of En-31 hardened to 62 HRC material to conduct the tests smoothly without any problems due to the environmental conditions. The range of loads can be applicable to this apparatus is 1 N to 200N with the variation in steps of 5N.

![Figure 4.24 Schematic view of Pin on Disc wear testing machine](image)

The variation in the size of the dead weights are available that can be added whenever required. The size of the dead weights is 0.1, 0.2, 1, 2 and 5Kg. The rotational speed of the disc is ranging from 200 rpm to 2000 rpm. It can be changed and infinitely variable in steps of 1 rpm. The applicable range of frictional load is up to 200N. The applicable least count is 0.1 N. The accuracy of 0.1 ± 2 % measured friction force in N can be obtained. The range
of wear measurement can be performed up to 2000 µm. The sensor used to measure the wear is ‘syscon’ make LVDT with a least count of 1 micron. The instrument is having the accuracy of 1 ± 1 % measured wear in microns. The general purpose wear track diameter is Φ50 mm to Φ100 mm and flexible to vary according to the requirements. The standard size of the Pin / ball diameter is 3mm, 6mm and 10mm. The loading system consists of dead weight that can be easily added or removed as per the requirements of the designers. The TAP make PNP type model APS-8 proximity sensor is connected with the system in order to measure the rotary measurements. The least count is 1 rpm and having the display accuracy of 1 ± 1 % measuring speed. The applicable range of sliding speed is between 0.5 m/s and 10m/s for the wear tests. The lubrication module is connected with re-circulation system. The measurements of wear and other parameters can be done with computer integrated data acquisition system. The multiple test reports can be compared with utilization of advanced comparative view. The safety interlocks systems are available to ensure the safe operations of the sample wear tests. The schematic view of components involved in a Pin on Disc wear test arrangement is presented in Figure 4.24.

![Figure 4.25 wear testing monitoring unit](image-url)
4.6.3 Preparation of wear test specimens

The sectioning of pin specimens of size 10mm X 10mm x12mm were machined by Electrical Discharge Machining (EDM). The sample specimens are presented in Figure 4.26. Before going to this wear test the specimen pins should be thoroughly cleaned and burns from the circumference must be removed. The contact surfaces were prepared by grinding against 600-grit silicon carbide paper and cleaned with alcohol. A pin-holder loaded the stationary pins vertically onto a rotating AISI-O1 tool-steel disc, which had been oil-hardened to 63 HRC. All experiments were conducted in air with temperature and relative humidity maintained between 20-25 °C and 55–67%, respectively. The weight of the cleaned specimen is measured before the contact of the pin with disc with the accurate weighing machine with an accuracy of 0.01 mg. The wear disc is cleaned with solvent and then allowed to dry for conducting the experiments. This step is to be necessarily repeated for each test to get the required accuracy of measurements.

4.6.4 Testing methodology

The selected pin specimen is clamped in the pin holder with the use of hardened jaws to the other end of loading lever tip. It is ensured that the pin is fitted with relevant size clamp. Prior to conduct the experiments the wear track radius is set. The pin is positioned in the disc between Φ50 to Φ100 so that wear can be used for many tests by proper positioning of the specimens at different diameter. For the wear rate calculations the position of the pin in wear track is very important. The sliding plate is unscrewed to loosen for fixing the correct position of the pin with the use of graduated scale and then clamp screw is tightened. The disc speed is set by the control of timer. By pressing the start push button and turn the knob on the controller in clockwise direction the disc will rotate. It is ensured that required testing speed is displayed in the monitoring and control unit. The process is monitored and allowed continuously to run for the remaining time in order to observe any
fluctuations. The desired velocity is based on the calculation from the speed and radius of the wear track. The required weights can be placed in the loading pan without shaking the equipment. Once start button is used the data is sent automatically to portable computer with the aid of sensors and data acquisition system. In the controller unit the acquired test parameters like wear, speed, friction force and room temperature are displayed. The same values are simultaneously displayed in the computer and the concerned graph is plotted. The necessary parameters are monitored, measured and recorded for further analysis calculations. A load cell is mounted on the lever are to measure the friction force. It is placed in between the pivot and pin. The maximum capacity to measure the load cell is 200N. The corrosion resistant high strength steel with high stability foil type strain gauge is used to measure the load cell. The tangential force acting on the pin due to the action of the holding beam is converted into the load cell. Then the deformation is sensed by the strain gauge and the corresponding measurement is recorded for further calculations. Since the strain gauge is directly connected with wheat stone bridge circuit the strain conditioning and balancing is automatically balanced and again displayed in the control panel. The stop button is pressed to finish the test. For our experiments, four normal loads (10, 15, 20 and 25 N) were applied using dead weights, and three sliding speeds (1, 1.5, and 2.0 m/s) were selected. The pin on disc machine is connected with computer as well as monitoring and control unit. The components of control unit include pre-set timer, pin temperature monitoring unit, wear monitor, friction force, sliding speed in rpm and power switch. The controlling and monitoring unit is presented in Figure 4.25.
4.6.5 Wear calculations

The sliding velocity and sliding distance can be derived by using the following mathematical expression.

\[
\text{Sliding velocity} = \frac{\pi DN}{60000} \tag{4.4}
\]

\[
D = \text{Diameter of wear track in mm.}
\]

\[
N = \text{Disc speed in rpm.}
\]

\[
\text{Sliding velocity in m/s.}
\]

\[
\text{Sliding distance} = \frac{\pi DN T}{60000} \tag{4.5}
\]

\[
T = \text{Time duration in sec.}
\]

The desired sliding velocity is achieved with the help of wear track and motor speed in rpm. Linear wear rate is directly observed and monitored by the application of linear variable differential transformer (LVDT). The sensor is placed at exactly same distance of pin from the pivot. The lever ratio of 1:1 can be used to calculate wear of the specimen directly by the LVDT. The plunger sensor is placed in the hardened pin projection. If the wear occurs in the pin then it will automatically uplift the lever arm in upward direction.
These changes are monitored and recorded in the wear measurement in the control panel. The least count of LVDT is 0.1 µm. The initial position is set in between positive and negative. Hence both type of wear can be monitored with this equipment and maximum range is 2 mm.

4.6.6 Data evaluation and reporting

The variation in the applied loads, percentage of reinforcement particles, sliding velocity and its effects on the wear losses are tabulated for further analysis. Then the data are plotted in the graphical representation. The trend and inferences are recorded. The losses in mass are converted into the losses in volume with the use of concerned densities.

4.6.7 Surface roughness test

The surface finish indicator is used to measure the surface finish of fabricated worn-out specimens. The term roughness is the relatively irregularities with finely spaced and superimposed on a waviness pattern. The product and its interaction with the environment are influenced by the surface roughness. It has been investigated that the surface texture greatly influences the functioning of the machined parts. The properties like corrosion resistance, wear resistance and fatigue resistance were greatly depend upon the surface texture. The Mitutoyo make surface roughness tester is used to measure the surface characteristics of the machined samples. The surface roughness tester is presented in Figure 4.27. The parts involved in this type of equipment are tracer head and amplifier. Usually the tracer head has a diamond stylus with a point radius of .0005 µin. The tracer head is moved on the upper surface of fabricated samples before and after the conduct of wear test. The movement caused by the irregularities in the surface is converted into the electrical fluctuations. The amplifier magnifies the fluctuations as signals then registered on meter. The meter reading will indicate the average height of the surface.
The surface irregularities can be measured in several forms like waviness, flaws, roughness, lay and profile. Normally the surface deviations are the departures from the nominal surface. Initially the tester is allowed to turn on for warm up. The machine is checked for the calibration by moving the tracer head on the test block. If necessary the calibration control may be adjusted. The cut-off range is set as 0.010. The surface to be measured is thoroughly cleaned to ensure the accurate readings and protecting the stylus. The readings are noted from the meter.

4.7 MATHEMATICAL MODELLING & OPTIMIZATION TECHNIQUES

Based on the data collected from the dry sliding wear test, the process parameters are optimized to get the desired response. The complete process with regression analysis, curve fitting and optimization techniques like Box-Behnken and Mixture design are explained with detail in Chapter 6.

4.8 ARTIFICIAL NEURAL NETWORK MODEL

The construction of Artificial Neural Network, types of learning, learning laws, learning with back propagation algorithm, predicting and evaluation of wear data, comparison of predicted versus experimental values and confirmation test are explained with detail in Chapter 7.
4.9 CORROSION STUDY

The need, types of corrosion, evaluation of corrosion, potentiodynamic polarization and cyclic impedance spectroscopy methods and their plotted curves are explained with detail Chapter 8.

4.10 SUMMARY

This chapter presents the details about selection of materials for the matrix and reinforcement, working principle of stir casting process and its safety precautions, manufacturing of composite specimens, micro structural studies of developed composite specimens, experimental investigations on density and its measurement and then comparisons, both macro hardness and micro hardness tests, tensile strength, impact strength, compression strength, and wears behaviour of the composite specimens by using dry sliding test with computerized pin on disc method. XRD, EDS, EBSD and Scanning Electron Microscope (SEM) studies to analyze the influence of particle size on wear mechanisms were also discussed.