

PREFACE

Tribology is the study of interacting surfaces in relative motion, a phenomenon that affects our everyday lives in several ways. The term *tribology* is based on the Greek word for rubbing and, although the term itself was not coined until 1966, there are instances of tribology in action from earlier times, when early tribologists used oil to facilitate sliding of large statues. Generally, tribology includes three key topics: friction, wear and lubrication. Friction is the resistance to relative motion, wear is the loss of material due to that motion, and lubrication is the use of a fluid (or in some cases a solid) to minimize friction and wear. The field is essentially interdisciplinary and utilizes aspects from mechanical engineering, materials science and engineering, chemistry and chemical engineering and more. It is technologically-relevant, scientifically-fascinating and economically-important. Friction is the primary culprit for low mechanical efficiency. It is responsible for loss of energy and material due to wear. Gradual failure of the components is aggregation of the wear loss, which eventually leads to failure. The need to replace the worn parts, the idle time during replacement, the manpower associated with it, the material processing and resources are some examples of direct and indirect losses incurred due to wear phenomenon, which need to be minimized. Lubrication (liquid or solid) is the key to reduce the frictional and wear losses.

It is one of the greatest challenges of the tribological systems to maintain low friction and low wear rate over a wide range of sliding conditions like load, speed and environment. Monolithic materials are not able to fulfill the requirements of low friction and wear. Hence, one is left with options like surface modification, wear resistant coatings or development of materials with self-lubricating and anti-wear properties. However, limitation of surface modification and coating techniques is that the modified surface

needs periodic overhauling. Therefore, development of new materials is a better alternative as it can play a vital role in fulfilment of the technological, environmental and social needs in relation to tribology. The goal of any material development for tribological application is to improve the efficiency of the system, reduce the energy consumption, cut short the man power and resources required for maintenance of the components and improvement in the life of the component. In a study conducted by Holmberg and Erdemir (2017) has claimed 23% of total energy consumption by the world's population accounts for tribological losses, of which 20 % is shared by frictional losses occurring at the tribo contacts and rest 3% is shared by wear loss or its maintenance cost. It can be inferred from the previous and recent data on economic impact of tribological generated losses, that overall a lot of money can be saved by minimizing these losses by using lubrication, surface modification/ coatings or developing new friction and wear resistant materials.

In many tribological systems it is not always possible to provide external lubrication. It could be either due to cost ineffectiveness, harsh environmental conditions, extreme pressure and inaccessible locations. Such applications urge for the development of self-lubricating materials which offer improved wear resistance along with low coefficient of friction and hence, the role of multi-phase composite materials becomes even more important. Composite materials are the mixture of two or more than two components which are physically distinct and chemically separable. In order to obtain desired properties suitable for a particular application, more than two dissimilar materials are mixed and fabricated to form the composites known as hybrid composites. These composites are difficult to fabricate by conventional methods of composite preparation Hence, some advanced sintering techniques like spark plasma sintering and microwave sintering have been evolved and being used.

Copper and its alloys are widely used because of their excellent electrical and thermal conductivities, better resistance to corrosion, ease of fabrication, good strength and fatigue resistance for making cables and wires, electrical contacts equipment and various other parts related to it apart from those used in automobile parts such as radiators and heat exchangers etc. However, poor strength, low anti-friction properties and low wear resistance of copper limits its application in tribological components, which can be enhanced by reinforcing it with solid lubricants and hard wear resistant materials. A number of solid lubricants (graphite, MoS₂, WS₂, *h*-BN, CNT, Ag etc.) either alone or in conjunction with other solid lubricant or hard phase (alumina, silica, zirconia etc.) have been used by several researchers to improve the mechanical and tribological properties of copper. It is not possible for a single phase to offer low and stable coefficient of friction (~ 0.2) and low wear rate over a broad range of load and speed conditions. Consequently, a different approach involving the fabrication of metal matrix composites (MMCs) reinforced by a solid lubricant and hard wear resistant material, or it could be the combination of two solid lubricants and one wear resistant phase or vice-versa may be required.

In light of the above, it becomes imperative to examine the tribological performance of self-lubricating copper based hybrid composites containing either a combination of a solid lubricating phases (s) and hard phase or a hybrid second phase which may improve the mechanical as well as tribological properties. Hence, the current study has been carried in two parts. The first one relates to the synthesis and tribological characterization of copper based composites containing iron, alumina, MoS₂ and *h*-BN. Three different composites Cu-Fe-Al₂O₃, Cu-Fe-Al₂O₃-MoS₂ and Cu-Fe-Al₂O₃-MoS₂-*h*-BN, designated as CA, CAM and CAMB, respectively, have been fabricated by spark plasma sintering. Pure copper specimen designated as PC has also been prepared for the

reference purpose. All the specimens (PC, CA, CAM, CAMB) have been tested under dry sliding condition using a ball-on-disc rotary tribometer at different loads of 2, 4, 6 8 N against EN31 steel ball of 6 mm for 6000 cycles and at a constant sliding speed of 0.5 m. s⁻¹. The major focus of this study is to investigate the effect of various phases on the tribological performance of composite, the occurrence of any synergetic action between a combinations of solid lubricants i.e. MoS₂ and *h*-BN and establishment of the probable wear mechanisms.

In another set of experiments, MoS₂ grafted graphene oxide nano particles are synthesized for reinforcement purpose. Graphene oxide is prepared by modified Hummers method and using hydrothermal approach MoS₂ nanoribbons are grafted on it. Copper powder and rGO-MoS₂ powders are mixed by ball milling and sonication, mixing process is followed by fabrication using spark plasma sintering (SPS). Composites containing a fixed amount of 2 wt. % rGO-MoS₂ are sintered at 600 °C, 650 °C, 700 °C and 750 °C and designated as CGM 600, CGM 650, CGM 700 and CGM 750, respectively, and their mechanical properties like hardness, UTS and YS have been determined by carrying out tensile test. The friction and wear characteristics of the composites as well as pure copper have been evaluated by carrying out wear tests against the 6 mm dia. EN31 steel ball at a fixed load and sliding speed of 4 N and 0.5 m. s⁻¹, respectively. The optimum sintering temperature has been determined on the basis of the mechanical and tribological properties and the composites containing four different (0.5, 1.0, 1.5 and 1.5 wt. %) concentrations of rGO-MoS₂ have been synthesized at the optimized sintering temperature, and have been designated as CGM 0.5, CGM 1.0, CGM 1.5 and CGM 2.0, respectively. The composites have been tested using a ball-on-disc tribometer under different loads of 4, 6, 8 and 10 N against EN31 ball and a fixed speed of 0.5 m.s⁻¹. The friction and wear results have been analyzed and optimum concentration

of rGO-MoS₂ providing the best friction and wear performance under the conditions used in the study has been determined. Further, the composites Cu-2.0 wt. % MoS₂ (designated as CM) and Cu-2.0 wt. % rGO (designated as CG) have been synthesized using SPS technique and their tribological performance has been compared with the composite Cu-2.0 wt. % hybrid rGO-MoS₂ by conducting wear tests against a counterface of EN31 steel ball at a load of 6N load and sliding speed of 0.5 m.s⁻¹. The worn surfaces of the composites have been analyzed by SEM, EDX and Raman spectroscopy to understand the wear mechanism.

Chapter 1 contains the introductory remarks highlighting the technological importance of the problem under investigation.

Chapter 2 begins with a brief description on composites and their types which is followed by a detailed survey on the processing routes to develop the metal based composites with special emphasis on the spark plasma sintering technique. The chapter also contains an exhaustive literature pertaining to the synthesis of copper based composites along with the effect of variables like sintering temperature, pressure and concentration of reinforcements on their mechanical properties like hardness, bending strength, toughness and tensile strength. A brief description of the laws and theories of friction, wear and types of wear also forms a part of the chapter. The chapter also presents an extensive literature on dry sliding friction and wear behavior of copper based composites containing hard/soft phase or their combination as reinforcement. The effect of concentration of second phase (s), load and speed on the friction and wear performance of such composites under different loading and speed conditions is also dealt with in detail based on the published literature. The chapter also sheds a light on the operative

mechanisms of wear prevailing in the dry sliding of such composites. The chapter ends with the formulation of the problem and the major objectives of the study.

Chapter 3 outlines the details of materials and the experimental procedures undertaken for synthesis and characterization of composites. In current investigation copper based composites Cu-Fe-Al₂O₃, Cu-Fe-Al₂O₃-MoS₂, Cu-Fe-Al₂O₃-MoS₂-*h*-BN, designated as CA, CAM, CAMB and pure copper specimen designated as PC have been synthesized by spark plasma sintering. The X-ray diffraction analysis has been employed to confirm the phases, whereas distribution of the phases has been analyzed using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX) elemental mapping. Density and hardness of composites is measured by using Archimedes principle and Vickers hardness tester, while tribological performance of the composites has been evaluated using a rotary ball-on-disc (DUCOM, India) tribometer against 6 mm diameter EN31 steel ball. The friction and wear tests have been carried out under different loads of 2, 4, 6 and 8 N and at a constant sliding speed of 0.5 m.s⁻¹ for 6000 number of cycles. Worn surfaces of the composites and counterface ball have been examined under the SEM to explore the wear mechanism, tribo-chemical analysis of worn track is done by X-ray diffraction and EDX and topography of the worn surface is examined utilizing the Atomic Force Microscopy (AFM).

The chapter also includes the detailed procedure followed for the synthesis of rGO-MoS₂ hybrid material and its characterization. Transmission electron microscopy (TEM) coupled with EDX has been employed for examining the morphology and elemental distribution of hybrid, whereas chemical features are probed with the help of X-ray Photoelectron Spectroscopy (XPS). Further, X-ray diffraction technique and Raman spectroscopy have been used for phase determination and confirmation. Copper

based composites containing 2.0 wt. % rGO-MoS₂ hybrid have been synthesized using spark plasma sintering at different sintering temperatures of 600, 650, 700 and 750 °C and designated as CGM600, CGM650, CGM700 and CGM750, respectively. Composites have been characterized by SEM, TEM, XRD and Raman spectroscopy. Density and hardness is measured for composites, which is followed by friction and wear testing on a rotary tribometre against EN31 steel ball at a load of 4 N and sliding speed of 0.5 m. s⁻¹ sliding speed for 6000 cycles. Based on the results of mechanical and tribological characterization, the optimum parameters of sintering have been determined and then composites containing four different rGO-MoS₂ content (0.5, 1.0, 1.5 and 2.0 wt.%) have been synthesized using optimized parameters and designated as CGM0.5, CGM1.0, CGM1.5 and CGM2.0, respectively. The tribological performance of these composites has been examined at different loads (4, 6, 8 and 10 N) and constant sliding speed (0.5 m. s⁻¹) for 6000 cycles. The composites containing rGO, MoS₂ and rGO-MoS₂ (2 wt. % each) have also been tested under the load of 6 N and 0.5 m.s⁻¹ sliding speed. The worn surfaces have been examined under the SEM coupled with EDX to establish the prevailing mechanisms of wear.

Chapter 4 describes the results on metallographic characterization of copper based composites Cu-Fe-Al₂O₃ (designated as CA), Cu-Fe-Al₂O₃- MoS₂ (designated as CAM) and Cu-Fe-Al₂O₃-MoS₂-*h*-BN (designated as CAMB). The presence of constituents has been confirmed by XRD, while the microstructure is analyzed by the scattered and backscattered mode of SEM. The elemental mapping reveals the agglomeration of Al₂O₃ at the grain boundary region of CA composite resulting in porosity, while a relatively dense microstructure with more uniformly distributed second phase has been observed for CAM composite. However, the composite CAMB has shown

some agglomeration of *h*-BN particles. The composite CAM has shown the highest density and hardness followed by the composites CA and CAMB.

The chapter also contains the results pertaining to friction and wear behavior of composites at different loads of 2, 4, 6 and 8 N and 0.5 m. s⁻¹ sliding speed. The coefficient of friction and wear rate have been observed to increase with increase in load from 2 to 4 N for pure copper as well as the composites CA, CAM and CAMB. However, a further increase in load from 4 to 8 N does not bring any significant change in coefficient of friction, except a drop in the value (from 0.93 to 0.32) for pure copper which has been attributed to the formation of a well compacted transfer layer of wear debris due to enhanced frictional heating. The wear rate is observed to decrease with increasing load for all the composites due to the formation of transfer layer of compacted wear debris confirmed by SEM micrograph, except for CA composite which has shown an increase and the same has been attributed to three body abrasion assisted fatigue wear caused by loose wear debris particles present on the worn surface. Composite CAM has exhibited the lowest wear rate and lowest coefficient of friction among all the composites which has been ascribed to the formation of compacted layer containing MoS₂. However, against expectation the composite CAMB containing a combination of MoS₂ and *h*-BN has shown a relatively higher wear rate and coefficient of friction indicating the absence of any synergetic action between the solid lubricants. A transition in the wear mechanism has been observed with change in loading conditions from 2 to 8 N for all the materials studied in the present investigation. Pure copper has shown a transition from mild adhesion at low load of 2 N to severe abrasion at 4 N which again changes to mild adhesion and plastic deformation on increasing the load to 8N. The composite CA has exhibited the delamination and oxidation as the operating wear mechanisms at the low loads, while wear mechanism has been observed to change to a combination of three body

abrasion and fatigue wear on increasing the load to 8N. The operative wear mechanism for CAM has been observed to be mild abrasion wear under all the loads whereas the same for CAMB is found to be a combination of plastic deformation and abrasion. In the end, results have been discussed in order to develop a coherent understanding of the effect of load and constituents on the mechanical and tribological behavior of composites.

Chapter 5 includes the results on the characterization of rGO, MoS₂ and rGO-MoS₂ by High resolution TEM, XPS, XRD and Raman spectroscopy of rGO-MoS₂. It is followed by the characterization of composites reinforced with 2 wt. % rGO-MoS₂ sintered at 600, 650, 700 and 750 °C, designated as CGM 600, CGM 650, CGM 700 and CGM 750, respectively. Microstructural features of the prepared composites have been analyzed by using SEM and TEM, while phase confirmation has been done using XRD and Raman spectroscopy. The hardness of the copper has been found to increase with the addition of rGO-MoS₂ which has been attributed to the restriction in movement of dislocation offered by the dispersed phase. However, the hardness has been observed to decrease with increasing sintering temperature which has been attributed to the non-uniform distribution and agglomeration of the rGO-MoS₂ which eventually results in the loss in densification as confirmed from SEM micrograph and punch displacement profile. The tensile strength has also been observed to decrease with increasing sintering temperature and the same has also been explained on the basis of the reduction in densification efficiency.

The results on the friction and wear behavior of the composites tested at a load of 4N and 0.5 m. s⁻¹ sliding speed against the 6 mm diameter EN31 steel ball for 6000 cycles are also included in Chapter 5. The composites have shown at least three times lower coefficient of friction and 110 times lesser wear rate than that of pure copper

which reflects the potential of rGO-MoS₂ as an effective solid lubricant. Among the composites CGM 700 exhibits the lowest coefficient of friction (0.059) and the lowest wear rate, which has been attributed to the formation of well-developed graphene and MoS₂ rich tribo-layer over the worn surface, the presence of which has been confirmed SEM and elemental mapping of the worn surface. The tribo-layer results in avoidance of direct metal-metal contact between the mating bodies and provides easy shearing capability at the interface which in turn reduce both the coefficient of friction and wear rate. The composite CGM 700 has been found to exhibit the optimized mechanical and tribological properties, hence, it is further tested at different loads of 6, 8 and 10 N to explore its tribological properties and the same have been compared with those observed for pure copper. The composite CGM700 has shown a marginal increase in both the coefficient of friction and wear rate with increasing load as against a significant increase for pure copper. The observed behavior for pure copper has been attributed to increase in abrasion with increasing load while marginal increase in friction and wear for composite has been attributed to the possible penetration of tribo-layer by the asperities of the counterface at increased loads. A mechanism, based on the contraction and expansion of graphene skeleton in the Cu-rGO-MoS₂ composites as a function of sintering temperature and sliding stress has been proposed to explain the relative changes in the friction and wear behavior among the Cu-rGO-MoS₂ composites. The self-lubricating properties of rGO-MoS₂ hybrid in composites and formation of rGO-MoS₂ containing tribo-thin film on the counter surface have played a vital role in improving the tribological performance of composites. The wear mechanism for pure copper has been observed to be the combination of plastic deformation, abrasion and adhesion, while Cu-rGO-MoS₂ composites sintered at different temperatures exhibited the mild abrasion and adhesion as the operating wear mechanism at low load (4N). However, the wear mechanisms for pure

copper and optimized composite CGM700 have been observed to be severe and mild abrasion, respectively, at loads beyond 4 N. In the end, results have been discussed in a comprehensive manner.

Chapter 6 begins with the presentation of results on the characterization of copper based composites, Cu-2 wt.% rGO, Cu-2 wt.% MoS₂ and Cu-2 wt.% rGO-MoS₂, designated as CG, CM and CGM, respectively, and Cu-0.5 wt.% rGO-MoS₂, Cu-1.0 wt.% rGO-MoS₂, Cu-1.5 wt.% rGO-MoS₂ and Cu-2.0 wt.% rGO-MoS₂, designated as CGM 0.5, CGM 1.0, CGM 1.5 and CGM 2.0, respectively. Composites are characterized by SEM and XRD for microstructural and phase analysis, which is followed by the density and hardness measurement. Composite CGM has shown the superior hardness and density as compared to that of CG and CM composite, which has been attributed to the good interfacial bonding between rGO-MoS₂ and copper matrix as confirmed by microstructural analysis of the composites. The density and hardness of composites containing different rGO-MoS₂ content increases with increase in rGO-MoS₂ content up to 1 wt. % due to uniform dispersion, whereas, a decrease in hardness and density occurs with increasing content beyond 1.0 wt. % due to the agglomeration of rGO-MoS₂.

Further, the chapter describes the results on friction and wear behavior of CG, CM and CGM composites and their comparison with pure copper. Pure copper exhibits the highest coefficient of friction (~ 0.77) and high wear rate, which is followed by CG and CM. However, the composite CGM has shown a steady and low coefficient of friction (~ 0.078) along with low wear rate. A relatively high coefficient of friction and wear rate shown by the pure copper have been attributed to its low hardness and soft nature resulting in severe abrasion and adhesion as confirmed by the SEM examination of the worn surfaces of pure copper. Among the composites CG exhibits high and gradually

increasing friction with high wear due to fatigue wear as confirmed from the large number of cracks observed on the worn surface. The coefficient of friction observed for composite CM reaches a maximum value of 0.22 with low wear rate owing to the formation of tribo-oxide layer comprising of MoS₂ particles as confirmed by SEM of the worn surface and the corresponding elemental mapping. The composite CGM has shown the low coefficient of friction and wear rate among all the composites i.e., CG, CM and CGM which has been attributed to the formation of rGO-MoS₂ rich tribo-layer and transfer layer formation over the counterface confirmed with the help of SEM, elemental mapping and Raman spectroscopy of the worn surface.

The chapter also presents the result pertaining to the effect of rGO-MoS₂ content and load on the friction and wear performance. Tribological testing of composites CGM 0.5, CGM 1.0, CGM 1.5 and CGM 2.0 has been conducted at the loads of 4, 6, 8 and 10 N and 0.5 m. s⁻¹ sliding speed for 6000 cycles against a 6 mm diameter EN31 steel ball on a ball on disc tribometer. The coefficient of friction is found to decrease with increase in rGO-MoS₂ content whereas the wear rate increases with increase in rGO-MoS₂ up to 1 wt. % content beyond which it decreases. Composite CGM 2.0 is observed to exhibit the lowest coefficient of friction (~ 0.2) among all the composite while composite CGM 0.5 has shown the lowest wear rate. A decrease in coefficient of friction with increasing content of rGO-MoS₂ has been accredited to the increase in lubricating phase content, while low wear rate at the 0.5 wt.% has been attributed to ductile behavior of composite due to low content of reinforcement phase and oxide layer formation. An increase in wear rate up to 1 wt. % content has been attributed to a fall in ductility, which results in brittle failure of surface and entrapment of loose oxide particles between sliding surface, which acts as third body and cause severe abrasion. However, a decrease in wear rate with increase in reinforcement content to 2 wt.%, has been attributed to the formation of a

compacted tribo-layer containing lubricating phase the presence of which has been confirmed with the help of SEM micrograph of worn surfaces, elemental mapping of the worn surfaces and wear debris. No significant change in coefficient of friction is observed for all the composites with increase in load. However, the wear rate has been observed to increase with increasing load especially in composites CGM 1.0 and CGM 1.5 which has been attributed to the increased tendency of peeling of the tribo-layer along with greater abrasion at high loads as confirmed from SEM micrographs. The wear mechanism is observed to be a combination of oxidation and adhesion for CGM 0.5, whereas two and three body abrasion are the dominating wear mechanisms for CGM1.0 and CGM 1.5. The dominating mechanism of wear for CGM2.0 composite is observed to be mild abrasion.

Chapter 7 presents the salient conclusions on the microstructural, mechanical and tribological characteristics of copper based composites synthesized in the present study along with the future scope of the study.