

EXPERIMENTAL PROCEDURE

The current chapter describes the details of materials and experimental procedures used in the present investigation. The chapter contains the details of the method used to synthesise graphene coating on bearing steel and the procedure undertaken to examine the tribological behaviour of coated steel under unidirectional as well as reciprocating sliding. The chapter also encompasses the process utilised for the preparation of water-based lubricant containing graphene oxide (GO) nanosheets and its evaluation under reciprocating sliding motion along with the techniques used for the characterisation of graphene oxide powder, coatings and worn surfaces.

3.1 PROCUREMENT OF MATERIALS

The cylindrical rods of bearing steel (GCr15) and stainless steel (SS 304) of 25.4 mm diameter procured from local market have been used in the present investigation. As bearing steel is mostly used in various machine parts and assemblies due to its availability, consistency in strength, high wear resistance and versatility, it was selected as the base material for graphene coating. However, for water-based lubrication, it can cause severe corrosion. Hence, stainless steel was selected for water-based lubricants containing graphene oxide, which is highly resistant to corrosion. Commercially available graphene oxide nano-sheets of thickness 0.8-1.2 nm and diameter 0.5-5 μm have been used as a graphene source in the present investigation. The graphene oxide powder has been procured from XFNANO Materials Tech. Co. Ltd., Nanjing, China.

3.2 DETERMINATION OF THE CHEMICAL COMPOSITION

The chemical composition of both bearing steel (GCr15), as well as stainless steel (SS304) used in the present study, has been determined through energy-dispersive X-ray spectroscopy (EDS, GENESIS, EDAX, Mahwah, NJ, USA) and the results of the analyses are presented in Chapters 4 and 5, respectively.

3.3 SAMPLE PREPARATION

The circular disc-shaped (ϕ 25 mm \times 7 mm) steel specimens have been prepared by cutting and turning operations on the lathe. The discs have been polished with different grades of emery papers (600#, 1200#, 2400#, and 4000#, respectively) followed by cloth polishing using the diamond paste to obtain a smooth and bright surface. The surface roughness of the polished specimens has been measured by a non-contact 3D optical surface profiler (Zygo NexView, AMETEK Inc., USA). The discs have been cleaned in an ultrasonic bath with acetone and ethanol for about 15 minutes each to remove the surface impurities, dust, oil, oxides layer, and any other contamination left during sample preparation.

3.4 SYNTHESIS AND TRIBOLOGICAL BEHAVIOUR OF GRAPHENE COATING

The following section describes the synthesis of graphene coating on nickel-plated steel and the procedure undertaken to examine the tribological behaviour of coated steel under unidirectional as well as reciprocating sliding.

3.4.1 SET-UP AND PROCEDURE FOR NICKEL ELECTROPLATING

The polished circular discs (ϕ 25 mm \times 7 mm) of bearing steel have been used for the deposition of graphene in the present study. A nickel layer has been electroplated on the surface of the steel disc to facilitate the graphene deposition. Before being plated with nickel, the samples have been chemically cleaned by immersing them in an aqueous solution of carbonate, hydroxide, phosphate, cyanide, and silicate of sodium for 5 minutes. The chemical cleaning is done to remove the impurities and to activate the metal surface to ensure better adhesion of plating metal with substrate metal. The voltage and current of 6 V and 15 A, respectively, have been used during chemical cleaning by making the samples as anode and a plate of cast iron as cathode. The schematic diagram of the typical setup used for chemical cleaning is given in Fig. 3.1. After cleaning, the nickel electroplating has been done on the disc specimens (connected to cathode) by submerging them in a solution of nickel chloride, nickel sulfate, and boric acid having a provision of continuous stirring using a mechanical stirrer during electroplating. A DC power source of 3 V has been used to connect anode (pure nickel plate) and cathode with a current flow of 5 A. Figure 3.2 presents a schematic diagram of standard setup used for nickel electroplating. The discs have been washed with water and dried after nickel plating.

3.4.2 CHARACTERISATION OF ELECTROPLATED NICKEL LAYER

The electroplated nickel layer has been characterised by optical microscopy (VHX - 6000, Keyence, Japan), and energy-dispersive X-ray spectroscopy (EDS, GENESIS, EDAX, Mahwah, NJ, USA). The disc has been cut through the cross-section and polished for measuring the thickness of the electroplated nickel layer using a scanning electron microscope (SEM, Quanta 200FEG, FEI, Netherlands).

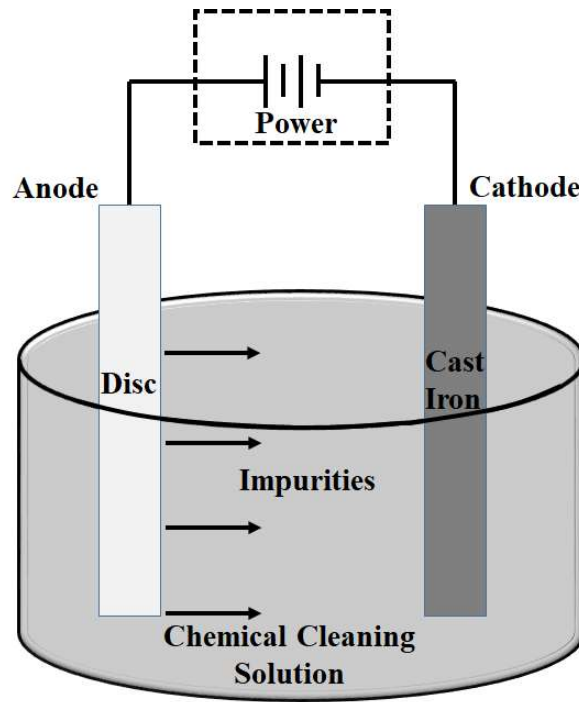


Fig. 3.1 Schematic diagram of a typical setup for chemical cleaning.

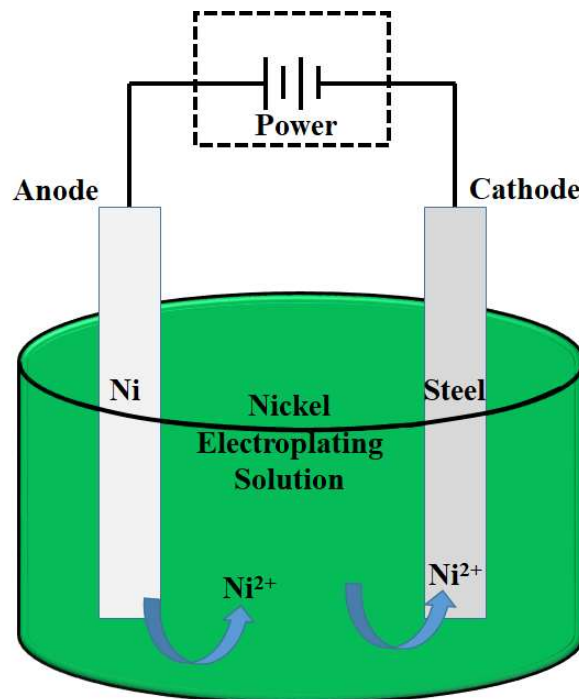


Fig. 3.2 Schematic diagram of a standard setup for nickel electroplating.

3.4.3 CVD SET-UP FOR GRAPHENE DEPOSITION

The graphene films on the nickel electroplated steel discs have been synthesised using a thermal CVD system (T-TCVDM-21, Technos Instruments, Jaipur, India) with acetylene as a hydrocarbon source and hydrogen gas as a reduction medium. A schematic diagram of CVD set-up consisting of a gas supply unit, a split tube furnace, and a vacuum system is presented in Fig. 3.3. The gas supply unit consists of the supply of hydrogen and acetylene gas with mass flow controllers attached to both gas supply lines to control the flow of gases. The split tube furnace (STF1200, Across International, USA) having a single constant heating zone with a quartz tube of 60 mm outer diameter and 1000 mm length with a pair of stainless steel vacuum sealing flange installed on the sides of the tube is used in the current study. The furnace has a maximum limit of the temperature as 1200 °C and Kanthal A1 (Fe-Cr-Al alloy) as a heating element for heating the tube to achieve a faster heating. A type K thermocouple has been used to sense the temperature of the furnace by placing it at the centre of the furnace.

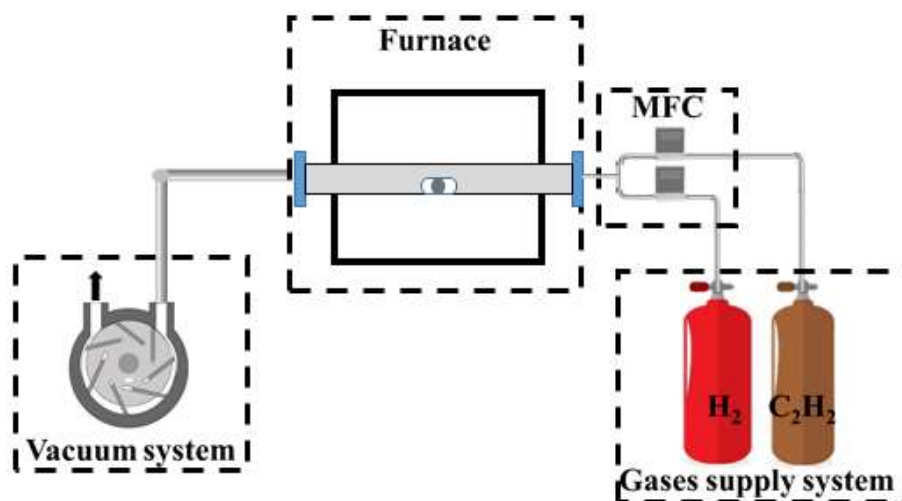


Fig. 3.3 Schematic representation of the thermal CVD set-up used for graphene synthesis.

3.4.4 GROWTH PROCEDURE AND DEPOSITION PARAMETERS

A typical temperature-time cycle for the growth of graphene is shown in Fig. 3.4. The disc to be coated is positioned in a ceramic boat, and then, the boat is pushed inside the quartz tube to place the boat in the centre of the furnace. After that, a vacuum of the order of 1.2×10^{-2} Torr is attained by using a rotary vacuum pump and maintained at this level. The samples are gradually heated from room temperature to predetermined growth temperatures, i.e., 650, 750, 850, and 950 °C, in 30 minutes and then annealed for 40 minutes under 20 sccm H₂ gas flow at the respective growth temperature. Annealing in the hydrogen environment helps for cleaning the native oxides over the nickel layer and, thus, promotes the C₂H₂ dehydrogenation over the nickel surface. The precursor gas, i.e., acetylene (C₂H₂), is allowed to flow for 20 minutes at a rate of 6 sccm along with H₂ (20 sccm). At higher temperatures, the decomposed carbon atoms from hydrocarbons are absorbed by the nickel layer. After completing the reaction stage, the flow of acetylene gas is terminated, and the samples are allowed to cool down naturally to room temperature in the hydrogen-rich environment. During the cooling stage, the formation of graphene occurs as a result of carbon precipitation over the surface.

Further, some experiments have also been carried out with various acetylene flow rates (6, 8, and 10 sccm) to grow graphene at 850 °C for 20 min and keeping the other conditions same. In order to analyse the effect of time on the growth of graphene, different growth times (10 and 20 min) at 850 °C have been used with a 6 sccm flow rate of acetylene while keeping the other conditions same. Table 3.1 presents the different conditions of temperature, flow rate, and reaction time variation for graphene growth. It costs approximate 2,000 Rs./sample (including material, nickel-plating, and CVD growth of graphene) to synthesise graphene.

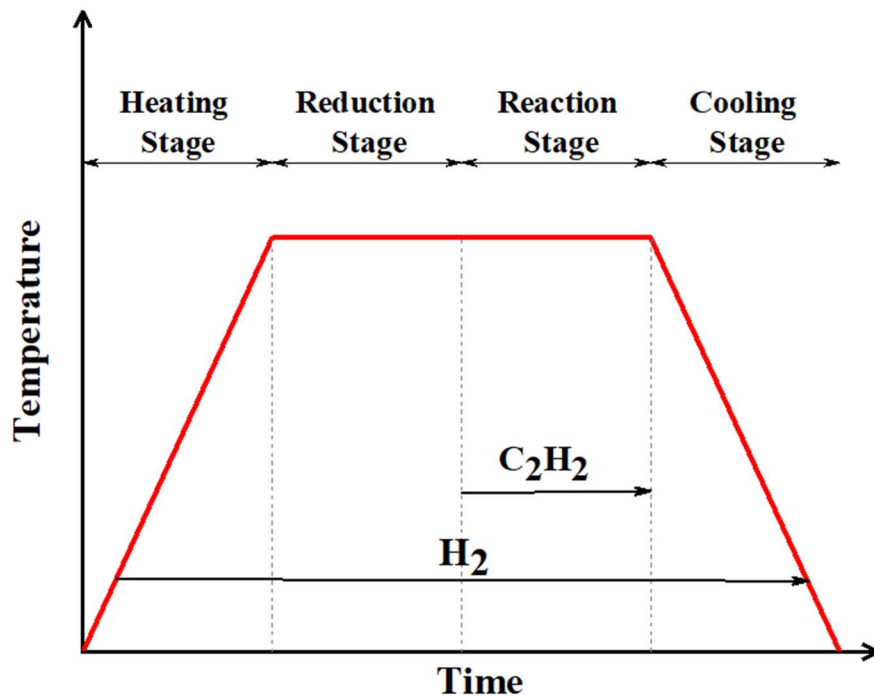


Fig. 3.4 Temperature-time cycle of a typical CVD growth of graphene.

3.4.5 CHARACTERISATION OF GRAPHENE FILMS

The morphologies of as-deposited graphene films have been studied by means of an optical microscope (VHX-6000, Keyence, Japan). The presence of graphene films on the surface is examined by high-resolution Raman spectroscopy (LabRAM HR Evolution, Horiba Jobin Yvon, France) using a laser excitation wavelength of 532 nm, laser power of 13 mW, scan range of 800-3000 cm^{-1} , and a scanning time of 0.1 second per spot. The size of the focal spot of the laser has been set to 1.25 μm in diameter. The surface roughness of graphene coatings is measured by a non-contact 3D optical surface profiler (Zygo NexView, AMETEK Inc., USA).

Table 3.1 Different conditions of graphene growth using CVD over nickel-plated steel.

Effects	Temperature (°C)	Reduction stage	Reaction stage	Cooling stage
Temperature variation	650	H ₂ (20 sccm) for 40 min	6 sccm (C ₂ H ₂) for 20 min	H ₂ (20 sccm)
	750			
	850			
	950			
Acetylene flow rate variation	850		6 sccm (C ₂ H ₂) for 20 min	
			8 sccm (C ₂ H ₂) for 20 min	
			10 sccm (C ₂ H ₂) for 20 min	
Reaction time variation	850	6 sccm (C ₂ H ₂) for 10 min		
		6 sccm (C ₂ H ₂) for 20 min		

The X-ray photoelectron spectroscopy (XPS) analyses with an applied power and beam diameter of X-rays as 23.56 W and 100.0 μm , respectively, have been performed using Quantera SXM (ULVAC-PHI, Kanagawa, Japan) with a monochromatic Al K α X-rays source of energy 1486.6 eV and angle of incidence as 45° for X-rays. The etching is performed by a sputtering argon gun to examine the elemental distribution along the depth. Peak fitting allowing to decompose the XPS spectra in different components assigned to different surface species, has been performed using the CasaXPS

processing software with a Shirley background. A high-resolution transmission electron microscope (HRTEM, Tecnai G2 20 TWIN, FEI, USA) has been utilised to measure the coating thickness and to reveal the structure of as-deposited graphene.

3.4.6 DRY SLIDING FRICTION AND WEAR TESTING

The friction and wear behaviour of synthesised graphene films have been examined using a ball-on-disc type of tribometer (UMT-5, Bruker, USA) at ambient conditions (temperature 25 °C and Relative humidity 40-50%) under both unidirectional as well as reciprocating sliding against a GCr15 steel ball of 6 mm diameter. The schematic representation of a ball-on-disc contact assembly is shown in Fig. 3.5.

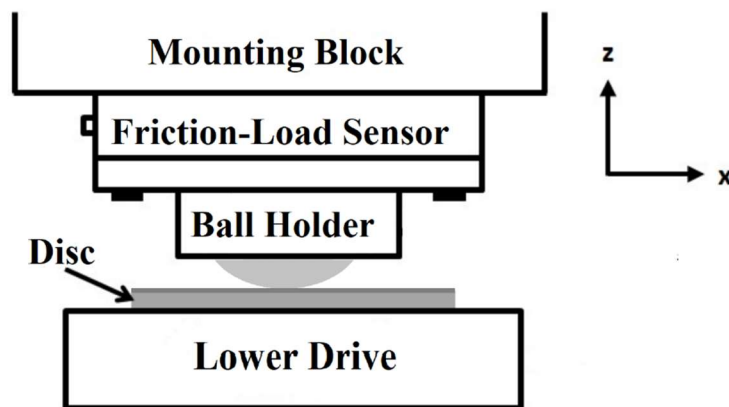


Fig. 3.5 Schematic representation of a ball-on-disc contact assembly for friction and wear tests.

In order to evaluate the friction and wear performance under unidirectional sliding, the disc has been set to rotate against the stationary counterpart (ball) with an average sliding speed of 0.07 m/s under an applied normal load of 0.5 N (average Hertzian contact pressure of 0.34 GPa). Each specimen under a set of experimental conditions has

been tested thrice to minimise the experimental error, and the average value has been reported. Initially, the friction and wear behaviour of graphene-coated bearing steel have been investigated for 800 cycles. To investigate the durability of graphene films over a period of time, the tribo-tests have also been conducted for a longer duration of 5600 cycles at a normal load of 0.5 N under atmospheric conditions.

For investigating the tribological performance under reciprocating sliding, the disc is made to reciprocate against the stationary counterpart (ball) with a frequency of 1 Hz (sliding speed of 0.01 m/s) over a stroke length of 5 mm. The four different applied normal loads of 0.1, 0.3, 0.5, and 1 N have been used for friction tests, corresponding to the average Hertzian contact pressures of 0.2, 0.28, 0.34, and 0.42 GPa, respectively.

The wear volume of the ball having a wear scar of effective diameter ‘ D ’ after tests has been determined by using equation (3.1) given below:

$$V = \left(\frac{\pi h}{6}\right) \left(\frac{3D^2}{4} + h^2\right) \quad (3.1)$$

Where, h is the height of material removed from the ball, which is calculated with the help of equation (3.2) given below:

$$h = R - \sqrt{R^2 - \frac{D^2}{4}} \quad (3.2)$$

Where, R is the original radius of the ball used for the friction test.

Further, the wear rate has been calculated using equation (3.3) as given below:

$$\text{wear rate} = \frac{V}{d \cdot L} \quad (3.3)$$

Where, V , L , and d are the total wear volume, applied normal load, and the total sliding distance, respectively.

The coefficient of friction during each run has been recorded through a data acquisition system in a computer that had an interface with the tribometer. The data from the starting to end of the test has been used to estimate the average coefficient of friction.

3.5 FORMULATION AND TRIBOLOGICAL BEHAVIOUR OF GRAPHENE OXIDE-WATER DISPERSION

The following section describes the preparation and tribological behaviour of water-based lubricant containing graphene oxide.

3.5.1 CHARACTERISATION OF GRAPHENE OXIDE POWDER

Graphene oxide powder has been characterised using Raman spectrometer (LabRAM HR Evolution, Horiba Jobin Yvon, France) by employing a laser with an excitation wavelength of 532 nm and a power of 13 mW with a scan range between 800 and 3000 cm^{-1} for per spot scanning time of 0.1 second. The focal spot diameter of the laser has been kept as 1.25 μm .

3.5.2 FORMULATION OF GRAPHENE OXIDE-WATER DISPERSION

Graphene oxide (GO) water dispersions containing different concentrations of 0.01, 0.05, 0.1, and 0.5 wt. % (GO), have been formulated by mixing Go in water followed by ultrasonication for 2 hours. Both the thickness and the average diameter of graphene oxide in dispersion have been characterised using atomic force microscope

(AFM) (Dimension Icon, Bruker, USA) and transmission electron microscope (TEM) (JEOL-2010F, Japan). For preparing the AFM and TEM sample, a very low concentration of graphene oxide is dispersed in water using ultrasonication. A drop of this dispersion is then put on the silicon wafer (in case of AFM) and copper grid (in case of TEM) and dried at 55 °C temperature in a vacuum oven before subjecting it to examination.

3.5.3 RHEOLOGICAL PROPERTIES OF GRAPHENE OXIDE-WATER DISPERSIONS

Rheological behaviour of dispersions has been explored at 25 °C with the help of a rheometer (MCR 302, Anton Paar, Austria) having cone and plate geometry with a 50 mm diameter plate and 1° cone angle over a range of shear rates from 1 to 1000 s⁻¹.

3.5.4 RECIPROCATING FRICTION AND WEAR TESTING

In order to examine the lubrication potential of formulated GO-water dispersions, the tribological tests have been performed under lubricated conditions using a multi-functional tribometer (Rtec instruments, USA) at room temperature with a ball-on-disc contact geometry under reciprocating motion. Figure 3.5 presents the schematic diagram of the ball-on-disc contact assembly used for the experiments. The stroke length and duration of the test have been kept as 5 mm and 3600 cycles, respectively. SS 304 stainless steel ball of 4 mm diameter has been used as counterface against the disc of SS 304. For all the lubricants having different concentrations (0.01, 0.05, 0.1, and 0.5 wt. %) of graphene oxide in water, the tests have been conducted under a normal load of 5 N and a sliding speed of 0.01 m/s. A graphene oxide-water dispersion volume of 100 µl is applied on the highly polished surface before starting each test, and no additional supply

of lubricant is made during the friction test. Each test under a given experimental condition has been conducted thrice and the average value is reported. The friction and wear tests have also been carried out using pure water as a lubricant under similar conditions for the purpose of comparison. The optimum concentration of GO in water has been determined on the basis of aforementioned experiments and then friction and wear testing have been performed under different normal loads of 5, 10, 15, and 20 N and different speeds 0.005, 0.01, 0.05, and 0.1 m/s for the optimised concentration of graphene oxide in water. Table 3.2 presents the experimental conditions used for evaluating the tribological performance of graphene oxide as an additive in pure water under reciprocating sliding for SS304 on SS304 tribo-pair.

3.6 EXAMINATION OF WORN SURFACES

The morphologies of the surfaces worn under different conditions of sliding, i.e., unidirectional and reciprocating under different loads, speeds, and for different concentrations of GO in water and wear scars on the counterpart (ball) have been examined under optical microscopy (VHX-6000, Keyence, Japan). The surfaces have also been subjected to Raman spectroscopy using a high-resolution Raman spectrometer (LabRAM HR Evolution, Horiba Jobin Yvon, Japan) with a laser excitation wavelength of 532 nm, laser power of 13 mW, the scan range of 800-3000 cm^{-1} , and scanning time of 0.1 second per spot with the size of the focal spot of the laser as 1.25 μm in diameter.

The worn tracks on the graphene-coated discs have also been analysed under a scanning electron microscope (SEM, Quanta 200FEG, FEI, Netherlands) equipped with an energy dispersive spectroscopy (EDS, GENESIS, EDAX, NJ, USA) to explore the possible mechanisms of wear. A high-resolution scanning electron microscope (HR-

SEM) (Nova Nano SEM 450, FEI, USA) equipped with energy-dispersive X-ray spectroscopy (EDS, Team Pegasus integrated EDS-EBSD, EDAX, NJ, USA) has been utilised to determine the chemical composition of the worn surfaces of ball and disc slid under lubricated conditions of graphene-oxide water dispersion.

A high-resolution transmission electron microscope (HRTEM, Tecnai G2 20 TWIN, FEI, USA) has been used to reveal the presence of the tribo-layer on the worn surfaces of both the ball and the graphene-coated disc after the friction test and to measure the thickness of this layer. However, a transmission electron microscope (TEM, JEOL-2010F, Japan) has been utilised to unravel the presence of the tribo-layer on the ball as well as on the disc surface after the friction tests under the lubrication condition of graphene oxide-water dispersion and to determine its thickness. The cross-sectional samples for TEM have been prepared using FIB (Lyra3, Tescan, Brno, Czech Republic) attached to the SEM facility. Additional metallic layers of Cr and Pt are sequentially deposited by ion sputtering on the surface of both the ball and the disc before the FIB process to prevent damage, spurious sputtering of the top portion of the specimen and to demarcate the location of the area of interest as well. The approximate thickness of deposited Cr and Pt are ~ 20 nm and ~ 2 μm , respectively. FIB in-situ lift-out technique has been used to prepare the TEM specimens from the worn friction surfaces. In this technique, the sample is extracted and transferred to a TEM half grid (lift-out grid of Cu with 4 posts), while it is still inside the FIB chamber. The thickness and diameter of the selected grid have been 25-30 μm and 3 mm, respectively. The samples have been prepared using rough milling followed by cutting, rough polishing, and final polishing before subjecting them to TEM examination.

Table 3.2 Experimental conditions used for investigating the tribological performance of graphene oxide as an additive in water.

Variables	Load (N)	Max. contact pressure (GPa)	Lubricants	Sliding speed (m/s)	Number of cycles
Concentration	5	1.42	water	0.01	3600
			0.01 wt.% GO in water		
			0.05 wt.% GO in water		
			0.1 wt.% GO in water		
			0.5 wt.% GO in water		
Load	5	1.42	0.1 wt.% GO in water	0.01	3600
	10	1.79			
	15	2.05			
	20	2.26			
Speed	5	1.42	0.1 wt.% GO in water	0.005	3600
				0.01	
				0.05	
				0.1	