CHAPTER 3

EXPERIMENTAL PROCEDURE

This chapter describes the details pertaining to procurement of materials used for synthesizing the reinforcements fabrication of copper based composites. Procedure to evaluate the friction and wear behavior of copper matrix composites and techniques adopted for characterization of samples and worn surfaces are also included in this chapter.

In quest of achieving low friction and low wear rate, two types of hybrid copper matrix composites have been fabricated, one of them contains the combination of hard phase and solid lubricants and another set of composites have been prepared containing hybrid reinforment of two 2D materials.

3.1 MATERIALS PROCUREMENT

This section highlights the materials, their size and purity, which have been used for the synthesis of reinforcement phase and composites. Materials procured for the synthesis of copper based composite containing the mixture of hard and soft phase is as follows: The powders of Cu (-325 mesh, 99.5% purity), Fe (250-300 mesh), Alumina (20-30 nm), MoS_2 (-325 Mesh powder, 99% purity) and hexagonal boron nitride (70 nm) have been procured from Sigma Aldrich, USA.

Material procured for the synthesis of rGO-MoS_2 soft phase is as follows: Sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$, 99.5%), thiourea (NH_2CSNH_2, 99%), and

graphite powder (< 20 μm) have been purchased from Sigma Aldrich, USA. Hydroxyl amine hydrochloride ($NH_2OH.HCl$, 99%), and sodium nitrate ($NaNO_3$, 98%) have been supplied by Alfa Aesar, USA. Potassium permanganate ($KMnO_4$, 99%, Fisher Scientific), sulfuric acid (H_2SO_4, 98%, Merck, Germany), hydrogen peroxide (H_2O_2, 30% aqueous solution, Loba Chemie, (Mumbai) India) and hydrogen chloride (37%, Fisher Scientific, USA) have been used.

3.2 SYNTHESIS OF rGO-MoS_2 REINFORCEMENT PHASE

The rGO-MoS_2 hybrid has been synthesized by following a two-step chemical approach. In the first step, graphene oxide (GO), a precursor to rGO-MoS_2 hybrid has been prepared by a harsh oxidation of graphite powder using a mixture of $NaNO_3$, H_2SO_4 and $KMnO_4$ as strong oxidizing reagents. The prepared oxidized product, known as graphite oxide is rinsed with 30% H_2O_2 and then 5% HCl solution to seize the oxidation process and remove the residues of oxidizing agents. It is followed by washing of graphite oxide with distilled water to remove the acid traces. The graphite oxide having expanded inter-lamellar spacing is exfoliated into the GO by using the probe sonicator. The aqueous dispersion of GO has been centrifuged at 5000 rpm. The supernatant having the fine sheets of GO is used for preparation of the rGO-MoS_2 hybrid. In this context, an aqueous solution of 1.21 g sodium molybdate dihydrate and 0.7 g hydroxyl amine hydrochloride is prepared by stirring at 90 $^{\circ}$C. It is followed by addition of 5 ml aqueous solution of 35% HCl under continuous stirring. Subsequently, 1.56 g thiourea is added and reaction mixture is stirred to obtain the homogenous solution. The 30 mL aqueous dispersion of GO (15.5 mg. mL^{-1}) has been thoroughly mixed with aqueous solution of reaction precursors of MoS_2. After that, the resultant reaction mixture is transferred into a Teflon-

lined stainless-steel autoclave which is then sealed properly. The autoclave has been kept in the electric oven at 230 $^{\circ}$C for 24 hours. The synthesized black color product is washed several times first with water and then ethanol to remove the reaction precursors and undigested salts. The black color product of rGO-MoS_2 hybrid is dried in the oven at 80 $^{\circ}$C for further characterization and composites preparation.

3.3 FABRICATION OF COMPOSITES

3.3.1 MIXING OF POWDERS

This section explains the mixing and powder sample preparation of copper matrix hybrid composites. Pure copper specimen is designated as sample PC, while Cu-Al_2O_3- Fe is designated as CA, Cu-Al_2O_3- Fe- MoS_2 sample is designated as sample CAM and Cu-Al_2O_3- Fe- MoS_2- *h*-BN composite sample is designated as CAMB. Metal powders have been weighed in required quantities using an electronic balance having an accuracy of 0.0001g, powders in appropriate ratio is mixed in pestle mortar for 15 mins prior to high energy ball milling (PM 200, RETSCH, Germany) to mix them thoroughly at a speed of 110 rpm for 45 minutes using acetone as the process controlling agent.

Copper based composites samples containing rGO-MoS_2 is mixed using the following procedure: The copper powder is gradually mixed into aqueous dispersion of rGO-MoS_2 hybrid with the aid of sonication. The obtained slurry is sonicated to obtain the uniform blending and then allowed to settle-down in the beaker. The supernatant water has been removed manually, and slurry is dried in the oven for 24 hours, which is followed by ball-milling of dried powder in the presence of 1% stearic acid. The ball-milling process is carried out for 4 hours at 150 rpm using steel balls of 10 mm diameter while keeping the ball to powder ratio is as 10:1.

3.3.2 SPARK PLASMA SINTERING OF COMPOSITES

Milled samples have been sintered using spark plasma sintering on Dr. Sinter SPS-625, Fuji Electronic Industrial Co. Ltd. (Japan) in IIT Roorkee. Composition, designation and sintering temperature of the hybrid composites is given in the Table 3.1. These samples have been held at the pressure of 30 MPa for 10 min. holding time, while 80 $^{\circ}$C is the heating rate.

Table 3.1 Composition, designation and sintering parameters of materials synthesized in this study.

Sample Designation	**Cu (wt.%)**	**Reinforcement (wt.%)**	**Sintering Pressure (MPa)**	**Sintering Temperature ($^{\circ}$C)**
Pure Cu **(C)**	100	-	30	900
Cu-Fe-Al_2O_3 **(CA)**	92	4 % Fe, 4% Al_2O_3	30	900
Cu-Fe-Al_2O_3-MoS_2 **(CAM)**	82	4 % Fe, 4% Al_2O_3, 10 % MoS_2	30	900
Cu-Fe-Al_2O_3-MoS_2-*h*-BN **(CAMB)**	82	4 % Fe, 4% Al_2O_3, 5 % MoS_2, 5% *h*-BN	30	900

Another set of samples containing rGO-MoS_2 have been sintered using spark plasma sintering. Thoroughly blended powder has been used to fabricate the Cu-rGO-MoS_2 composite by spark plasma sintering. The Dr. Sinter SPS-625 Spark Plasma Sintering Machine (Fuji Electronic Industrial Co. Ltd, Japan) has been used to fabricate the composites at sintering pressure of 49 MPa, while keeping a holding time of 5 mins at a heating rate of 100 $^{\circ}$C. min^{-1} to obtain composites (Table 3.2). The DC pulse current is used to disperse the spark plasma energy between the particles of powder to form highly dense and compact composites. Schematic diagram of spark plasma sintering machine is shown in Fig. 3.1.

Table 3.2 Designation, composition and sintering temperature of the composites.

Samples Designation	Copper (wt. %)	Reinforcement (wt. %)	Sintering Temperature (˚C)
PC	100	_	800
CGM 600	98	2 wt. % rGO-MoS_2	600
CGM 650	98	2 wt. % rGO-MoS_2	650
CGM 700	98	2 wt. % rGO-MoS_2	700
CGM 750	98	2 wt. % rGO-MoS_2	750
CGM 0.5	99.5	0.5 wt. % rGO-MoS_2	700
CGM 1.0	99	1 wt. % rGO-MoS_2	700
CGM 1.5	98.5	1.5 wt. % rGO-MoS_2	700
CGM 2.0	98	2.0 wt. % rGO-MoS_2	700
CG	98	2 wt. % rGO	700
CM	98	2 wt. % MoS_2	700
CGM	98	2.0 wt. % r GO-MoS_2	700

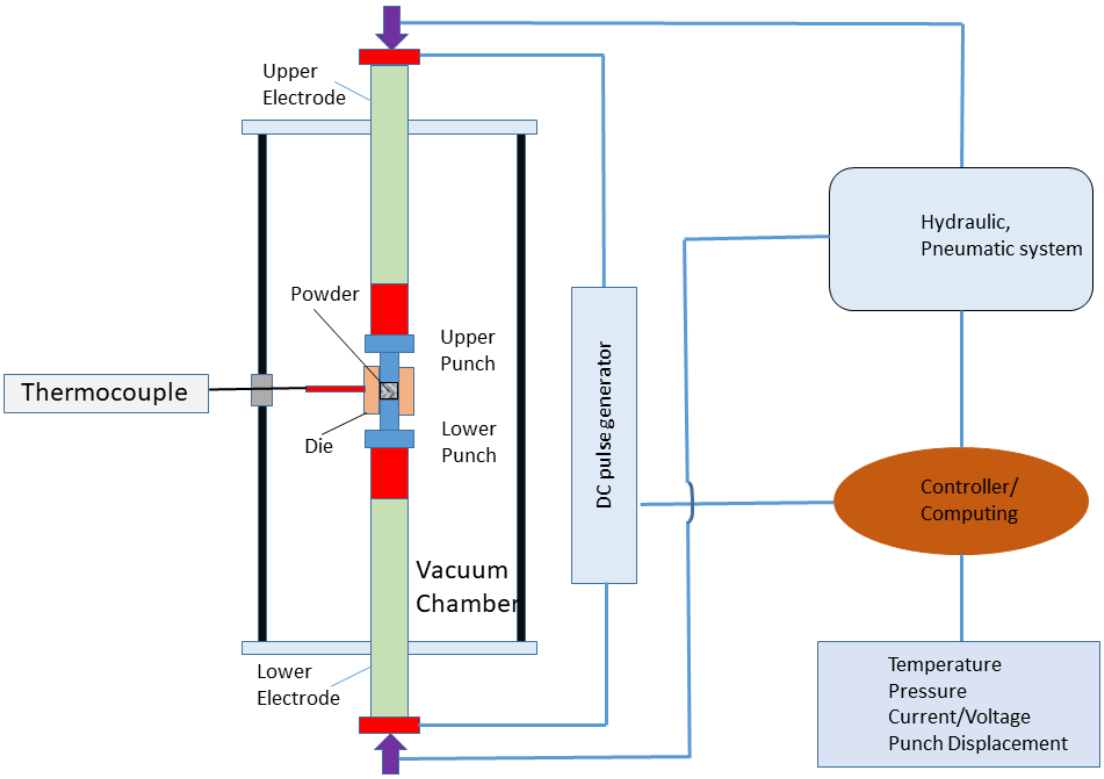

Fig. 3.1 Schematic diagram of a typical spark plasma sintering machine.

3.4 CHARACTERIZATION OF rGO-MoS_2 AND COMPOSITES

Powders are characterized In order to check the morphology, composition and chemical structures of the synthesized hybrid materials, the powders have been subjected to different characterization techniques. The microstructural features and elemental mapping of rGO-MoS_2 hybrid is probed by using a JEM 2100, JEOL transmission electron microscope. The high-resolution transmission electron microscopic (HRTEM) images have been captured at accelerating voltage of 200 kV. Transmission electron microscopy samples are prepared by drop-casting of ethanolic dispersion of rGO-MoS_2 hybrid on the carbon coated TEM grid. The chemical features of rGO-MoS_2 hybrid have been examined by the X-ray photoelectron spectroscopy (XPS) using the PHI 5000 Versa Probe III scanning XPS microprobe (Physical Instruments Inc.) spectrometer equipped with Mg K_α line as an X-ray source. The X-ray diffraction (XRD) patterns of rGO-MoS_2 hybrid and Cu- rGO-MoS_2 are recorded in the 2θ range of 10°-70° using an X-ray diffractometer (SmartLab, Rigaku, Germany) equipped with Cu K_α radiation source. The Raman spectra of rGO-MoS_2 hybrid and Cu-rGO-MoS_2 composites are probed using the RM 1000 (Renishaw, UK) Raman spectroscope equipped with a solid-state diode laser of 785 nm excitation. The microstructure, particularly the distribution of rGO-MoS_2 hybrid in the Cu-rGO-MoS_2 composites is examined by scanning the microscopic images in the scattered mode using the scanning electron microscope (EVO 18, Carl-Zeiss Microscopy, LLC). The high-resolution microscopic structure of Cu-rGO-MoS_2 composite are examined by capturing TEM images using the FEI Tecnai G^2 20 TWIN microscope. To capture TEM images, Cu-rGO-MoS_2 composite sample has been mechanically polished up to 50 μm thickness followed by electro-polishing to obtain a very fine sample.

3.5 PHYSICAL AND MECHANICAL PROPERTIES EVALUATION

Density measurement is done by Archimedes principle. The mechanical properties in terms of Vickers hardness and tensile strength are measured for copper and Cu-rGO-MoS_2 composites. The Vickers hardness (MH-5-VM, Hengyi Precision instrument Co. Ltd; China) is probed by applying a load of 300 g for 10 seconds. The reported values are average of eight measurements taken at different points on each sample. The tensile tests have been carried out using flat samples (4 mm × 4.8 mm) for a 15 mm gauge length and 1 $mm.s^{-1}$ ramp rate using the tensile testing machine (Instron 5982, USA). Schematic diagram of tensile sample is shown in Fig. 3.2.

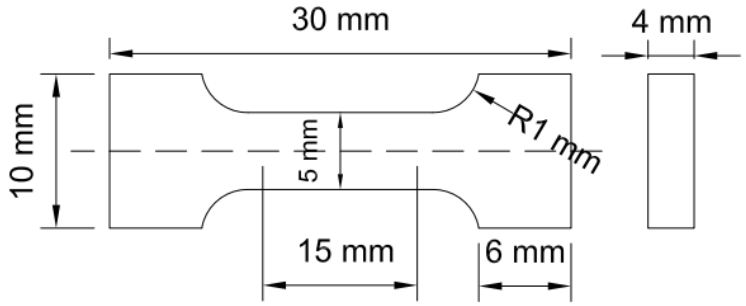

Fig. 3.2 Schematic diagram of flat tensile sample.

3.6 FRICTION AND WEAR TESTING

Dry sliding wear tests for the pure Cu and the composites have been conducted according to ASTM standard 133, using a pin/ball-on-disc rotary micro-tribometer supplied by M/S DUCOM, Bangalore (India). Schematic diagram of ball on disc setup is shown in Fig 3.3. . The torque moment on the sample is calibrated in terms of friction force as indicated on the machine, using a fixed distance of lever arm of the

apparatus. Tangential force has been monitored continuously during the wear test and the data is acquired in the PC attached to the machine which is supplied along with the tribometer. The friction coefficient is determined from the friction force and the normal loads; only pre-calibrated dead loads have been used.

The tests have been conducted at ambient conditions having relative humidity in the range of 45 to 55 %, against the EN31 ball of 6 mm diameter as counter face, hardness of the steel ball is noted as 62 HRC. The disc specimens have been polished up to 4/0-grade emery paper, subsequently specimens have been polished on cloth wheel with brasso and kerosene to have average surface roughness of 0.3µm. Both the disc and ball have been cleaned by acetone and dried before conducting the test. Testing conditions corresponding to hybrid composites is shown in table 3.3. The wear tests have been conducted at 2, 4, 6 and 8 N and fixed sliding velocity of 0.5 $m.s^{-1}$ for 6000 cycles.

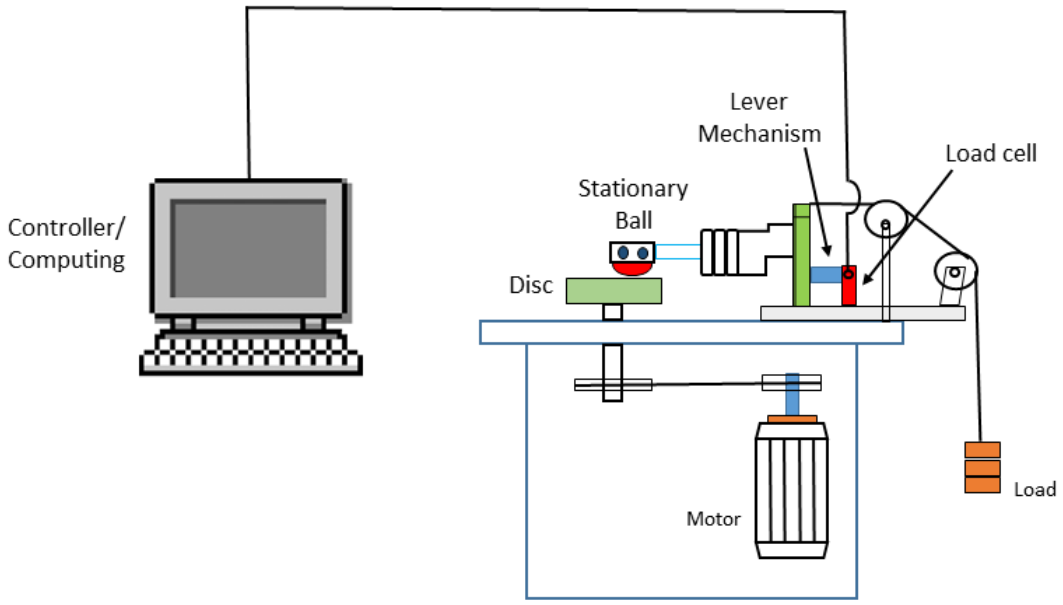

Fig. 3.3 Schematic diagram of ball/pin on disc tribotester.

Table 3.3 Tribological testing parameters for hybrid composites.

Composition	Sliding Speed	Load	Number of Cycles
PC	$0.5\ m.s^{-1}$	4 to 8 N (in the step of 2N)	6000
CA			
CAM			
CAMB			

Copper matrix composite samples with varying sintering temperature (designated as CGM 600, CGM 650, CGM 700 and CGM 750), with variable rGO-MoS_2 wt. % (designated as CGM 0.5, CGM 1.0, CGM 1.5 and CGM 2.0) and derivative phase of rGO-MoS_2 reinforced in copper matrix are compared on the basis of their tribological performance. Testing conditions for all set is given in Table 3.4.

Table 3.4 Tribological testing conditions for composites containing rGO-MoS_2.

Variables	Composition	Sintering Temperature (°C)	Sliding Speed	Load	Number of Cycles
Sintering Temperature	**CGM 600**	600	$0.5\ m.s^{-1}$	4 N	6000
	CGM 650	650			
	CGM 700	700			
	CGM 750	750			
	PC	800			
Composition	**PC**	800	$0.5\ m.s^{-1}$	6 N	8000
	CG	700			
	CM	700			
	CGM	700			
Composition and Load	**CGM 0.5**	700	$0.5\ m.s^{-1}$	4N to 10 N (in step of 2N)	6000
	CGM 1.0	700			
	CGM 1.5	700			
	CGM 2.0	700			

After the tribo test, each sample is cleaned with acetone to remove the worn debris. Each test has been conducted thrice with fresh surfaces of tribo-pair and the average values are reported here. Since, mass loss is too low in to be measured in some cases, the wear rate of each sample have been calculated by measuring the profilograph of worn track. Volume loss is calculated from the product of profilograph area and perimeter of wear track circle. Dividing the wear loss from the sliding distance gave the value of volumetric wear loss. It can be also be written in mathematical expression as follows:

$$W = \frac{Volume\ loss}{Sliding\ distance} = \frac{Ap \times \pi D}{\pi D \times N}\ \text{mm}^3.\text{m}^{-1} = \frac{(mi - mf)}{\rho} / L$$

Where A_p is area of profile, D is Diameter of wear track and N is number of cycles.

3.7 CHARACTERIZATION OF WORN SURFACES

The surfaces of pure Cu as well as its composites, worn under different conditions of load and speed have been examined under SEM to determine the prevailing wear mechanisms The worn surface of counter face balls and the wear debris have also been subjected to scanning electron microscopy using FEI, Nova Nano SEM and EVO-18 Carl ZEISS both coupled with EDX are used as per the resolution and magnification requirement for surface examination. Atomic Force Microscope (AFM) (NTEGRA PRIMA, NT-MDT, Russia) has been utilized to examine the topographic features of each worn surface, topography under tapping mode. RM 1000 (Renishaw, UK) is utilized for Raman mapping and Raman spectroscopy of worn surface, raman mapping is done in order to determine the effect of tribostress on the reinforcement phase distribution and their chemical structure. A laser excitation of 514 nm is used to obtain the signature of rGO and MoS_2 on a selected area of 600 nm^2.