CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Introduction

The materials, experimental setup, several characterization instruments, and complex techniques utilized to conduct the experiments to meet the study's objectives are all described in detail in this chapter. A description of the equipment and techniques used to characterize the microstructures and mechanical and tribological properties of the produced composites has also been provided. Pure copper has also been cast and characterized to compare its qualities with the produced copper-based hybrid composites. Figure 3.1 illustrates a steps flow diagram for fabricating of copper-based hybrid composites.

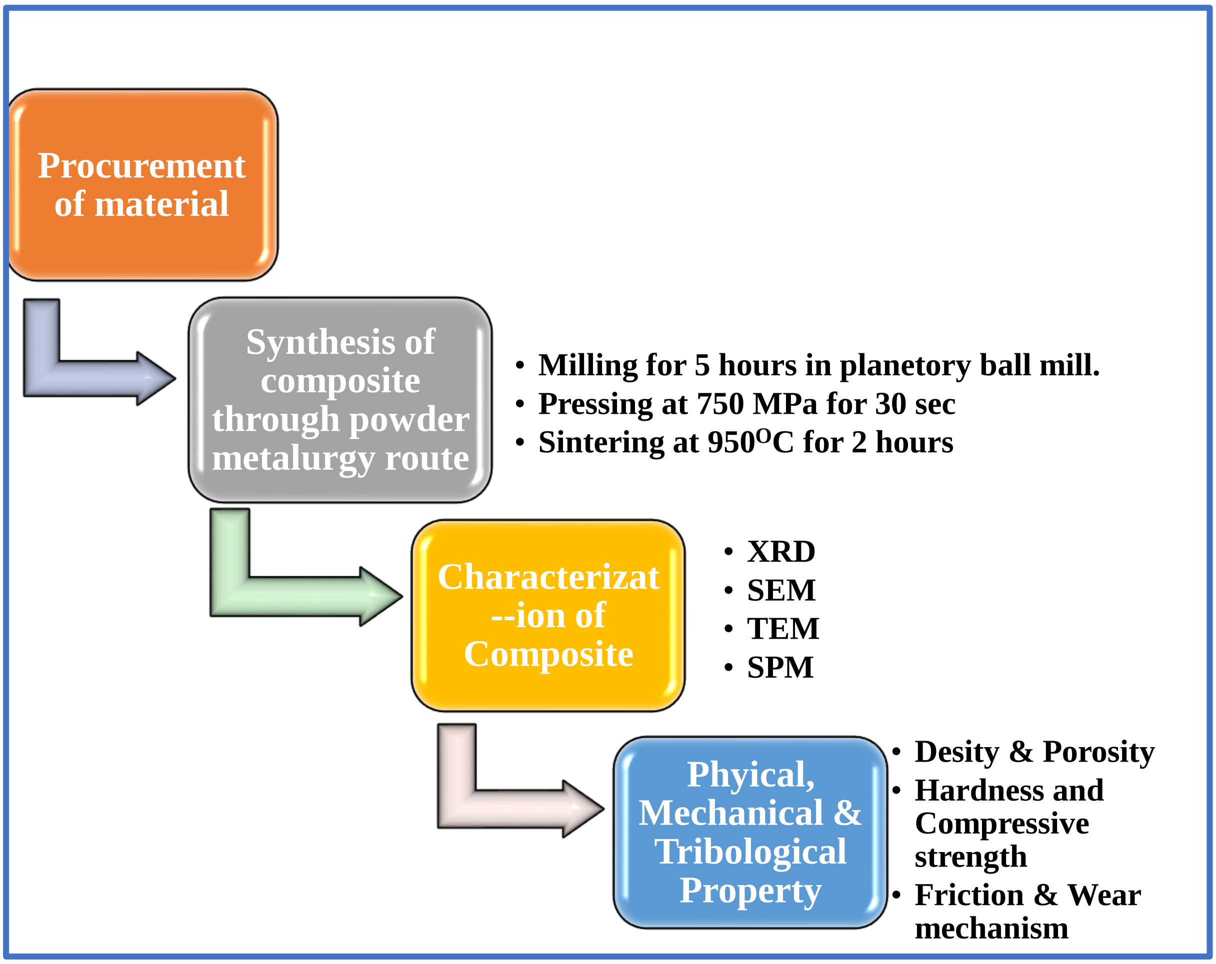

Figure 3.1 Flow diagram for synthesis and characterization of copper-based hybrid composite.

3.2 Material selection for Preparation of copper matrix composites

the copper metal matrix composites were developed by combining the pure copper powder with two wt.% chromium (purity 99% purchased from Sigma Aldrich), electrolytic copper (purity 99.5% purchased from CDH in Gujarat, India) with 354 mesh mean particle diameters, boron carbide (average particle size 90 mesh, 98.0% purity purchased from CDH in Gujarat, India), silicon carbide (average particle size 220 mesh, 99.0% purity purchased from CDH in Gujarat, India) and graphite (average particle size 150 mesh, 95.0% purity purchased from CDH in Gujarat, India) in different concentrations. The composition of the specimen and the coding materials employed in the investigation are shown in Table 3.1

Table 3.1 Specimen's Compositions and its Coding

<table>
<tr><th colspan="5">Cu-B_4C -Gr composites</th></tr>
<tr><th>S. No.</th><th>Specimens Code Name</th><th>Compositions</th><th>Purity (%)</th><th>Total Weight (%)</th></tr>
<tr><td rowspan="4">**1**</td><td rowspan="4">**CU01/C1**</td><td>Copper</td><td>99.5</td><td>100</td></tr>
<tr><td>Chromium (Cr)</td><td>99.0</td><td>0</td></tr>
<tr><td>Graphite (Gr)</td><td>95.0</td><td>0</td></tr>
<tr><td>Boron carbide(B_4C)</td><td>98.0</td><td>0</td></tr>
<tr><td rowspan="4">**2**</td><td rowspan="4">**CU02/C2**</td><td>Copper</td><td>99.5</td><td>95</td></tr>
<tr><td>Chromium (Cr)</td><td>99.0</td><td>2</td></tr>
<tr><td>Graphite (Gr)</td><td>95.0</td><td>1.5</td></tr>
<tr><td>Boron carbide(B_4C)</td><td>98.0</td><td>1.5</td></tr>
<tr><td rowspan="4">**3**</td><td rowspan="4">**CU03/C3**</td><td>Copper</td><td>99.5</td><td>92</td></tr>
<tr><td>Chromium (Cr)</td><td>99.0</td><td>2</td></tr>
<tr><td>Graphite (Gr)</td><td>95.0</td><td>3.0</td></tr>
<tr><td>Boron carbide(B_4C)</td><td>98.0</td><td>3.0</td></tr>
<tr><td rowspan="4">**4**</td><td rowspan="4">**CU04/C4**</td><td>Copper</td><td>99.5</td><td>89</td></tr>
<tr><td>Chromium (Cr)</td><td>99.0</td><td>2</td></tr>
<tr><td>Graphite (Gr)</td><td>95.0</td><td>4.5</td></tr>
<tr><td>Boron carbide(B_4C)</td><td>98.0</td><td>4.5</td></tr>
<tr><th colspan="5">Cu-SiC-Gr composites</th></tr>
</table>

S. No.	Specimens Code Name	Compositions	Purity (%)	Total Weight (%)
1	**S1**	Copper	99.5	100
		Chromium (Cr)	99.0	0
		Graphite (Gr)	95.0	0
		Silicon carbide (SiC)	99.0	0
2	**S2**	Copper	99.5	95
		Chromium (Cr)	99.0	2
		Graphite (Gr)	95.0	1.5
		Silicon carbide (SiC)	99.0	1.5
3	**S3**	Copper	99.5	92
		Chromium (Cr)	99.0	2
		Graphite (Gr)	95.0	3.0
		Silicon carbide (SiC)	99.0	3.0
4	**S4**	Copper	99.5	89
		Chromium (Cr)	99.0	2
		Graphite (Gr)	95.0	4.5
		Silicon carbide (SiC)	99.0	4.5

3.3 Preparation of the copper-based hybrid composites

The present study involved the development of novel composite specimens through the conventional powder metallurgy technique. For every composite, the material was blended in a ball mill, as shown in Figure 3.2 (c), for 5 hours at 250 rpm. The ball-to-powder ratio was taken as 10:1 (R & Rao, 2018). The homogenous blended mixture was compacted in a die set using a hydraulic press shown in Figure 3 (b) at 750 MPa. Three specimens were prepared from each composite mixture. The die set involves a die, plunger, and bottom pallet, as shown in Figure 3.2 (a), which were made up of die steel. The compacted green pellets that were obtained from the die have a thin crown edge on one side of their flat circular area; they are removed smoothly from it before sintering. The compacted green pellets were followed by the sintering process; in this process, an argon control atmospheric furnace is used. In this process, the green specimen is placed in an inert environment, which is achieved by applying a vacuum to the chamber to suck out all the air and then supplying it with argon to make the environment inert.

The sintering temperature was kept at 950 °C, the holding time was 1.5 hours, and the temperature rise and fall were maintained at 5 °C per minute. The other metal oxide formation during the sintering process was controlled using an inert environment made of argon (Stalin et al., 2021). The sintered specimens had the same shape as the green specimens, although they had a different surface finish, as shown in Figure 3.2(d). The sintered samples were then polished via emery paper of grades 600, 800, 1000, 1200, 1500, and 2000 for microstructural analysis and other characterizations. The density of the developed samples was measured using the Archimedes principle, and a pin-on-disc tribo-tester was used for the tribological behaviours.

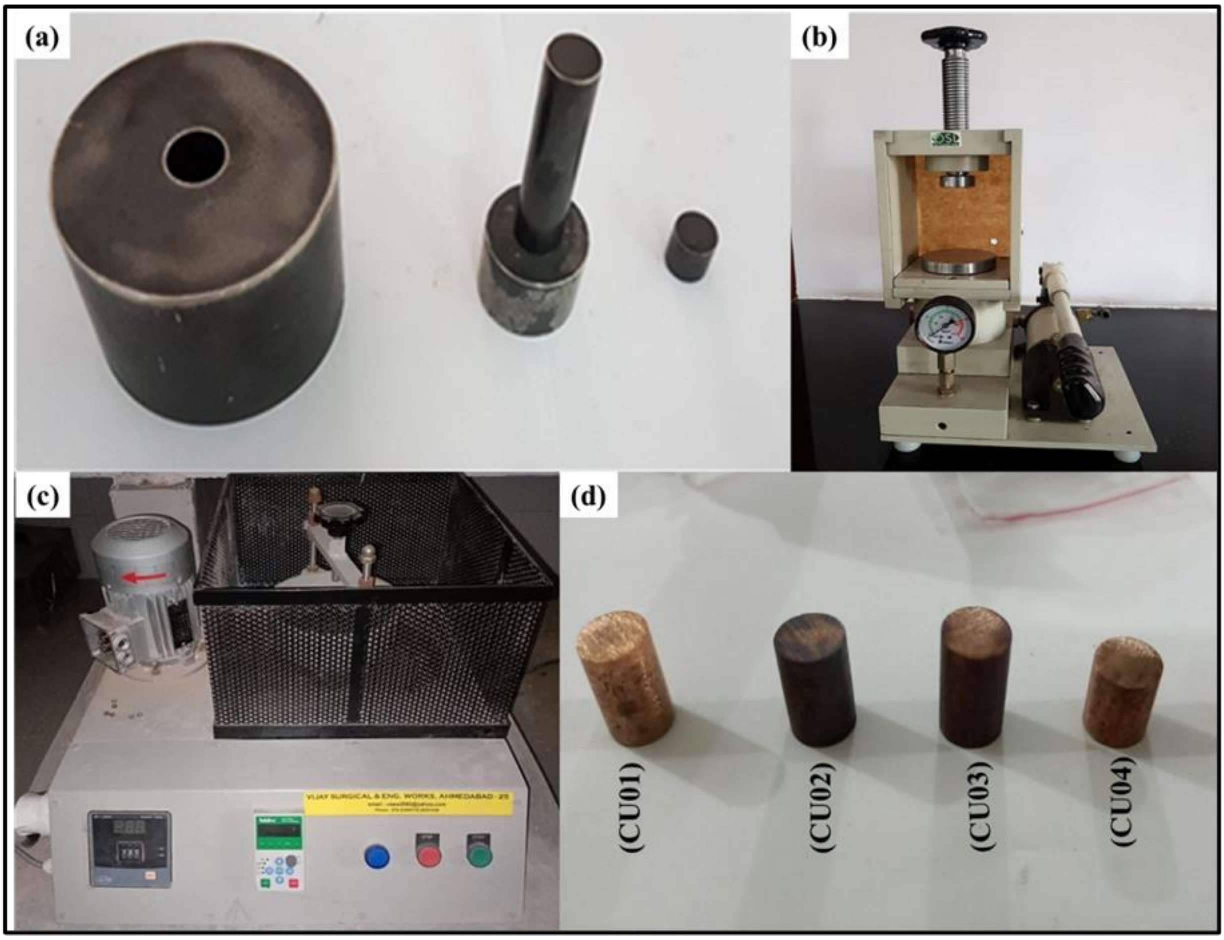

Figure 3.2 (a) Die, Plunger, and Pallet; (b) Hydraulic Press Machine; (c) Ball Milling Machine; (d) Sintered Specimens

3.4 Characterizations of Copper Composites

The subsequent sub-section provides a comprehensive account of the methods and procedures employed to Analyse the microstructural, mechanical, electrical, and tribological properties of the copper matrix and copper composites in the current study.

3.4.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis is a technique used to detect the existence of various phases, determine the crystallographic parameters, and evaluate the level of crystallinity. X-ray diffraction (XRD) examination involves directing a beam of X-rays over a specimen, where the X-rays interact with the atoms present in the material. When the X-rays interact with the crystal lattice, they experience diffraction, resulting in the formation of a distinct diffraction pattern. The peaks in this pattern correlate to the spatial arrangement of the atoms within the crystal lattice. Analysing the positions, intensities, and forms of the diffraction peaks can yield valuable insights. Additionally, it determines several crystal phases inside the composite by analysing the unique diffraction patterns generated at each stage. Moreover, lattice parameters, unit cell diameters, and crystal symmetry are among the crystallographic properties of the composite that can be determined by XRD examination. These characteristics provide insightful information on the crystal structure, facilitating a more profound comprehension of the material's characteristics.

An X-ray diffraction analysis was conducted on copper matrix and composite specimens to determine the lattice strain, crystallite size, and phases present. The Rigaku Desktop Miniflex II X-ray diffractometer (Tokyo, Japan) was used to analyze X-ray diffraction (XRD). The XRD was conducted with a Ni-filtered Cu-K† emission (λ=1.5406Å) at an operating voltage of 40 kV and a current of 30 mA. The scanning rate was set at 2^{o}/min, and the analysis was conducted in the angle (2θ) range of 20–80°.

To determine the interplanar spacing, d, for each intensity peak and its corresponding value of 2θ, Bragg's equation (Eq. 3.1) was applied. This law detects distinct phases with the assistance of X-ray diffraction statistical information (JCPDS).

$$\mathbf{2d\sin\theta = n\lambda} \tag{3.1}$$

where, **θ** - Incident angle

λ - Wavelength of the X-ray

n - An integer representing the order of the diffraction.

3.4.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a useful technique employed to analyse and describe the microstructure of materials. Scanning electron microscopy (SEM) enables the analysis of the external structure of copper-based hybrid composites, including the characteristics of particles or grains, such as their form, size, and texture. Images with excellent resolution can be generated by this method, making it possible to analyze the microstructure and locate any imperfections or abnormalities. Because the electron beam's wavelength is far shorter than that of visible light, it is possible to observe minute details and characteristics at the micro and nanoscale. It facilitates the analysis of grain boundaries, phase distribution, and porosity inside the material. By examining the microstructure, scholars can obtain useful insights into the composite's formation, consolidation, and processing conditions, which significantly impact the composite's physical and mechanical characteristics. In order to conduct elemental analysis, SEM is frequently coupled with energy-dispersive X-ray spectroscopy (EDX). By detecting and analysing the distinctive X-rays that the specimen generates, EDX can map the elements throughout the surface of the composites and determine their elemental composition. Investigators can evaluate the material's homogeneity and distribution using SEM. It offers crucial insights into the characteristics and possible uses of the material by assisting in the knowledge of its shape, microstructural characteristics, and elemental appearance.

The originally prepared specimens underwent polishing using emery paper with grades ranging from 400 to 2000. Subsequently, the sintered samples were employed for microstructural analysis. The samples underwent a polishing process utilizing alumina powders to eliminate any surface scratches. The micrographs of the pieces were obtained through scanning electron microscopy. The current research employed a Nova Nano SEM 450 model manufactured by FEI Company of USA (S.E.A) PTE, LTD, to obtain scanning electron microscope images at different magnifications. The present study conducted an elemental mapping analysis utilizing the EDS technique to ascertain the distribution of phases in sintered specimens with varying compositions. The identification of phases in composites was carried out through X-ray diffraction analysis.

3.4.3 High-Resolution Transmission Electron Microscopy (HRTEM)

A transmission electron microscope (Model: Tecnai G2 20 TWIN; Company: FEI Company of USA (S.E.A.) PTE, LTD) was used to characterize the copper composite. The highly efficient HRTEM method thoroughly examines a material's microstructure and nanoscale characteristics. A particular HRTEM model provides advanced capabilities for material imaging and analysis. To construct the composite specimen, it was thinned to a thickness that permits electron transmission.

Important details regarding the crystalline structure, grain boundaries, imperfections, and interfacial interactions of the composite are revealed by HRTEM investigation. It makes it possible to measure elements, including crystallographic orientation, lattice spacing, and particle size. The form and arrangement of the composite's constituents are revealed by high-resolution photographs taken from HRTEM, revealing insights into its microstructure.

HRTEM analysis along with energy-dispersive X-ray spectroscopy (EDS: TEAM EDS SYSTEM with Octane Plus SDD Detector Company: EDAX Inc.) and selected area electron diffraction (SAED). Crystal structure and crystallographic orientations are easily identified and determined with SAED. By offering elemental analysis, EDX enables investigators to look at how the elements inside the composite are split.

3.4.4 Density and Porosity Measurement of Copper Composites

The Archimedes principle is used to obtain the density of the developed composite. The volume of the asymmetric microwave sintered sample is obtained using the Archimedes principle. First, the Dry weight is measured, and then the different sintered samples are soaked for 4 hrs in 80 0^C warm water in a water bath. Then, the suspended weight of the sample is calculated using the density measurement machine.

The density of sintered specimens was measured using the Archimedes principle as per the American Society for Testing and Materials (ASTM) B328 standard. Five readings were taken for each sintered specimen, and their mean was considered and reported. Archimedes' principle states that when an object is submerged in a fluid, it experiences an upward force equivalent to the weight of the fluid displaced by the object. As a result, when an object is submerged in a liquid, its apparent weight decreases by a value equal to the weight of the volume of liquid displaced. The experimental density of the specimen was determined by using Equation (1), which involves the mass and volume values of the object.

$$Experimental\ density = \left(\frac{wt.of\ specimen\ in\ air}{loss\ in\ specimen\ wt.}\right) \times density\ of\ water \tag{1}$$

However, the theoretical density of each sintered specimen was determined using the mixture rule.

The theoretical density (ρ_{th}) of the samples was calculated from the rule of mixtures and the formula for computing the theoretical density is given as,

$$\rho_{th}= V_m\rho_m+V_p\rho_r$$

Where ρth is the theoretical density of the composite, Vm is the volume fraction of matrix material, ρm is the density of the matrix, Vr is the volume fraction of reinforcements, and ρr is the density of the reinforcements.

The porosity of the sintered specimen was evaluated using equation (2). Porosity impacts the mechanical behaviours of the developed materials, so it should be measured and analysed.

$$Porosity = \left(1 - \frac{Experimental\ Density}{Theoretical\ Density}\right) \times 100 \tag{2}$$

3.4.5 Hardness Measurement of Copper Composites

In structural analysis, engineering design, and material development, the hardness test is a mechanical test used to assess a material's property. Any material's ability to withstand long-term deformation from abrasion, wear, indentation, and scratches is referred to as its hardness. To determine a relationship between hardness and other material characteristics, hardness testing is more important. The hardness of unreinforced copper and developed composite specimens was evaluated using a Vickers hardness tester (Model HTA RVM 50) with an applied load of 5 kgf and a dwell period of 10s. Before the hardness measurement, all the specimens were polished using emery paper grades of 2000. Five readings were collected for each sintered sample to eliminate reading errors, and the average of these readings was taken and reported as the hardness value. The hardness was determined using the following equation (3):

$$\boldsymbol{HV = 1.854\frac{F}{d^2}} \tag{3}$$

F is the load in (kgf), and d is the average length of the two diagonals(R. Singh et al., 2023). HV stands for the Vickers hardness number, and the indentation is measured in terms of the length of the two diagonals. The coefficient 1.854 corresponds to the geometric constant of the Vickers indenter.

3.4.6 Compressive Strength of Copper Composites

In compliance with ASTM standard E9, compression tests were performed to examine the composite material's response to compressive force. The compression tests were conducted using the screw-driven Instron$^{\text{TMTM}}$ Universal Testing Machine, with an initial strain rate of

10 s^{-1} at ambient temperature. Specimens of a cylindrical shape, measuring 20 mm in height and 10 mm in diameter, were prepared for the test. Every specimen set conducted five tests. Lubricating oil was positioned between the specimen and the compression machine's plate to lessen friction. The proportion of the decline remained at 49%. The specimen's end surfaces were preserved perpendicular to its axis.

3.4.7 Tribological Measurement of Copper Composites

The tribological behaviours of developed composites and unreinforced copper were studied using pin-on-disc tribo-testing equipment (Figure3.3) (supplied by DUCOM Instruments India) under dry sliding conditions. The wear specimens were prepared from both developed composites and unreinforced copper into cylindrical pins of 10 mm in diameter and 18 mm long. This cylinder-shaped wear pin was kept in a holder for the first stage, which holds it in vertical positioning against an EN31 hardened steel counter disc with a hardness of 62 HRC. The specimen was held stationary against the 100-millimeter-diameter revolving counter disc that was part of the pin-on-disc device. The counter disc was composed of EN-31 hardened steel with 62 HRC. Table 3.2 lists the composition of the hardened steel counter disc. The standard carbon steel utilized in EN-31 hardened steel has been case-tempered to a hardness of 62 HRC.

Table 3.2: EN-31 hardened steel counter disc composition details

Elements	**Si**	**Mn**	**C**	**P**	**Cr**	**S**	**Fe**
Wt. %	0.09.34	0.35-0.70	1.0-1.20	0.06	1.1-1.5	0.04	Balance

The hardened steel counter disc can rotate against the stationary surface of the wear pin. Each wear pin was tested under three different normal loads, such as 10 N, 20 N, and 30 N, and at two different sliding speeds of 1 m/s and 2 m/s for a constant sliding distance of 2000 m (2 km). Four tests were run on each specimen set to avoid reading errors. Before performing the tribological test, each wear pin was polished with emery paper grades up to 2000, and the disc was cleaned with acetone to eliminate any tiny debris or dust from it to avoid inaccuracy in the wear test reading. The complete weight readings were taken using the weighing machine with model no. KEA-210 supplied by K. Roy Instruments Pvt. Ltd. Varanasi with a least count of 0.001 g. 2 km sliding distance was tested for wear and friction, and once the sliding distance was reached, the weight loss was computed. To calculate the weight loss, the specimen was removed from the holder after sliding a distance of two kilometres, allowed to cool to room temperature, and then gently cleaned with a brush to remove any loose wear debris. It was then weighed and reattached in the same way. and place it within the holder to prevent sliding disorientation. The specimen was weighed both before and after the run using analytical balancing equipment. Using Archimedes' method to estimate the density of the corresponding composite, the weight loss data were translated into volume loss. For reproducibility, each test was run four times at a fixed weight and sliding distance of two kilometres. The average volume loss was reported at the end of each time period. The frictional force was displayed on a control panel on the machine. The friction coefficient was calculated by dividing it by the normal load using the friction force.

The wear rate and coefficient of friction were evaluated using formulas (4) and (5), as shown below:

$$\textit{Wear rate } (mm^3/km) = \frac{\Delta M}{\rho_{act} \times L} \tag{4}$$

$$\textit{Coefficient of friction} = \frac{F}{N} \tag{5}$$

Where ΔM is weight loss, ρ_{act} is the sintered specimen's actual density, L is the total distance (km), F is the frictional force, and N is the normal applied load. This made it easier to plot how the coefficient of friction changed as the sliding distance increased. The friction coefficient measurements were then averaged throughout the sliding distance to get an average friction coefficient for a given test, which has been used to examine how the friction coefficient changes under different loads.

3.4.8 Evaluation of Deteriorated Surface

To identify the predominant wear mechanisms, the surfaces of pure Cu and its composites that have been worn under various load and speed circumstances have been analyzed using Scanning electron microscopy (SEM).

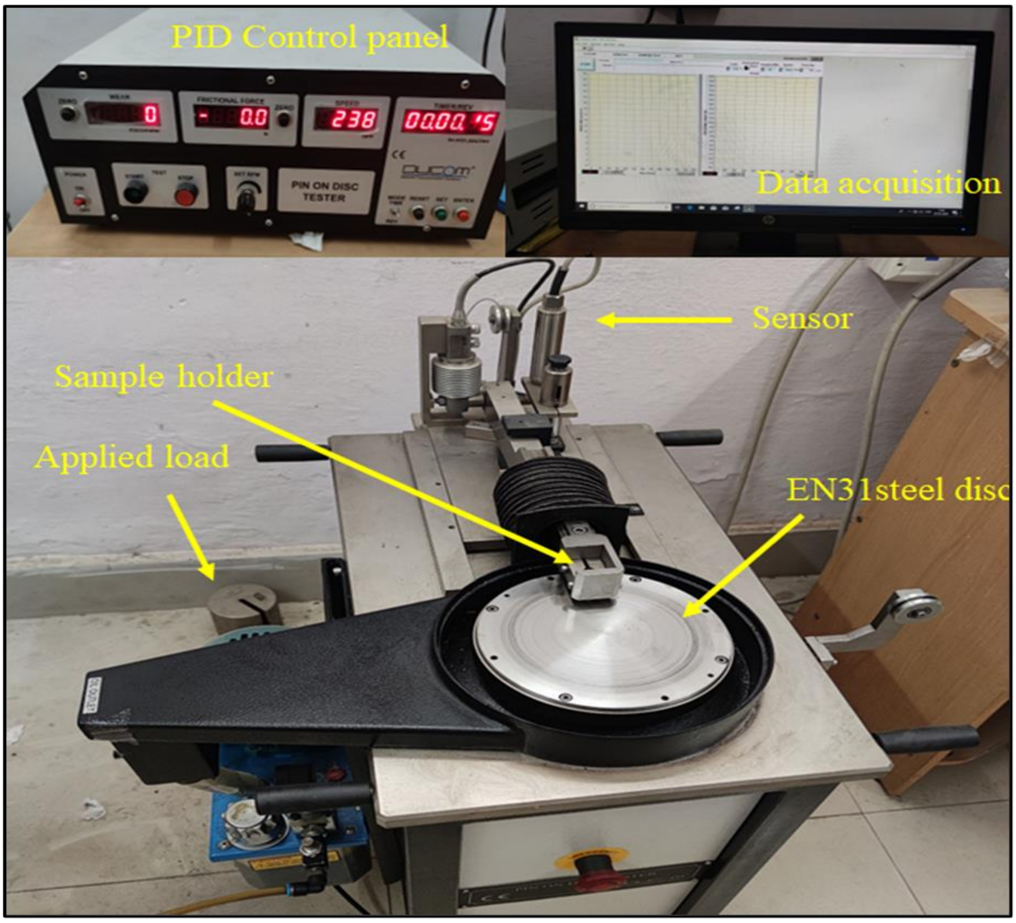

Figure 3.3 Pin-on-disc tribometer with counter disc of EN-31 steel

Using FEI, Nova Nano SEM, paired with EDS, scanning electron microscopy has also been applied to the worn surface of counter face balls and wear debris, depending on the resolution and magnification needed for surface investigation. afterward the completion of the wear test, a surface analysis was conducted on the deteriorated surface using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) system. To enhance comprehension of the wear mechanisms, the deteriorated surfaces of the samples were analyzed via atomic force microscopy (AFM) provided by NT-MDT Service & Logistics Ltd.