CHAPTER 2

EXPERIMENTAL DETAILS

2.1 INTRODUCTION

The present chapter provides the details of the materials, experimental set-up and different characterizing equipment and the elaborate procedures used to carry out the experiments for fulfilling the objectives of the current study. The machinery and procedures adopted for characterization of microstructures, mechanical and tribological characteristics of the fabricated composites have also been described.

2.2 MATERIALS AND METHODS

The present work used three different materials: Cu powder (45 µm average particle size and 99.5% purity procured from CDH, Gujrat India), Graphite (Gr) powder (7–9 µm average particle size and 99% purity procured from CDH, Gujrat India) and TiC (<200 nm average particle diameter and 99.9% purity procured from Sigma Aldrich, USA) powders). Table 2.1 depicts the properties of the materials used in the study.

Tables 2.1 Properties of the materials used in the current study

Property	**Cu**	**Graphite (Gr)**	**TiC**
Usage type	matrix	reinforcement	reinforcement
Density (g/cm^3)	8.96	2.21	4.93
Particle size (µm)	45	7-11	<200 nm
Purity (%)	99.5	99	99.9
Melting point (°C)	1084	3550	3068

2.2.1 Preparation of the Copper-Graphite-TiC composite

The synthesis of Copper-Graphite-TiC (Cu-Gr-TiC) composite comprises of three steps (a) milling of desired composite powder in a planetary ball mill; (b) compaction in compaction die; (c) sintering in a furnace. The alloying powders were pre-heated in a hot air oven at 100ºC to remove the moisture content associated with powder particulates. The powders were weighed according to the desired weight percentages by a METTLER TOLEDO balance with an accuracy of 0.1 mg. The purpose of mechanical alloying is to reduce the particle size and morphology and it also improves the dispersion of the reinforcement in the matrix phase. The three powders were mechanically mixed by means of a high-speed ball mill (RETSCH PM400). The milling was done at 300 rpm for 5 hours using tungsten carbide balls (ϕ10 mm) with powder-to-ball weight ratio of 1:5. The composite powders were milled for 20 minutes with an interval break of 15 minutes so as to avoid overheating without the use of any control process agent (dry condition).

The composite powders milled for five hours were then compacted using a die-punch arrangement with help of 8 mm diameter die. The die and punch were coated with zinc stearate for easy sample removal. The compaction pressure was 700 MPa. After compaction consolidation of milled powders occurs and a green compact sample were obtained.

The green compacts were then sintered in an argon atmosphere using a tubular furnace (Nabertherm GmbH Germany-RHTH 120–300/18). Sintering causes the transformation of poor mechanical bonds of the green compact to a strong metallic bond. Initially the Cu-Gr samples were sintered at different temperatures of 900ºC, 950ºC and 1000ºC and a sintering time from 1 to 2 h. Then, after optimization all the samples were sintered at

950ºC for 1.5 h of sintering time. The sintered samples exhibited a cylindrical form, with a diameter of 6 mm and a length of 12 mm.

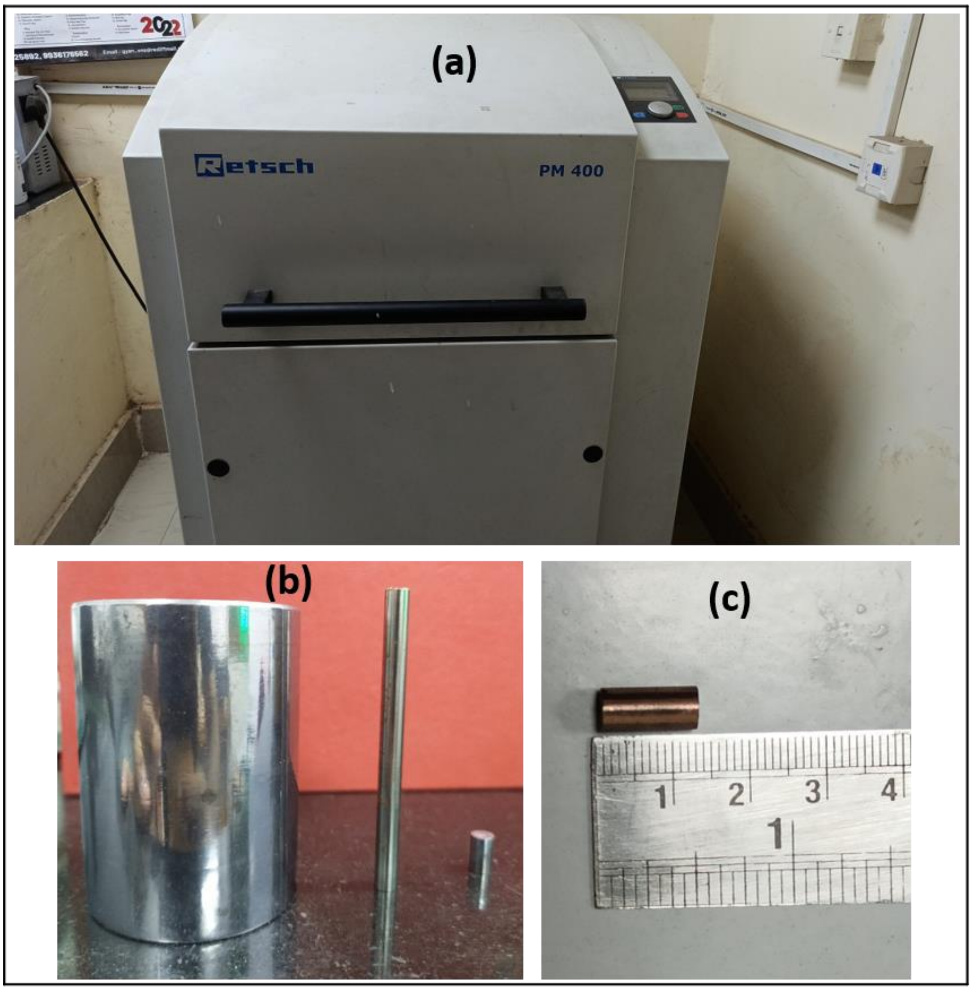

Fig. 2.1 (a) PM400 milling machine, (b) Compaction die and punch and (c) Sintered sample

Further samples of desired shape and size were cut as per requirements of various tests such as Optical microscopy, XRD characterization, Hardness, Tribological test etc. Along with pure copper sample, four composites with varying TiC amount 0, 1.5, 3.0 and 4.5 wt.% and keeping graphite amount (5 wt.%) constant were fabricated as shown in Table 2.2.

Table 2.2 Samples with different composition

S. N.	Composition	Nomenclature
1	Pure Copper	Cu
2	Copper- 5wt.% Graphite	Cu-Gr
3	Copper- 5wt.% Graphite-1.5wt.% TiC	T1.5
4	Copper- 5wt.% Graphite-3.0wt.% TiC	T3.0
5	Copper- 5wt.% Graphite-4.5wt.% TiC	T4.5

2.3 X-RAY DIFFRACTOMETER FOR PHASE ANALYSIS

The phases incorporated into the Cu, Cu-Gr and TiC reinforced composites were examined using a Rigaku MiniFlex 600, X- ray Diffractometer using Cu-Kα radiation (wavelength 1.5 A). The experimental setup involved varying the 2θ angle within the range of 10^o to 100^o at a scanning rate of 5^o per minute. In order to identify different x-ray peaks, the 'd' values obtained from XRD patterns were compared with the standard d-spacing values available in the JCPDS database. This comparative analysis allowed for the detection and matching of characteristic x-ray peaks with their corresponding d-spacing values from the database.

2.4 DENSITY AND POROSITY

The density of sintered samples was obtained with the help of Archimedes principle using ASTM B328 standard. At least five values were measured for each set and their average has been considered.

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

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

Where, ρ_{th} : the theoretical density of the composite, V_m : the volume fraction of matrix material, ρ_m : the density of matrix, V_r : the volume fraction of reinforcements and ρ_r : the density of the reinforcements.

In powder metallurgy technique, the mechanical characteristics of composites are significantly influenced by the porosity. The porosity in the sintered product may develop during sintering by the trapping of gases and due to thermal gradient among the different powders. Thus, the percent porosity (%P) was also determined using following equation:

$$P = \left(1 - {}^{\rho_{act}}/_{\rho_{th}}\right) \times 100$$

2.5 MICROSTRUCTURAL CHARACTERIZATION

The microstructure features of the sintered samples were analysed using both optical microscope (OM) and scanning electron microscope (SEM).

2.5.1 Optical Microscope (OM)

A Leica Metallux-3 microscope equipped with an image analyzer was utilized to conduct microstructural investigations through optical microscopy. Preparation of sample for the microstructural examination was done by following the standard metallographic procedures. Initially, a series of 600–2500 grit SiC emery papers were used to grind the sintered samples. Further, the samples were polished with alumina powders using a rotating polishing machine. The polished samples were etched using an etchant (10 g Fe_3Cl +10 ml HCl + 100 ml distilled water). Then, samples of all compositions were studied under optical microscope. The analysis of the average grain size of composites was conducted in accordance with the ASTM E112 standard (1996) and was calculated using line intercept method.

2.5.2 Scanning Electron Microscope (SEM)

The scanning electron microscopy of the polished and etched sintered samples was accomplished with Carl ZEISS EVO 18 FEI scanning electron microscope (SEM) or NOVA Nano SEM 450. However, for identifying the distribution of various elements, the energy dispersive spectroscopy (EDS) elemental mapping study of sintered samples with varying compositions was also performed.

2.6 MECHANICAL CHARACTERIZATION

2.6.1 Hardness

The Vickers hardness of sintered pure copper and the composite samples was obtained using a Leco LM248AT hardness tester. Before the hardness test, the sintered samples were properly polished with diamond paste. For each sample set, five readings were taken and their average value was reported. The applied load was 0.5 kgf and dwell time is 30 s according to ASTME92 standard.

2.6.2 Compressive strength

Compression tests were conducted to analyze the response of the composite material under compressive loading in accordance with the ASTM standard E9-89. The 100 KN screw-driven Instron™ Universal Testing Machine was employed for the compression tests, with an initial strain rate of 10^{-2} s^{-1} at room temperature. Cylindrical specimens measuring 12 mm in height and 6 mm in diameter were prepared for the test and three tests were performed for each sample set.

2.7 TRIBOLOGICAL MESEAUREMENT AND WORN SURFACES STUDY

2.7.1 Wear and Friction

A standard pin-on-disc (POD) tribometer (Ducom TR-20 M26) procured from DUCOM, India was utilized for analysing the wear performance of the samples under dry and lubrication conditions at ambient environments. The sintered samples in the shape of cylinder with length 12 mm and diameter 6 mm were used for wear test. The ASTM G99-95a standard was followed for the wear test. An EN31 steel disc with a hardness of 60 HRC was utilised as a counter surface for pin samples. The data acquisition was done with help of WINDUCOM software. Surfaces of the pin sample were properly polished up to 2000 grit SiC coated emery paper, and then acetone cleaning was done to ensure smooth contact between mating surfaces. Similar procedure was done for the disc surface before each test. After each test acetone was utilized for cleaning the disc to get rid of any leftover debris. The weight loss of the test samples was evaluated using a precision balance METTLERTOLEDO of 0.1 mg accuracy. Wear tests under dry sliding condition were performed at different applied loads (10 N to 40 N), sliding distances (1000 m to 4000 m), and sliding speeds (0.75 m/s to 3 m/s). Wear tests under lubricating sliding condition were performed at different applied loads (10 N to 70 N), sliding distances (2000 m to 8000 m), and sliding speeds (0.75 m/s to 3 m/s). Each experiment was conducted three times to assess the repeatability and consistency of the obtained results. Wear and friction data are presented in terms of wear volume, wear rate, wear coefficient, and coefficient of friction.

Wear volume is defined according to ASTM standards G99, 2010:

$$Wear\ Volume = \frac{\Delta w}{\rho} X\ 1000$$

Where wear volume in mm^3,

Δw is weight loss in g, ρ is density in g/cm^3

The wear rate and COF were computed from the Equation (2.1) and (2.2), respectively [J. Salguero et al., 2018]:

$$Wear\ Rate\left(\frac{mm^3}{m}\right) = \frac{\Delta W}{\rho_{act} X\ d} \qquad \text{Eqn. 2.1}$$

$$COF = \frac{f}{N} \qquad \text{Eqn. 2.2}$$

Where ΔW is the initial mass minus final mass (g), ρ_{act} is the actual density of sintered sample; d is the total sliding distance travelled (m), f is the frictional force and N is the normal applied load. The wear coefficient provides a more detailed measure to describe the wear properties of a material. It is calculated using the equation following (Eqn. 2.3): [Banerjee et al., 2020]:

$$\text{Wear coefficient (K)} = \frac{\Delta W * H}{\rho * L * d} \qquad \text{Eqn. 2.3}$$

Where, ΔW-weight loss, H-hardness (HV), ρ-density, L-applied load and d-sliding distance.

The Table 2.3 displays the characteristics of synthetic motor oil utilized for lubrication [M.S. Charoo et al., 2016].

Table 2.3 Characteristics of SAE20W40 motor oil

Properties	**Kinematic viscosity at 40^0C** (mm^2/s)	**Dynamic viscosity at** -10 °C (mPas)	**Density** (kg/m^3)	**Flash point,** (°C)	**Pour point, in** (°C)	**Viscosity Index**
Values	116	2800	879	236	-30	135

2.7.2 Surface topography

A scanning electron microscope FE-SEM (Nova Nano SEM 450) attached with EDS was employed for examination of worn surfaces to comprehend the wear mechanism. The NTEGRA Prima Atomic force microscope (AFM) was also utilized for studying the topographical parameters of the worn surface by following ASTM E2859-11 standard. An atomic force microscope works by scanning a sharp probe across the surface of a sample while measuring the interactions between the probe and the sample. These interactions help to generate a detailed topographic map of the sample surface, providing information on its features (roughness, topography) at the nanoscale. They have been used to assess the roughness value (Ra) and surface imperfections of the worn-out surfaces.

2.8 STATISTICAL MODELLING USING RESPONSE SURFACE METHODOLOGY

With the use of Design Expert 13.0 software, tribological characteristics of the composites were optimized. A quadratic model was established based on the best-fit model. Design of experiments (DOE) is an important tool which can be used for various experimental conditions. RSM is an effective mathematical approach for experimental design, modelling and optimisation of output. Response Surface Methodology (RSM) is a cost-effective and potent optimization technique that minimizes the number of required experiments. Typically, linear or quadratic polynomial functions are utilized in RSM to elucidate and explore experimental conditions. Second-order models are frequently favoured in RSM due to their flexibility, providing a robust approximation to the actual response. Several assumptions of the RSM comprise:

Linearity: The relationship between the response variable and the input variables is assumed to be linear within the experimental region. This allows for the use of linear and quadratic models to represent the relationship.

Independence: The experimental runs are assumed to be independent of each other. This means that the value of the response variable for one run does not depend on or influence the value of the response variable for another run.

Normality: The residuals (the differences between the observed and predicted values) are assumed to be normally distributed. This assumption is important for the validity of statistical tests and confidence intervals.

Central composite design is mostly favoured in fitting of quadratic models in the response surface experiment setup. There are three steps in central composite design (CCD): experimental design, development of model and final result analysis. In this work, CCD is used for the optimisation of responses which are wear rate and COF with respect to input variables. Input variables (wear parameters) taken were: Load (A), Sliding distance (B) & wt.% TiC (C) and they are also called as independent factors. Throughout the tribological test velocity was kept constant at 1.5 m/s. Table 2.4 and Table 2.5 illustrates the distinct factors with their maximum and minimum levels (values) utilized for designing the experiment for dry and lubricating sliding conditions, respectively.

Table 2.4 RSM input parameters for the composites under dry sliding condition

Factor	**Unit**	**-α**	**+α**	**Low (-1)**	**High (+1)**
A: Load	N	20	40	20	40
B: Sliding distance	M	2000	4000	2000	4000
C: TiC content	Weight %	1.5	4.5	1.5	4.5

Further assuming the response parameter values lies between these levels. Axial points are positioned symmetrically in CCD about the central point and their distance from centre is known as alpha (α). For the face-centered CCD designs, alpha values vary from +1 to -1. The more than one (>1) alpha value means point is outside of cube, equal to one (=1) means point lies on the face of the cube, whereas less than one (<1) alpha means point lies within the cube. However, the experiment runs are in randomized sequence.

Table 2.5 RSM input parameters for the composites under lubricating sliding condition

Factor	**Unit**	**-α**	**+α**	**Low (-1)**	**High (+1)**
A: Load	N	30	70	30	70
B: Sliding distance	M	4000	8000	4000	8000
C: TiC content	Weight %	1.5	4.5	1.5	4.5