CHAPTER 2

LITERATURE REVIEW

Recent years have witnessed increasing efforts to develop composites possessing enhanced mechanical and tribological properties due to the requirements of efficiency, durability, and environmental compatibility put forth by the advanced technological systems. A number of novel materials having improved properties have been developed and the quest still continues. Some recent studies have demonstrated the efficacy of two-dimensional (2D) nanomaterials as potential reinforcements in different matrices due to their high modulus of elasticity, high strength, and ultralow friction as indicated by Ji et al (2020).

Sliding friction and wear are highly complex phenomena and become more complicated while dealing with composites due to the involvement of multiple-phases which may have their own distinct response to sliding. The research community has been exploring the dry sliding friction and wear behavior of composites under different conditions, in order to develop the understanding of the underlying mechanisms. However, despite several years of research it is still difficult to predict the behavior. Though, several models and laws have been developed for predicting the friction and wear of composites, but each has its own limitations and there is no single model which holds well in every condition. The different factors like surface roughness, load, speed, plastic deformation, adhesion, two or three body abrasion, fatigue spalling, delamination, oxidation, tribolayer formation and tribo-chemical reactions account for the complexity of phenomena. Apart from these, material properties, chemical and microstructural features of the material also play a crucial role in governing the friction and wear behavior of composites. The friction and wear performance of metals like copper has been shown to improve by the addition of hard/soft lubricating phase or a combination of these (Hong et al., 2011; Mallikarjun et al. 2017, Yu-nan et al., 2019).

The chapter begins with a brief description on the composites, their types and techniques used to fabricate the composites with special emphasis on spark plasma sintering (SPS) which is followed by a detailed review of literature on the mechanical properties of copper based composites containing different (hard, soft or a combination of them) reinforcements. The chapter also provides a short description on the fundamentals of friction including some basic theories of friction and wear highlighting the basic types of wear and Archrad's law. The chapter also includes a few studies underlining the tribological potential of rGO-MoS_2 hybrid which is the subject of the current investigation. An exhaustive literature on the tribological properties of copper based composites containing hard phases, 2D materials and other solid lubricant forms a major part of the chapter. The research gap is identified on the basis of the critical evaluation of the literature and the problem formulation along with the research objectives are presented at the end of the chapter.

2.1 COMPOSITE AND ITS TYPES

Composite materials are the mixture of two or more than two components which are physically distinct and chemically separable, with matrix as the major and continuous phase, reinforcement as the discontinuous and minor phase. Composites are developed to attain the desired properties for a specific service requirement which cannot be provided by a monolithic material. The composites have been classified on the basis of (i) matrix i.e. metal, polymer and ceramic, (ii) reinforcing phase i.e. fiber (long or short), whiskers, particulate and (iii) geometry of reinforcement i.e. continuous fiber, discontinuous fiber and wire. Figure 2.1 shows the typical classification of composites based on the matrix.

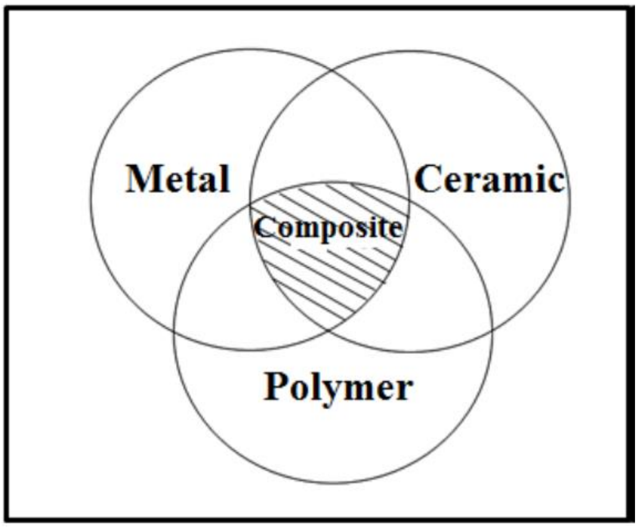

Fig 2.1 Matrix based classification of Composites. (Rosso et al., 2006)

Among all the above discussed composites, metal matrix composites are being used across the world for a wide range of applications due to their superior properties like high toughness, high specific modulus, high thermal conductivity, low thermal coefficient of expansion etc. In comparison to polymer matrix composite, MMC's show better fire resistance, high temperature capabilities, higher transverse strength, high stiffness, high shear strength and better compressive strength. Moreover, metal matrix composites also have an edge over the ceramic matrix composites due to high toughness, moisture resistance, high electrical and thermal conductivity, resistance to thermal shock and easy to work on (joining, shaping, and manufacturing).

2.1.1 PROCESSING TECHNIQUES FOR COMPOSITES

There are various processing techniques which are used for development of metal matrix composites. Mainly it depends upon the state of matrix material at the time of processing. These processes can be classified into five major categories as illustrated in Fig. 2.2.

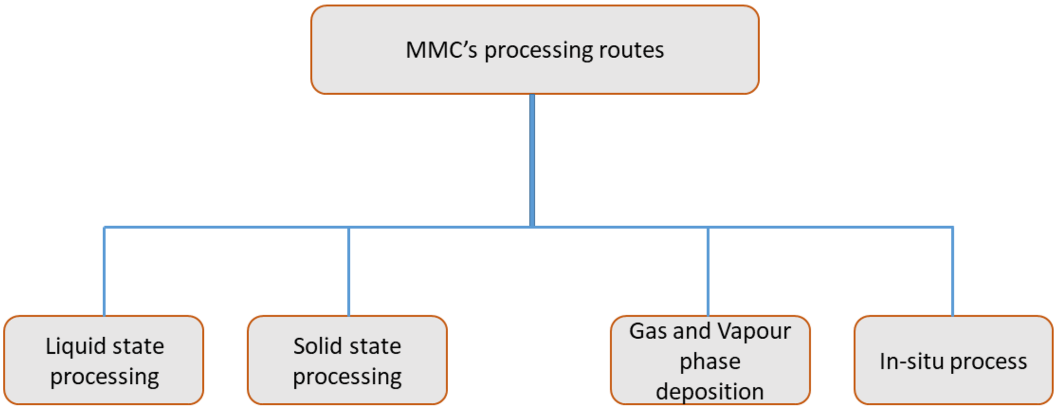

Fig. 2.2 Classification of the processing routes to develop MMCs.

2.1.1.1 Liquid State Processing

In **liquid state processing** the particulates of reinforcing phase are incorporated in the molten metal during the composite preparation, which is followed by mixing and casting of the melt. The liquid phase processing has been further classified into three categories, namely, melt stirring, gas pressure infiltration and squeeze casting. In **melt stirring technique**, reinforcement phase is added into molten metal and mixed with the help of the stirrer, which is then allowed to solidify. It is simple composite preparation technique but high temperature can degrade the quality of reinforcement phase. Another type of liquid phase processing technique is **gas pressure infiltration** technique, where molten metal is infiltrated in a ceramic preform by the means of gas pressure. The advantage of this technique over other liquid phase processing is pore free casting. The **squeeze casting** is also a type of liquid phase processing technique, where molten metal is forced to fill the preform with the help of pressure applied by ram displacement, preform is kept at the lower fixed part of the setup.

2.1.1.2 Solid State Processing

In this process metal is reinforced with particulates with mixture of blended elemental powders. There are certain steps prior to the final consolidation part involved in this process and **powder metallurgy and diffusion bonding** fall under this category.

(i) Powder Metallurgy (P/M)

It involves the mixing of matrix and reinforcements in powder form with appropriate proportion which is followed by compaction under pressure and sintering at elevated temperature to allow the diffusion to take place. Figure 2.3 depicts the steps followed for preparing a composite via P/M technique. The method provides a flexibility to incorporate any type or any form of reinforcement like whiskers, fibers or particulates. It is highly versatile process and allows to combine dissimilar materials which cannot be done by any other processes.

Mixing and Blending: Mixing is done to obtain uniform dispersion of all phases. Elementary powders are mixed and a homogeneous mixture of secondary powder is achieved, with powder particulates that are properly sized and well distributed with well-defined morphology. Lubricants are also mixed with powders to lower down the friction and wear of compaction dies as abrasive or hard particles can abrade the die surface during compaction. Several parameters like milling time, milling vial and ball material, milling environment, ball to powder ratio, processing control agent and ball size etc.

affect this process. However, mixing time is a critical factor. Excessive mixing should be avoided as it can result in hardening of particles.

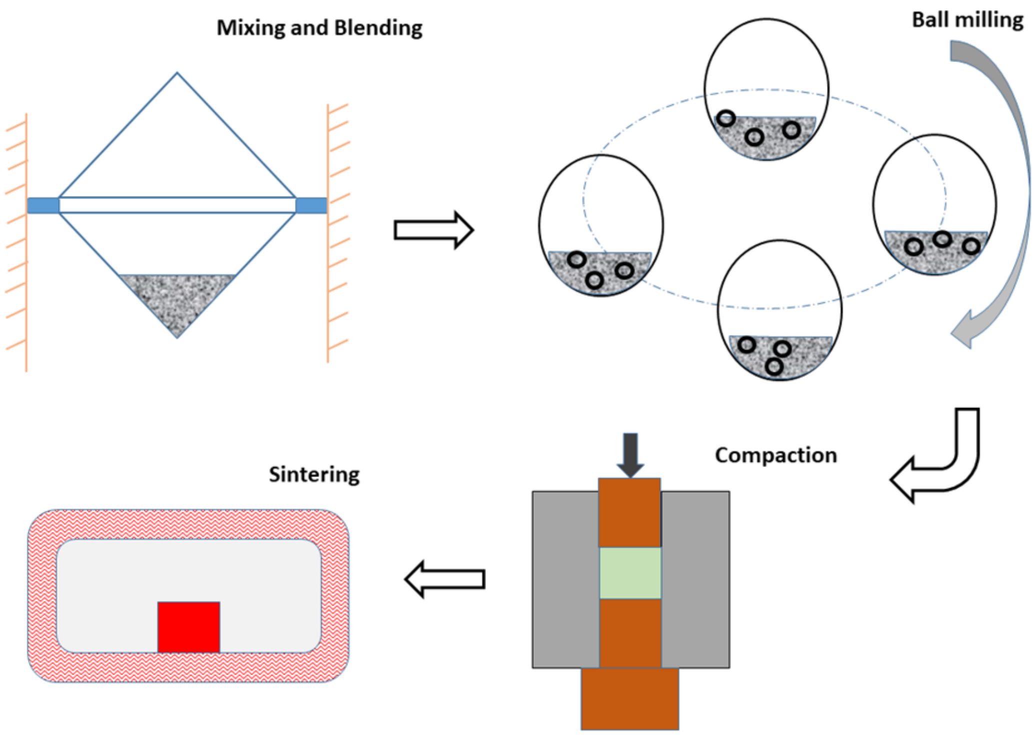

Fig. 2.3 Steps involved in powder Metallurgy process.

Among all mixing methods, high energy ball milling is the most commonly used due to its efficiency and efficacy in providing uniform dispersion of small reinforcement phase particles to matrix phase. Planetary ball mill is extensively used for mixing process as it reduces the size of the powder apart from mixing them. It consists of a jar mounted on eccentric sun wheel, both of them revolve in opposite direction and synchronize the centrifugal force alternately.

Compaction: Compaction is the process of compacting the mixed powders in a die by application of high pressure at room temperature to form green compact. It provides the green strength to the compacts by particle sliding and interlocking and plastic deformation. The density of the compact increases and porosity decreases with increasing compaction pressure (Garg, 2007).

Sintering: In this process compacts are heated to allow the fusion of pores between the interlocked particles which results in increase in density and strength. It involves three stages: in first stage interparticle welding takes place between the loosely stacked particles, and the weld grows as the sintering time increases (German, 2016). In second stage network of pores becomes unstable and it starts shrinking which is followed by stage three in which pore gets vanished. Figure 2.4 shows the different stages of sintering and the diffusion which occurs during the process.

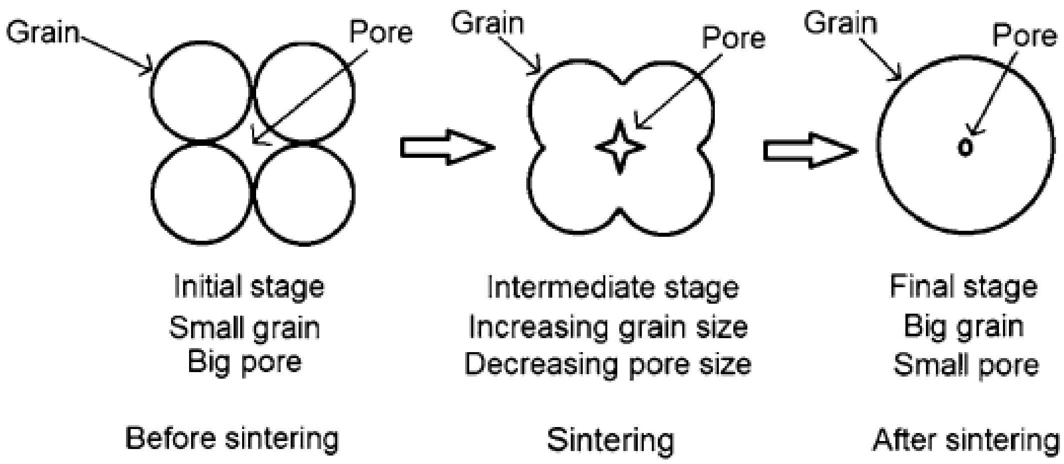

Fig 2.4 A schematic diagram of sintering (Ayatimur et al., 2014)

There are various techniques of sintering like conventional sintering, microwave sintering and spark plasma sintering which have been employed to produce composite materials. In **conventional sintering process** preformed powders are heated for diffusion, temperature is lower than melting point and it can last for several minutes to hours. While, **microwave sintering** is closely associated to dielectric properties, which are seen as indicators when material is exposed to microwave irradiation. **Hot isostatic pressing** is the sintering technique which involves the simultaneous heating and application of pressure to achieve high densification. In **spark plasma sintering process** joule heating takes place and a simultaneous load is applied throughout during the consolidation process. This sintering occurs at significantly less temperature than the melting point and offers several advantages over other sintering techniques like very less sintering time, avoid the coarsening of grains, ability to sinter the phases with high difference in sintering tendency.

(ii) Diffusion bonding

It is a solid state processing, in which fibers and metal sheets/foils embedded alternatively to form sandwich structure. The foil and fiber sandwich is then compressed and heated above the melting point of foil material, thus wetting the fiber and spreading the metal all over structure.

2.1.1.3 Gas and Vapor Phase Deposition

The gas and vapor phase techniques can be categorized mainly into two: the spray processes and the vapor deposition processes.

(i) Spray Deposition

The spray deposition processes involve fragmentation of a stream of molten metal in fine droplets (300 µm or less) by using a high-speed cold inert gas (argon or nitrogen) jet, that are sprayed together with the reinforcement particulates and collected on a substrate or mold where the semisolid metal droplets recombine and solidify to produce the composite material. (Srivatsan et al., 2006; Haghshenas et al, 2015) The droplets get flattened on impacting the substrate when they strike at very high velocities in molten or partially solidified state and weld together to form the composite as shown in Fig. 2.5. Though, the recombining of the splats occurs after the high energy impact over the substrate, the chances of porosity formation still exist due to difference in coefficient of thermal expansion of different constituents, thus it becomes necessary to apply the secondary process like forging to achieve high densification. The spray process is basically a hybrid rapid solidification method because the metal undergoes a rapid transition from the liquidus to the solidus which is followed by a slower cooling from the solidus to room temperature as indicated by (ASM hand book, 2001; Campbell et al. 2010; Asthana et al., 2015).

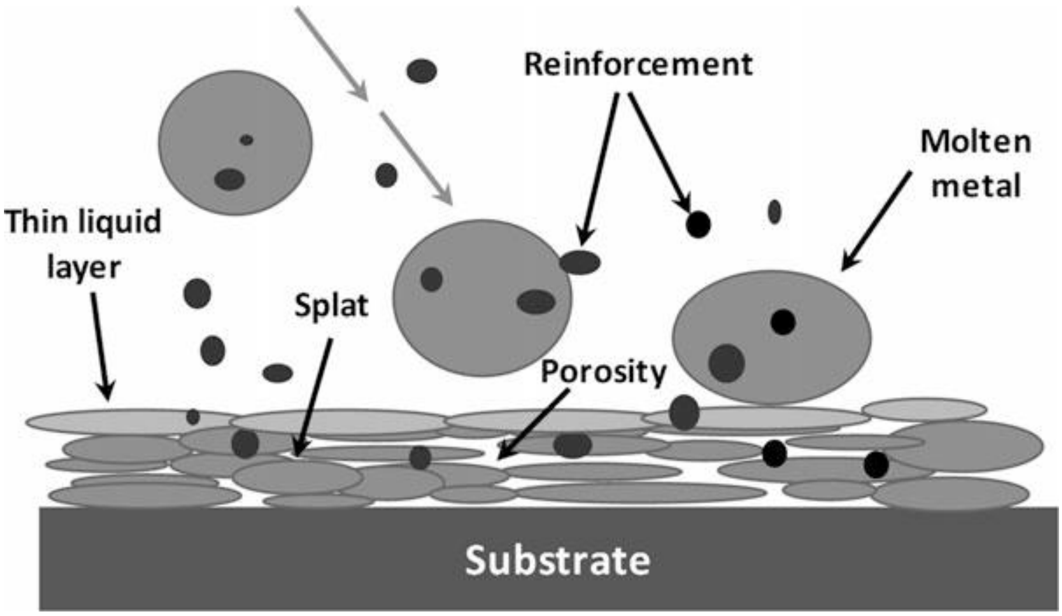

Fig. 2.5 Schematic diagram showing co-deposition of a metallic matrix and reinforcing particulates via thermal spray process (Asthana et al., 2015).

(ii) Vapor Phase Deposition

The process consists of several methods like Electron Beam/Physical vapor Deposition (EB/PVD), Physical vapor deposition (PVD), Chemical Vapor Deposition (CVD) and Plasma Assisted Chemical Vapor Deposition (PACVD). In EB/PVD fibers are passed through the region of high partial pressure of the melt deposit, where condensation occurs in order to produce a relatively thick coating on the substrate. (Shi et al., 2011; Li et al., 2004; Guo et al., 2002) The multiple number of evaporation sources can be used in this technique and composition can be varied by controlling the evaporation rate of the sources. There are various advantages of vapour phase deposition like high range of compositions can be prepared, there is no mechanical disturbance of interfacial region, uniform thickness can be achieved and thickness can be controlled etc. There are two major vapor deposition techniques available in the market: physical vapor deposition and chemical vapor deposition. **Physical vapor deposition** is a vacuum deposition technique, in which, material transforms from condensed phase to vapor phase then again get condensed as a film over the substrate, whereas **Chemical vapor deposition** is a process in which solid materials are vaporized and deposited on the substrate in the form of thin film by a chemical reaction.

2.1.1.4 In-Situ Processing

The in-situ processes can be classified in two brad categories (i) controlled solidification of melts (Zhang et al., 2013; Hu et al., 2012; Gunjishima et al, 2002: Zhang et al., 2016) and (ii) chemical reaction between two phases (Zhang et al., 2018; Yin et al., 2005; Sui et al. 2014; Peng et al., 2000; Singla et al. 2015). The major advantage of in-situ composite materials is that the reinforcing phase is generally homogeneously distributed, and spacing or size of the reinforcement may be adjusted in several cases by the solidification or reaction time. The interfaces are clean, mutually compatible and coherent because the constituent phase crystallizes in situ rather than combined from separate sources. However, the system selection and the reinforcement orientation are limited, and the process kinetics (in the case of reactions), or the shape of the reinforcing phases, is sometimes difficult to control as indicated by (Cuvas et al., 2018).

2.2 SPARK PLASMA SINTERING (SPS)

It is a novel sintering technique, which has been proved to be the most effective one for the research and development of new materials. It is a pressure sintering technique in which axial pressure is applied with simultaneous heating of the powder sample by means of plasma generation occurring at the gap sites of the particles due to electric discharge of DC pulse energizing. Quasi-static application of compressive force leads to morphological changes and increases the contact between particles and activates grain boundary diffusion, lattice diffusion and plastic deformation in order to increase the densification. A high heating rate increases the activation energy for grain boundary diffusion rather than surface diffusion, which helps in densification even at a low temperature simultaneously preventing the grain coarsening as well. In addition to the joule heating produced by electric current and plastic deformation, it produces DC pulse voltage between powder particles and effectively makes use of spontaneous heat generation by discharge between powder particles (Guillon et al., 2014). Thus, it provides two major advantages compared to conventional sintering: (i) makes high energy pulse focus at the grain junction point, thus saving the energy and (ii) High energy and low voltage pulse current generates instantaneous spark plasma and high localized temperatures between particles resulting thus, in optimum thermal diffusion and grain boundary migration. A schematic diagram of SPS is shown in Fig. 2.5. While processing an electrically conducting material, current flows through the sample rather than die and interaction of current takes place in following ways: (i) current passes through the porous powder beds, (ii) Peltier effect; between punch and powder and (iii) at interfaces and electro-migration. Since powder mixtures are not homogeneous and have different electrical conductivity at each point, a complex network of current flow forms, which is the result of initial packing structure. Then Joule heating occurs through percolating current path and formation of heat spots occurs at different locations where the local temperature exceeds the average temperature value. This mechanism leads to the formation of composite with fine microstructure.

2.3 COPPER BASED COMPOSITES AND THEIR MECHANICAL PROPERTIES

Copper based Composites containing different types (hard, soft or a combination of these) of reinforcements have been synthesized by several researchers through various processing techniques to attain desired mechanical properties for a particular service condition and the parameters of processing and content of reinforcements have been optimized. The following section presents the results of some researches on the preparation and evaluation of mechanical properties of Cu based composites.

Xu et al. (2020) studied the effect of in-situ formed nano WC and graphene, formed by impregnated reduction of W-Cu-graphene nano platelets on strengthening of copper based composites synthesized by Powders sintered at different temperatures (700, 800 and 900 ˚C) and reported that W-Cu-GNP composite exhibited 118% increase in yield strength (YS) with only 23% compromise in ductility attributing the increase in YS to a good dispersion of in-situ formed nano particles in the matrix. The strength was found to increase with increase in sintering temperature up to 800 ˚C and a further increase in temperature led to a decrease in strength.

Cui et al. (2020) developed the copper based composites containing (50 vol. %) graphite flakes and (0, 0.5, 1 and 3 wt. %) Mo particles by hot pressing technique at 1000 ˚C and 10 MPa pressure, while Cu-Mo composites were also developed by the same technique. It was found in the investigation that bending strength increased with increase in Mo content for Cu-Mo composites, while for Cu-Gr-Mo composites an increase in bending strength took place up to 1 wt. % of Mo content followed by a decrease with further increase in Mo content. Cu-Mo composites have been reported to possess better bending strength compared to Cu-Gr-Mo composites due to loss in ductility due to formation of Mo_2C.

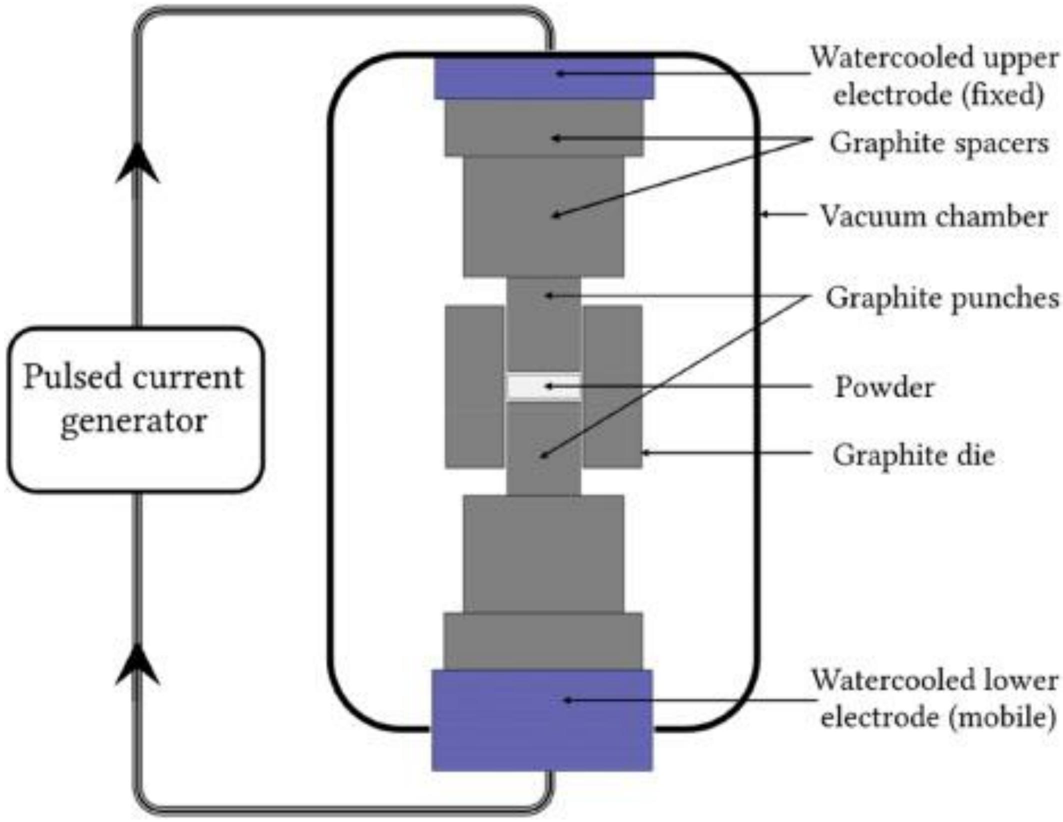

Fig. 2.6 Schematic diagram of Spark plasma sintering of powder sample (Guyot et al 2012)

Ghambheri et al. (2020) developed the copper based composite containing (0.4, 0.8, 1.6 and 3.2 vol. %) Ag decorated rGO using SPS at a sintering temperature of 800 °C and pressure of 35 MPa and indicated an increase in hardness till 1.6 vol. % addition of reinforcement followed by a decrease with increase in its content to 3.2 vol. %. It has further been reported that the strength increased with increase in reinforcement content up to 0.8 vol. % and decreased thereafter till 3.2 vol. % whereas elongation decreased with increase in reinforcement and it has been attributed to the change in fracture mechanism from ductile to brittle mode with increase in graphene content.

Li et al. (2020) developed *in situ* (0.07 wt. %) graphene reinforced copper based composites by calcination of polyethylene glycol and copper mixture in Ar and H_2 atmosphere followed by SPS at 850 ˚C and 50 MPa pressure and observed that composite had higher tensile strength (UTS of 254 MPa) than that of pure copper (208 MPa) with an attendant reduction in ductility. The strengthening effect has been ascribed to the load transfer between graphene and copper, thermal mismatch, grain refinement and orowan strengthening.

In order to analyze the effect of CNT content on mechanical properties of Cu based composites, the composites having an interconnected architecture of (0, 0.2, 0.4, 0.6 and 0.8 wt. %) CNT/W were developed by Zhang et al. (2020) using spraying pyrolysis of CNT/W powders and two stage SPS with initial sintering of compacts at 773 K for 5 min at 20 MPa followed by heating at 1073 K for 10 min at 50 MPa. An increase in tensile strength and elongation with increasing content of reinforcement up to 0.6 wt. % due to good dispersion caused by the weakening of van der Walls forces between CNT's by W particles has been reported. However, a further increase in the CNT-W content led to a decrease in tensile properties due to agglomeration as indicated by authors.

Cheng et al. (2019) studied the effect of nickel iron coated graphite/ copper composite prepared by electroless plating and spark plasma sintering at 850 ºC for 20 min holding time and 35 MPa pressure and achieved a good interfacial bonding between graphite and copper due to formation of Fe_3C and $FeNi_3$ with resulted increase in relative density, bending strength, hardness and compressive strength.

Chen et al. (2019) determined the optimum sintering temperature by fabricating Cu based composites containing 1.5 vol. % CNT-GO hybrid by SPS at temperatures of 823, 923, 1023 and 1123 K and 50 MPa pressure testing their mechanical properties and prepared the Cu-1.5 Vol. % GO and Cu-1.5 Vol. % CNT at the optimized temperature to analyze the effect of hybridization on the tensile properties. It has been reported that composite sintered at 1023 K had the maximum tensile strength and that Cu-CNT-GO composite showed better tensile properties than standalone composites due to formation of Cu_2O at the interface which increased the load transfer efficiency of the composite by lowering the interfacial energy.

Zhang et al. (2019) developed copper based powder metallurgy (P/M) composites containing (0, 0.1, 0.4 wt. % GO) graphene and a fixed amount of 0.5 wt. % carbon fiber (CF) at a compaction pressure of 50 MPa, followed by sintering at 900 $^{\circ}$C in a hot press vacuum furnace at 30 MPa pressure for 2 h. The hardness and yield strength were found to increase with increase in GO content and the authors have attributed it to the orowan strengthening, good interfacial bonding and spatial geometric distribution, which contributed in hampering the dislocation movement.

Chu et al. (2019) synthesized a Cu-Cr matrix composite reinforced by plasma treated and untreated (1 vol. %) graphene oxide (GO) sheets by SPS at 1053 K and 50 MPa pressure for 8 min and reported that an improvement of 103 % and 18% in yield strength (YS) and ultimate tensile strength (UTS) of Cu-Cr alloy. Also, YS and UTS of plasma treated GO reinforced composite have been reported to be 37% and 24%, higher than those of untreated GO reinforced composites which has been attributed to increase in (Cr_3C_7) carbide formation at edges and the basal plane of graphene due to plasma treatment, leading good interfacial bonding between graphene and the matrix. In another study, the same authors (Chu et al., 2018) prepared copper matrix composite reinforced by plasma treated and untreated (0.5 and 1 wt. %) graphene sheet and reported that composites reinforced by plasma treated graphene have higher TS and YS and that both increased with increase in graphene content. In a similar study, Zhang et al. (2019) compared the mechanical properties of Cu based composites reinforced with (0.2 wt. %) Cu electroplated graphene nano plates (GNP) as well as plain GNPs prepared by SPS and reported a significant improvement in tensile strength for electroplated Cu/GNP composite in comparison to plain Cu/GNP composite due to the good wetting facilitated by oxygen mediated bonds at the interface of copper and graphene which helped in the load transfer between matrix and graphene. However, Salvo et al (2019) observed a decrease in hardness of Cu by adding 1.0 wt. % graphene nano sheets (GNS) and with increasing sintering temperature and attributed it to the change in grain size with sintering temperature as well as with the addition of GNS as graphene sheets acquire the grain boundary positions and limits the grain growth.

Chen et al. (2018) developed Cu- 1.5 vol. % GO, Cu-1.5 Vol. % CNT, Cu-1.5 Vol. % CNT-graphene (GO) hybrid by SPS at 1023 K with 100 K/min heating rate at 50 MPa pressure for 10 min and found significant improvements in micro hardness, YS and UTS increased in comparison to pure copper due to thermal mismatch and orowan strengthening. The authors also reported that Cu-CNT-GO composite had superior properties than Cu-GO or Cu-CNT composites and attributed it to the presence of an interconnected network which favored the efficient load transfer at interface.

Wang et al. (2018) prepared Cu coated carbon nano tubes (CNTs) reinforced copper matrix composites containing 0, 0.25, 0.5, 1.0, 1.5 and 2.0 vol. % of CNT via spark plasma sintering at sintering temperature and pressure of 750^0 C and 50 MPa, respectively for 5 min time with a heating rate of 100^0 C/min followed by hot rolling at 700^0 C to obtain a total 50 % reduction and reported an increase in tensile strength till 1.0 Vol. % addition of CNT followed by a decrease thereafter.

Luo et al. (2017) fabricated Cu-0.6 wt. % rGO and Cu- 0.6 wt. % Ag-rGO composites by sintering at 700 ˚C in a vacuum hot press at 50 MPa for 45 min and compared with pure copper prepared following same route. The authors reported that the addition of rGO enhanced YS and UTS by 93% and 98%, respectively, due to dispersion strengthening by rGO particulates and Cu-Ag-rGO composite showed higher strength than Cu-rGO composite caused by the good interfacial bonding between Ag-rGO and matrix due to presence of Ag.

Yue et al. (2017) synthesized 0, 0.5, 1.0, 1.5 and 2 wt. % graphene nano sheets (GNS) reinforced copper matrix composite by vacuum hot pressing at a pressure of 25 MPa at a sintering temperature of 850 ˚C for 1 h and found that % elongation, hardness and UTS increased on adding GNS up to 0.5 wt. % due to thermal mismatch, grain refinement and load transfer between GNS and matrix improves strength. However, these properties decreased with increasing GNS content further due to change in fracture mode from ductile to brittle.

Si et al. (2017) synthesized graphene nano platelets (GNP) reinforced copper matrix composite to investigate the effect of carbide layer on its microstructure and properties. Initially, GNP were mixed with Ti and V in the presence of molten salt slurry in planetary ball mill at 250 rpm for 12 h to obtain TiC and VC coated GNPs, which were blended with copper by mixing them into alcoholic solution of Cu ions by addition of NaOH to form $Cu(OH)_2$ / GNP slurry followed by heating of slurry at 60 ˚C for 4 h to get Cu_2O/GNP. The obtained powder was then sintered by SPS at 700 ˚C for 5 min holding time at the pressure of 35 MPa with a heating rate of 50 ˚C/min. An increase of 40 % in tensile strength has been reported by the authors attributing it to the filling of Cu-GNP gap carbide interlayer.

Chen et al. (2016) studied the effect of graphene content (0.2, 0.4, 0.6, 0.8, 2 and 4 vol. %) on microstructure and mechanical properties of copper matrix composite. Composites were sintered by SPS at 700^0 C and 50 MPa pressure for 5 min. Mechanical properties like yield stress, hardness, elastic modulus were found to improve with increase in GNP content upto 0.6 vol. % followed by a decrease beyond that due to agglomeration of GNPs. Similarly, Gao et al. (2016) prepared 0, 0.1, 0.3 and 0.5 wt. % GO reinforced copper based composites via SPS at a temperature of 900 ˚C and 25 MPa for 1 h and suggested that UTS decreased with increasing GO content, while elongation first increased up to 0.3 wt.% addition of GO and decreased thereafter.

Zhang et al. (2016) prepared Cu-rGO and Cu-GNP composites containing 0.05, 0.1, 0.3, 0.5 and 1 wt. % of reinforcements at a sintering temperature of 600 ˚C for 5 min and at a pressure of 45 MPa using SPS technique and reported that the YS and TS decreased with increasing content of GNP, whereas, deceased with increasing rGO content. The observed behavior has been attributed to the orowan strengthening and mismatch in coefficient of thermal expansion in case of rGO and tendency of agglomeration in case of GNP.

Akbarpour et al. (2013) developed a copper based composite reinforced by (2, 4 and 6 vol. %) SiC nanoparticles by vacuum hot pressing process to investigate the effect of SiC content on mechanical properties and reported an increase in strength with addition of SiC particles due to grain refinement.

Samal et al. (2013) prepared 1, 3, 5 and 10 vol. % graphite reinforced copper matrix composites via conventional P/M route and 1 and 5 vol.% graphite containing composites fabricated by SPS to compare their mechanical properties. It has been reported that the composites fabricated from spark plasma sintering exhibited better properties like hardness, density and compressive strength compared to those prepared by conventional route due to fine grain morphology. However, compressive strength and elastic modulus decreased with increase in graphite content while hardness and flexural strength increased.

Rajkovic et al. (2012) examined the effect of milling time (10, 15 and 20 h) on the mechanical properties of Cu based composites having both nano and macro sized alumina particles reinforced copper matrix composite and reported that the maximum micro-hardness was obtained for a 10 h milling time which decreased slightly with the increasing milling time till 20 h.

Akhtar et al. (2009) fabricated 69 and 77 vol. % TiC reinforced composites having pure copper, Cu-Ti-Al and Cu-Ni-Co as matrices via powder metallurgy route to study the effect of TiC content on the mechanical properties and indicated that hardness and bending strength of composites improved with increasing TiC content due to good solubility of TiC in matrix alloy. However, Cu-Ni-Co matrix composites exhibited better mechanical properties compared to other matrices.

Peng (2007) synthesized in-situ Ti_3AlC_2 particulate reinforced copper matrix P/M composites by hot press vacuum furnace containing 0, 20, 30 and 40 wt. % of Ti_3AlC_2 and reported that composite having 20 wt. % reinforcement showed optimum hardness, flexural strength and toughness which decreased for higher contents of Ti_3AlC_2 due to the agglomeration of particulates and subsequent pore generation.

2.4 FRICTION AND WEAR

2.4.1 FRICTION

The resistance encountered by one body in moving over another is known as friction. Every surface has asperities, and frictional force arises due to the interaction of these asperities of two mating surfaces. Frictional force is the sum of the resistance offered by all the individual asperity contact sites. Coulomb (1785) proposed the basic laws of Friction: The **first law** states that, friction is directly proportional to normal load. While according to **second law**, the friction force is independent of apparent area of contact between the contacting surfaces and **third law** says that, the kinetic friction force is independent of sliding velocity, once the motion starts. Apart from these laws, some theories have also been developed with time, one of the famous theory proposed by Bowden and Tabor (1950) and known as **Adhesion theory** of friction, states that when two precisely clean surfaces are pressed against each other at room temperature, strong junctions are formed due to cold welding and adhesion without any interdiffusion or re-crystallization of metal atoms taking place at these junctions. A force is needed to break these junctions to move one body over other. Yet another theory on friction proposed by Coulomb (Year) known as **Asperity interlocking theory** says that when two surfaces are placed in contact with each other, both touch each other at discrete points known as asperities. Applied load is born by these asperities and they deform plastically on the application of load. When sliding occurs soft asperities deform under the application of load and leads to frictional resistance. **Molecular attraction theory** proposed by Hardy (1931) states that friction is because of molecular attraction. Origin of this theory is partial irreversibility of bonding force among the atoms. Such molecular attraction works over short distances and thus discriminates between real area of contact and apparent area of contact. It is also known as the extension of adhesion theory. Bowden and Leben **(1939)** proposed the **Stick-slip Theory** also considered as the alternative theory of adhesion, which assumes that one surface rests over the other at junctions. Once surface starts to slide over another, a rise of temperature occurs at these junctions, which results in local welding at the junctions. This leads to resistance to motion, i.e friction. Sliding occurs on account of applied force by tearing apart of these welds.

2.4.2 TYPES OF WEAR

The gradual loss of material loss of the material from the solid bodies which are in relative motion is known as wear. Mechanical properties of rubbing surfaces, chemical interaction and testing conditions affect the wear process. The wear of materials has been classified on the basis of the operative mechanisms and major types of wear are (i) abrasive (ii) adhesive, (iii) erosive, (iv) fatigue and (v) corrosive wear.

Adhesive wear occurs due to formation of micro-junctions caused by welding between opposing asperities of two rubbing surfaces. In other words, adhesive wear occurs in the form of material transfer when two bodies slide against each other or pressed against each other. Applied load on a body is supported by asperities. Due to less apparent area, load on the asperities are high enough to deform them and adhere to each other forming the micro-joints. The motion of the bodies' results in rupturing of the joints and rupture takes place from non-deformed region. Material transfer takes place in this manner from counter-body.

Archard (1953) provided an expression for adhesive wear loss. According to the expression, wear loss is directly proportional to the applied load and inversely proportional to the hardness of the material. It can be expressed as:

$$W = \frac{k\,L}{H} \tag{2.1}$$

where W is the wear rate, L is applied load, H stands for hardness of material and k is the wear coefficient.

Abrasive wear occurs when loss of material is caused by protuberance of hard material that are forced against soft material. It depends upon type of contact and contact environment. If there are two rubbing parts involved in friction process than wear is known as two body wear. In this mode of abrasive wear, asperities of hard body cause the material loss from the soft body while sliding. If the material loss occurs due to entrapment of hard particles between two mating surfaces, it is called third body abrasion. When material loss takes place from a solid body by the impingement of fluid or solid particles, such type of damage is known as **erosive wear**. In this type of wear, particles do the mechanical action on the solid surface through repeated deformations and cutting. Particles with some velocity impinge on the surface and cause pits, subsurface deformation. Particles are also detached from the surface due to cyclic crack growth occurred from superficial or subsurface microcracks. Such type of material loss is known as **fatigue wear.** Another type of material loss due to cyclic load is known as **fretting wear.** It is the material loss due to cyclic rubbing of two surface at very low amplitude. It can cause cracks on the surface, and lead to catastrophic failure. Wear due to corrosion or oxidation during sliding in the presence of corroding medium is known as **Corrosive wear**. It can also occur during dry sliding or in the presence of some gas. Excessive use of anti-wear agents or other chemical interaction can also cause corrosive wear. Harsh environmental conditions like high temperature, sea water, and high acidic or basic medium can also cause this type of wear.

2.5 TRIBOLOGICAL POTENTIAL OF rGO-MoS_2 HYBRID

The rGO and MoS_2 are two very popular and extensively used 2D materials having the lattice layered structure (Jiang et al., 2015) and a number of investigations (Chen et al., 2016 and Yi et al., 2020) have been conducted to analyze their effect as additive in lubricants in improving their lubricating capability or as a reinforcement in composites and coatings to provide them self-lubricating character. However, only a limited studies have been carried out pertaining to the investigation of tribological potential of rGO-MoS_2 hybrid as a self-lubricating agent lubricant in metal matrix composites. Chen et al. (2020) prepared rGO-MoS_2 by hydrothermal approach and functionalized it with hyper branched polysiloxane (HBPSi) containing cyclo-phosphazene (HBPSi-CPP). The authors prepared bismaleimide resin matrix composites by precipitation polymerization containing (0, 0.2, 0.4, 0.6, 0.8 and 1.0 wt. %) rGO-MoS_2 hybrid as a reinforcement and examined their dry sliding friction and wear using a pin-on-disc tribometer against the steel counterface. Both the coefficient of friction and wear rate have been reported to decrease with increasing content of rGO-MoS_2 till 0.4 wt. % beyond which both of these increased. The observed behavior has been attributed to dendritic structure, good dispersion of reinforcement and good interfacial bonding obtained for 0.4 wt. % reinforced composite. In another study, Chen et al. (2015) fabricated cast bismaleimide resin matrix composites reinforced with (0, 0.2, 0.4, 0.6, 0.8 and 1.0 wt. %) cyclotriphosphazene coated rGO-MoS_2 and examined their tribological behavior by conducting tests at a load of 196 N and speed of 200 rpm speed using a ball-on-disc rotary configuration against a counterface of steel. The coefficient of friction and wear rate have been reported to decrease with increasing reinforcement content up to 0.4 wt. % due to its unique layered structure and synergetic effect of reinforced phases. However, the coefficient friction and wear rate increased with increase in amount of reinforcement beyond 0.4 wt. % due to agglomeration.

In order to analyze the effect of a combination of rGO and MoS_2, Zhang et al. (2017) deposited four types of coatings i.e. pure epoxy, epoxy-MoS_2 and epoxy- GO and rGO-MoS_2-epoxy by air spraying in a nitrogen atmosphere followed by curing at 70 ˚C on steel substrate and investigated their tribological performance by carrying out tests in vacuum using ball-on -disc configuration at the load of 10 N and sliding speed of 0.033 $m.s^{-1}$ speed. The rGO-MoS_2-epoxy coating has been shown to provide the minimum friction and moderate wear rate compared to other coatings highlighting thus, the effectiveness of rGO-MoS_2 as a reinforcement over either rGO or MoS_2.

2.6 DRY SLIDING OF COPPER BASED COMPOSITES

Copper based composites have been studied extensively for its tribological behavior under different loads, sliding speed and composition by many researchers. Some of the studies are presented here:

2.6.1 CONTAINING A SOFT/LUBRICATING AND HARD PHASE

Copper based composite containing 1, 2, 3, 4, 5 and 6 wt. % of silver coated or uncoated graphite with addition of Ni to improve the wettability have been prepared by Wang et al. (2020) to analyze the effect of graphite content on their tribological behavior by carrying out tests using a pin-on-disc setup against U75V steel pins at a speed of 0.065 $m.s^{-1}$ and contact pressure of 0.77 MPa. The authors observed a decrease in coefficient of friction and wear rate with increasing graphite content and reported that the composites containing silver coated graphite exhibit much lower friction and wear rate than those containing uncoated graphite. The improvement in performance has been attributed it to the synergistic lubricating action of silver and graphite. Kavocik et al. (2008) investigated the effect of copper coated and uncoated graphite content on copper matrix composites friction behavior and found that friction coefficient decreases with increase in graphite content for both coated and uncoated samples. However, coated samples exhibited better frictional properties than the uncoated ones, attributed to good interfacial bonding between copper matrix and graphite. In an another study, Moustafa et al. (2002) studied the tribological behavior of 8, 15 and 20 wt. % copper coated and uncoated graphite reinforced copper matrix composites prepared by powder metallurgy and found the similar results.

Zhu et al. (2020) examined the effect of addition (20, 30, 40, 50, 60 vol. %) of foam copper prepared by electroless plating on the friction and wear the behavior of copper based composite containing different amounts (20, 30, 40, 50, 60 Vol. %) of graphite particles fabricated by ball milling and subsequent pressing at 100 MPa followed by sintering at 780 $^{\circ}$C for 2h by conducting reciprocating wear test at a load of 10 N and speed of 0.1 m.s^{-1}. The authors reported that coefficient of friction decreased with increasing graphite content for composites with or without foam whereas the wear rate increased. However, composites containing copper foam exhibited low friction and wear rate compared to composites without foam and attributed it to the formation of a friction layer having 3D network structure of a foam part from lubricious effect of graphite.

Ming et al. (2017) explored the effect of graphite content and sliding speed on tribological behavior of copper based P/M composites containing 3, 6, 12, 15 and 18 wt. % graphite using a pin-on-disc tribometer against HI3 steel disc at a normal pressure of 0.5 MPa and sliding speeds ranging from 3.14 m.s^{-1} to 47.1 m.s^{-1} and reported a decrease in wear rate with increasing speed and graphite content attributing it to the formation of a transfer layer counter surface. However, the coefficient of friction has been reported to decrease up to 6 wt. % of graphite followed by an increase thereafter and the same has been attributed to the formation of tongue layer which raised the friction.

Sun et al. (2019) investigated the effects of Sialon ($Si_4Al_2O_2N_6$) content and the counterface on the friction and wear performance of spark plasma sintered Cu based composites containing different amounts (0, 5, 10 and 20 wt. %) of Sialon at different loads of 3, 5, 7 N and a speed of 0.2 $m.s^{-1}$ on rotary ball on disc tribometer against alumina and steel ball. The authors reported an increase in coefficient of friction with increase in Sialon content whereas an increase in wear rate has been reported till 5 wt. % addition followed by a decrease further till 20 wt. %. Both coefficient of friction and wear rate have been reported to be lower against alumina ball than steel ball and improved behavior has been ascribed to grain refinement and good interfacial bonding of Sialon with Cu.

The tribological behavior of P/M processed Cu based composites having 0, 5, 10, 20 wt. % $AlMgB_4$ has been studied by Chen et al. (2016) at a load of 10 N and sliding speed of 0.188 $m.s^{-1}$ using a ball on disc configuration. Both the coefficient of friction and wear rate have been found to decrease with increasing content of $AlMgB_4$ content and the authors have attributed it to the formation of smooth lubricating and wear resistant film containing CuO, B_2O_3 and H_3BO_3 over the worn surface.

Zou et al. (2017) studied the tribological behavior of cast *in-situ* Cu-based composites containing 0, 0.5, 1 and 1.5 wt. % TiB_2 by conducing sliding wear tests at the loads of 15, 30, 45 N and sliding speeds of 0.020, 0.120 and 0.180 **$m.s^{-1}$** using a pin-on-disc tribometer against a counterface of structural steel and reported that wear rate increased with increasing load and sliding speed, whereas it decreased with increasing amount of TiB_2 and the same has been attributed to the increase in deformation resistance with increasing content of TiB_2. In a similar study, Pellizzari et al. (2017) examined the effect of load on the tribological behavior of Cu-0.5 wt. % TiB_2 against HSS steel disc at different loads of 50, 100 and 200 N and a fixed sliding speed of 0.6 $m.s^{-1}$ and reported an increase in wear rate with increase in load. Similarly, Tu et al. (2003) studied the dry sliding behavior of Cu based cast in-situ composites containing 0.5, 1.5 and 2.5 wt. % TiB_2 against medium carbon steel disc. It has been reported that wear rate increased with both the load and the speed and decrease in wear rate with increasing content of TiB_2 was reported due to decrease in plastic deformation with addition of TiB_2 content.

In order to explore the effect of addition of alumina on the friction and wear behavior of P/M processed Cu based composites containing 0, 2, 4 and 6 wt. % nano-alumina, Li et al. (2015) carried out ring-on-block tests at different loads of 5, 10, 15, 20, 25, 30 N and a sliding speed of 0.84 ms^{-1} against medium carbon steel and reported that both coefficient of friction and wear rate decreased with increasing amount of alumina till 4 wt. % followed by an increase beyond that. The authors attributed it to the change in wear mechanism from adhesive wear to abrasion due to increasing amount hard phase. In another study, Fathy et al. (2012) examined the effect of load and speed on the friction and wear behavior of alumina reinforced copper matrix composites and reported that an increase in wear rate with increase in load as well as speed due to crack formation with increased tribostress. A decrease in wear rate with increasing content of alumina has also been reported by authors due to increase in hardness which improved the resistance against abrasion. Similarly, Eddine et al. (2013) also reported an improvement in the friction and wear performance of pure copper by reinforcing it with alumina.

Tribological behavior of copper matrix composite reinforced with copper coated $NbSe_2$ and CNT containing a total of 15 wt. % ($NbSe_2$ + CNT) has been studied by Chen et al. (2015) using a ball-on-disc rotary tribometer against 440 C stainless steel ball at the loads of 1, 1.5, 2, 3 and 5 N and a fixed sliding speed of 0.053 ms^{-1}. It has been reported that the wear rate and coefficient of friction increased with increasing with composite containing 12 wt. % $NbSe_2$ and 3 wt. % CNT exhibiting superior tribological characteristics. The observed behavior has been attributed to the formation of lubricating layer on the complete worn out region for this particular content.

Lin et al. (2011) studied the tribological characteristics of copper/CNT composites having 5, 10, 15, 20 vol. % of CNT using a vane-on-disc set up against S45C martensitic steel at normal pressures of 0.44, 0.74, 1.04 MPa and sliding speeds of 1.23, 2. 45, 4.9 ms^{-1} and reported that coefficient of friction decreased with increasing CNT content whereas the wear rate was initially increased on adding CNT up to 5 vol. % due to low amount of lubricant available at the sliding interface, decreased thereafter till addition of 15 vol. % CNT due to availability of adequate amount of lubricant before increasing again for high content i.e. 20 vol. %, addition due to agglomeration of CNTs and resulting brittleness of material.

Raj Kumar et al. (2011) investigated the tribological behavior of microwave sintered copper matrix composites containing 5, 10, 15 and 20 vol. % copper coated CNT at the loads ranging from 12 to 60 N and a sliding speed of 2.77 ms^{-1} against EN 30 disc using a rotary pin-on-disc tribometer and observed an increase in both coefficient of friction and wear rate with increasing load and attributed it to the tendency of fragmentation of copper matrix with consequent generation of loose debris at contact interface leading to an increase in the friction and wear. It has further been reported that coefficient of friction as well as wear rate decreased with increase in CNT up to 15 vol. %, followed by an increase thereafter due to agglomeration of CNT at higher contents.

Rajkumar et al. (2011) investigated the tribological characteristics of copper matrix composites containing with TiC (5, 10 and 15 vol.%) and graphite (5 and 10 vol.%) by conducting tests on a pin-on- disc setup at different loads of (write values of load) and sliding speeds 1.25 and 2.5 ms^{-1} against EN30 steel and found an increase wear rate and coefficient of friction with increasing load. It has also been reported that low graphite and TiC content resulted in high wear rate and low friction whereas high graphite and TiC exhibited converse effect and the same has been attributed to change in wear mechanism from oxidative and plastic deformation wear to oxidative and delamination wear.

Dhokey et al. (2008) studied the wear behavior of Cu-20 vol. % SiC particulates composites fabricated by powder metallurgy by carrying out dry sliding tests at different loads of 15, 25, 45, 65 N and sliding speeds of 0.6, 1.2, 1.8, 2.4 ms^{-1} against SAE 52100 steel as the counterface using a rotary pin-on-disc tribometer and indicated that the wear rate increased with increasing load whereas it decreased with increasing sliding speed. A decrease in wear rate with speed has been attributed to the formation of mechanically mixed layer which protects the surface against wear whereas the increase in wear rate with increasing load has been ascribed to the augmented adhesion due to increase in plastic deformation.

Gautam et al. (2008) investigated the tribological behavior of cast Cu- 4 wt. % Cr-4 wt. % SiC composites by conducting dry sliding wear test on pin-on-disc set up against 4615 steel at the loads of 10 to 40 N and fixed sliding speed of 0.786 ms^{-1} covering a total sliding distance of 1398 m and reported an increase in wear rate and decrease in coefficient of friction with increasing load. However, the composites showed a lower coefficient of friction and wear rate in comparison to pure copper which has been attributed to the presence hard carbide particles which improved the hardness of the composites and reduced the real area of contact.

Zhan et al. (2004) synthesized copper based composites containing 10 vol. % SiC and (0, 3, 7 and 10 vol. %) graphite particles by compacting at 150 MPa pressure and sintering at 820 ˚C in ammonia atmosphere followed by repressing and examined their friction and wear characteristics against GCr15 steel ring using a block-on-ring tribometer at a speed of 0.42 $m.s^{-1}$ and loads of 20, 50 and 110 N load. The coefficient of friction and wear rate have been reported to decrease with increase in graphite content and it has been attributed to the formation of graphite rich layer over the worn surface with increasing graphite content. However, wear rate increased with increasing load whereas the coefficient of friction did not show any significant change with respect to load.

Tribological performance of 4 to 16 vol. % nickel coated CNT reinforced copper matrix composites prepared by powder metallurgy have been investigated by Tu et al. (2001) by carrying out tests at the loads ranging from 10 to 50 N using a pin-on-disc machine at a sliding speed of 0.0047 ms^{-1} against the diamonds pin. It has been reported that the coefficient of friction decreased with increase in load and CNT content, whereas wear rate increased with increasing load and decreased with increasing content of CNT. The decrease in friction with increasing CNT content has been attributed to the reduced contact between metal surface and diamond pin due to modification of surface by lubricious effect of CNT.

2.6.2 COPPER BASED COMPOSITES REINFORCED 2 D MATERIAL

Sadoun et al. (2020) investigated the effect of addition of graphene nano platelets (GNP) on the tribological performance of Cu-5 wt. % ZrO_2 - (0, 0.5, 1 and 1.5 wt. %) GNPs hybrid composites prepared via powder metallurgy technique at 950 ˚C sintering temperature in H_2 atmosphere by carrying out wear tests at different sliding speeds of 0.4, 0.7, 1.0 $m.s^{-1}$ and normal loads of 5, 10, 15, 20 N against a pin of stainless steel pin using a pin-on-disc tribometer and reported a decrease in coefficient of friction with increase in graphene content and a decrease in wear rate with increase in graphene content up to 0.5 wt. % followed by an increase thereafter. However, no significant variation was observed at a particular speed.

Pratik et al. (2020) coated rGO by copper using electroless deposition followed by activation and sensitization and synthesized (0.25, 0.5, 0.75 and 1.0 wt.%) rGO reinforced Cu matrix composites via spark plasma sintering at a temperature of 750 $^{\circ}$C and pressure of 50 MPa. The authors examined their tribological behavior by carrying out pin-on-disc test at 10 N load and 150 rpm against alumina ball and reported a decrease in coefficient of friction with increase in graphene content till 0.5 wt. %, however, an increase in graphene content beyond 0.5 wt. % exhibited the increase in coefficient of friction and due to agglomeration.

The tribological behavior of Cu-40 Vol. % rGO-WS_2, Cu-40 Vol. % rGO and Cu-40 Vol. % WS_2 composites prepared by P/M technique has been investigated by Lu et al. (2020) by conducting tests at a load of 80 N and a speed of 0.2 $m.s^{-1}$ using ring-on-disc tribo-tester at against a counterface of 1045 steel and reported that Cu- rGO composite performed better than other composites due to the formation of a well-developed tribo-oxide film on the worn surface.

Xian et al. (2020) investigated the effect of cobalt addition (0, 0.25 and 0.5 wt. % Co) on the tribological performance of Cu-0.2 wt. % graphene nano platelets reinforced composites prepared via hot pressing at 900 $^{\circ}$C by carrying out tests on a ball-on-disc tribometer against SiC ball at a load of 1N load for 2000 cycles. The coefficient of friction and wear rate have been reported to decrease with addition of GNP in pure Cu, which further decreased on adding Co up to 0.25 wt. % due to increased interfacial bonding. However, increase in amount of Co beyond 0.25 wt. % resulted in an increase in coefficient of friction as well as wear rate as indicated by authors.

Xue et al. (2019) studied the tribological behavior of $MoSe_2$/ MoO_x (x =2, 3) reinforced copper based P/M processed composites by carrying out tests against the 440 steel ball at different loads of 1, 3, 5 and 7 N and a fixed sliding speed of 0.17 m. s^{-1} using a ball-on-disc configuration of tribometer and observed a decrease in coefficient of friction and wear rate with the addition of reinforcement phases due to their synergetic effect. However, a decrease in coefficient of friction and an increase in wear rate with increasing load has been reported by them.

Lian et al. (2019) examined the synergic action between graphene oxide (GO) and Ti_3AlC_2 in improving the tribological performance of Cu based composites by synthesizing the copper matrix hybrid composite reinforced with GO and Ti_3AlC_2 via hot press sintering and compared with the composites containing either GO or Ti_3AlC_2 alone by carrying out ball-on-disc tests at loads of 1, 2, 3 to 4N against steel ball and reported a significant reduction coefficient of friction coefficient and wear rate for hybrid composite attributing it to the synergetic action between GO and Ti_3AlC_2.

He et al. (2018) studied the friction behavior of copper based composites containing (0.05, 0.1, 0.15 and 0.2 wt. %) of graphene nanosheets prepared through sintering in a vacuum tube. A decrease in coefficient of friction with increase in graphene content due to the formation of graphene rich tribo layer at the tribo interface has been reported by the authors.

Gao et al. (2018) investigated the tribological behavior of (0.1, 0.3 and 0.5 wt. %) graphene reinforced copper matrix composites fabricated by electrostatic self-assembly and powder metallurgy by performing tests on a rotary pin-on-disc rotary tribometer against GCr 15 disc under different loads of 10, 15, 20 and 25 N and speeds of while 120 r/min, 240 r/min and 480 r/min. It has been reported that coefficient of friction and wear rate increased with for graphene content up to 0.3 wt. % followed by a decrease after that and the same has been attributed to the uniform dispersion of graphene till 0.3 wt. % and the agglomeration thereafter. Both coefficient of friction and wear rate have been reported to decrease with load up to 15 N and increase beyond due to pull out of graphene sheets at higher tribostress.

Goudarzi et al. (2018) evaluated the tribological performance Cu based composites containing 1 to 10 wt. % MoS_2 at 1, 2 and 4 N loads and 0.2 ms^{-1} sliding speed for a sliding distance of 1000 m against AISI52100 steel pin using a pin-on-disc setup and reported a decrease in coefficient of friction and an increase in wear rate with increasing load. The composite containing 2.5 wt. % MoS_2 was found to provide the least friction coefficient and wear rate for all testing conditions which has been attributed to the presence of a well-developed tribo-film over the surface of the composite. The operative mechanisms of wear have been reported to be abrasion and delamination.

Xiao et al. (2018) studied the tribological behavior of (10, 20, 30 and 40 vol. %) WS_2 reinforced copper matrix composite fabricated by powder metallurgy (P/M) route by carrying out reciprocating wear sing a ball on disc setup against GCr15 ball at a load of 10 N a frequency of 4 Hz for a stroke length of 5 mm and observed a decrease in coefficient as well as wear rate with increasing WS_2 content.

Zhang et al. (2016) examined the tribological behavior of copper matrix composite reinforced by 1.0 wt. % carbon fiber (CF) and 2.5 wt. % reduced graphene oxide (rGO) prepared by SPS and freeze drying and compared with composite containing 2.5 wt. % rGO alone using a Pin-on-disc tribometer against GCr15 disc as counter face at a load of 20 N and sliding speed of 1.6 ms^{-1} and reported that coefficient of friction coefficient and wear rate decreased with addition of CF in the copper matrix along with increase in hardness. It has been ascribed to the hindrance to the movement of dislocation offered by carbon fibers along with formation of lubricating film on the surface due to cooperative effect of both the fillers.

Kovalchanko et al. (2012) investigated the tribological behavior of 1, 5, 10 and 15 wt. % MoS_2 reinforced copper matrix P/M composites at the loads of 10, 20, 40 and 80 N and sliding speed of 0.15 $m.s^{-1}$ using pin-on-disc tribometer against steel disc and found a decrease in coefficient of friction and wear rate with increasing MoS_2 content. However, the coefficient of friction was reported to decrease with load, whereas the wear rate increased with increase in load. The observed behavior has been attributed to the formation of a transfer layer at the counter face which reduced friction and wear with increase in MoS_2 content. In a similar study, Xiao et al. (2017) examined the effect of MoS_2 (0, 5, 10, 20, 30 and 40 vol.%) content on long term dry sliding wear behavior of copper matrix composites prepared through powder metallurgy route at fixed load and sliding speed of 5 N and 0.42 ms^{-1}, respectively, against AISI 52100 steel disc using pin-on-disc configuration for a sliding distance of 15 km and observed a decrease in coefficient of friction with increasing amount of MoS_2 ascribing it to the presence of lubricating phase which promotes smooth sliding. However, the wear rate increased with increasing reinforcement up to 10 vol. % followed by a decrease beyond that and attributed it to the deleterious effect associated with soft phase which causes voids and crack formation due to brittle phase formation at the interfacial region.

Lu et al. (2016) studied the effect of (0, 0.5, 1.0, 1.5 and 2 wt. %) multi-layer graphene (MLG) on tribological properties of $CuSn_5Bi_5$ alloy based composites synthesized by P/M route by conducting tests using a ball-on-disc setup against a hardened steel ball at a normal load of 2 N and sliding speed of 0.26 ms^{-1} and reported a decrease in coefficient of friction as well as wear rate with increase in MLG content up to 1.0 wt. %, with an increase in both beyond that content till 2.0 wt. %. The improved friction and wear performance till 1.0 wt. % has been attributed to the formation of a tribo layer due to the alignment of MLG at the sliding interface.

The effect of graphene content (2.5, 5, 7.5 and 10 vol. %) on the tribological properties of copper matrix composites prepared by powder metallurgy has been investigated and compared with graphite reinforced composites having same content by Li et al. (2015) at a load of 2 N and sliding speed of 1.0 $m.s^{-1}$ using GCr 15 ball as counter face. A decrease in both, coefficient of friction and wear rate with increase in graphite and graphene contents has been observed by the authors. It has also been reported that the graphene reinforced composites exhibit substantially less friction and wear rate than that of graphite reinforced composites and the same has been accredited to the formation of more compacted tribo-layer for graphene reinforced composites than for graphite reinforced ones.

In order to explore the possibility of a synergetic action for a combination of solid lubricants Chen et al. (2008) prepared graphite and *h*-BN reinforced copper matrix composites containing different percentages of them via P/M technique by keeping the total amount i.e. 10 wt. % of (*h*-BN+ graphite) of the lubricants fixed and carried out tests using a block-on-ring setup against an AISI 52100 steel ring at different loads and sliding speeds of 50, 75, 100 and 125 N and 1.04, 1.56, 2.08 and 2.6 respectively. It has been reported that coefficient of friction increased with load, whereas no significant effect of sliding speed could be observed. On the contrary, wear rate decreased with increasing sliding speed, whereas no change has been reported with load. However, the composite having 8 wt. % of graphite and 2 wt. % *h*-BN showed the lowest coefficient of friction and wear rate due to a synergetic action between *h*-BN and graphite at this particular content.

Kato et al. (2003) analyzed the friction and wear behavior of Cu-Sn based composites containing 0 to 40 vol. % uncoated graphite, Cu coated graphite, uncoated MoS_2 and Cu coated MoS_2 at a fixed load and speed of 125 N and 0.3 $m.s^{-1}$ using a cylinder-on-plate testing set up and reported that coated graphite and coated MoS_2 reinforced composites performed better than the uncoated ones. It has also been reported that the coefficient of friction and wear rate Cu coated graphite decreased with increasing content of reinforcement whereas wear rate of MoS_2 reinforced composites decreased with increasing amount of MoS_2. The authors concluded that graphite exhibits superior tribological properties than MoS_2 as the reinforcement phase and attributed it to the formation of brittle $CuMo_2S_3$ during sintering and absence of MoS_2.

2.7 FORMULATION OF THE PROBLEM

A critical review of literature presented above suggests that despite a large number of investigations carried out to examine the tribological performance of copper based hybrid composite containing either a hard phase or a soft lubricating phase and a combination of both (hard and lubricating phase), there is a lack of studies conducted on evaluating of the friction and wear behavior of Cu based hybrid composites containing

MoS_2, *h*-BN and nano-alumina, despite their excellent lubricating properties and hardening capabilities. Moreover, a combination of solid lubricants i.e. MoS_2 and *h*-BN may act in a synergistic manner to reduces friction at the interface and provide effective lubrication over a range of working conditions like load, speed and temperature. Hence, it becomes imperative to explore (i) the tribological potential of MoS_2, *h*-BN and Alumina reinforced copper based composites and (ii) possibility of any synergistic action between MoS_2 and *h*-BN. One may also infer from the above review of the literature that limited studies have been conducted on the evaluation of tribological potential of rGO-MoS_2 hybrid (rGO graphted by MoS_2) nano-particles, that too as additives in the lubricants, however, it's potential as a reinforcement in self-lubricating metal matrix composites has not yet been explored. Therefore, it would be proper to synthesize metal based composites containing rGO-MoS_2 hybrid as a reinforcing phase and analyze the effect of its content on their tribological behavior under dry sliding conditions.

In view of the above, the present study is being conducted to explore the tribological behavior of novel Copper based composites containing nano Al_2O_3, Al_2O_3-MoS_2 and Al_2O_3-MoS_2-*h*-BN and to examine their tribological characteristics by carrying out dry sliding wear test under different loads with an objective to explore the probability of any synergetic action between a combination of solid lubricants. Further, looking into the present trend of research, the present study also envisages to unravel the friction and wear behavior of copper based composites containing rGO-MoS_2 hybrid nano particles. The composites containing a fixed amount of rGO-MoS_2 may be synthesized at different sintering temperatures to determine the optimum temperature based on the examination of their mechanical properties and tribological performance. Copper based composites containing different contents of rGO-MoS_2 may then be prepared at this optimized sintering temperature and their friction and wear characteristics may be evaluated at different working conditions to explore the effect of reinforcement content on coefficient of friction and wear rate. Pure copper specimen and composites containing same amount of either MoS_2 or rGO alone may be prepared and tested under similar conditions for the purpose of comparison. The study also intends to establish the prevailing mechanisms of wear under the conditions used in the investigation for this new class of composites.

2.8 OBJECTIVES OF STUDY

In light of the above, present study has been carried out with the aim to fulfill the following objectives:

i) To fabricate Cu-Fe-Al_2O_3, Cu-Fe-Al_2O_3-MoS_2 and Cu-Fe-Al_2O_3-MoS_2-*h*-BN composites by spark plasma sintering and explore their friction and wear behavior under different loads.

ii) To explore the possibility of a synergetic action between MoS_2 and *h*-BN in reducing friction.

iii) To synthesize rGO-MoS_2 hybrid by grafting MoS_2 on rGO and characterize it.

iv) To fabricate and characterize the tribological properties of copper based composites containing rGO-MoS_2 at different sintering temperatures to determine the optimum sintering temperature.

v) To synthesize and characterize the Cu-rGO, Cu-MoS_2 and Cu-rGO-MoS_2 composites containing different amounts of rGO-MoS_2 hybrid and to evaluate their tribological performance at different loads.

vi) To establish the dominating mechanisms of wear.