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RESEARCH

Solid Lubrication in Iron Based Materials – A Review

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A B S T R A C T

The wide choice of materials available today has posed a major challenge for designers and engineers to select the most suitable material and manufacturing process for any engineering application. The mechanical and tribological properties have been a great concern, as the life of a product significantly depends upon these two aspects. Researchers have developed various composites with different compositions comprising of metals or metals with non metallic fillers to enhance these properties economically. Development of various Iron based antifriction composite materials is one amongst such composites as these are readily available with low cost. Sintered steels are also being used in gears and bearings due to economic and technical characteristics. Thus, new compositions with improved wear and friction properties have become a thrust area for tribologists and designers in the research world. This paper presents a review on various solid lubricants used in ferrous based compositions in order to enhance the mechanical and tribological properties.

1. INTRODUCTION

There has been a rapid growth in the development of engineering materials worldwide during the past few decades. The issue of material conservation, energy conservation, longevity, etc. has become a challenging task before designers, engineers and materials scientists in the development of new materials in the research environment [1]. Ferrous materials contain iron as prime constituent and play a significant role in engineering applications due to its low cost, ease of manufacture, better strength, toughness, ductility and availability. These materials can be alloyed and heat treated to achieve desired mechanical properties. Ferrous metals such as mild steel, carbon steel and, stainless steel are in use for a number of engineering applications [2].

Iron is alloyed with other metals like graphite, copper, phosphorus, nickel, etc. in order to change the microstructure so that the properties for a given application are easily met. Pre-alloyed ferrous powders when used with various additives such as copper, nickel, graphite, etc. results in high strength martensitic microstructures [3].

In this paper, various compositions of iron which are widely being used for various engineering applications are discussed. Solid lubricants and their behavior have also been comprehensively reviewed. The main objective of this paper is to review various ferrous based self lubricating composites which are developed by adding one or more solid lubricants in order to enhance the tribological properties.

2. IRON BASED COMPOSITIONS

2.1 Iron – Carbon system (Fe-C)

Iron is alloyed with carbon (graphite) to improve mechanical strength, hardness, hardenability, etc. Fe and C powders in the proportion of 93.3 % and 6.67% by weight% (wt %) were mechanically alloyed in a high-energy mill (shaker type) under inert atmosphere for different time intervals, which resulted in fabrication of nanocrystalline alloys in amorphous matrix of pure elements. Size of the crystallite reduces with increase in alloying time, which makes alloy more amorphous due to considerable change in the microstructure of material and in the chemical composition. Such alloys after sintering exhibits improved mechanical and tribological properties [4].

The morphology and distribution of graphite can also affect the friction and wear of iron-based materials. When, 0.8 wt% of carbon is diffused in iron, the amount of pearlite increases, which results in strength enhancement whereas 0.5 wt% carbon leads to decrease in strength. Thus, the occurrence of different phases in iron depends upon the carbon content to a larger extent [5].

2.2 Iron-Copper system (Fe-Cu)

The strength of iron can be improved by the addition of copper as it melts and rapidly dissolves in iron. During sintering, 2 wt% of copper dissolves in the solution and the excess (if any) remains there, in free state which results in the formation of a copper rich solid solution. Large pores occur in iron-copper (Fe–2wt%Cu) composition due to the fact that copper melts at 1083°C and spreads between iron particles and leads to the swelling of the compact. At room temperature, the solubility of copper in iron is around 0.4 wt% which results in the precipitation of excess copper [5]. This is the reason for the formation of homogeneous clusters of copper in Fe-matrix after sintering.

2.3 Iron-Copper-Carbon system (Fe-Cu-C)

The combined features of copper and carbon in iron matrix can be obtained by forming a Fe-Cu-C composite. The rapid diffusivity of copper in iron is the main reason for growth in the volume of compact leaving behind equal volume of porosity in Fe matrix. The addition of copper by 1 wt% reduces the strength and also influences the sensitivity of sintered carbon on dimensional variation as shown in Fig. 1, whereas, addition of 2 wt% copper results in better mechanical properties [6].

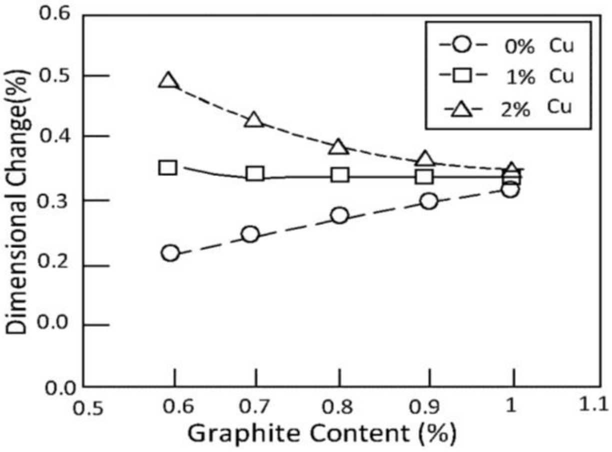

Fig. 1. Effect of carbon on Dimensional change of Fe-Cu-C composite [7].

The dimensional change due to copper is effected by the addition of carbon to Fe-Cu-C composites. The effect of addition of copper powder to Fe-Cu-C composites by different methods such as atomized copper, diffusion alloyed Fe-Cu and chemically bonded copper have been studied and it was observed that addition of copper does not cause any significant change in the mechanical properties and microstructure [7]. The microstructure and the mechanical properties of Fe-Cu-C composites can also be significantly improved by increasing the temperature during sintering [8].

2.4 Iron-Carbon-Copper/Nickel system (Fe-C-Cu/Ni)

The addition of nickel, carbon and, copper to iron in amounts of 2-4 wt% , 0.4-0.8 wt% and, 2 wt% respectively results in nickel steels [6]. Addition of nickel to Fe-C enhances the diffusivity of iron which leads to increase in pearlite and decrease in ferrite contents. Nickel rich areas also form at certain places. Thus, nickel steels show increased strength, ductility and also possess high strength when subjected to heat treatment.

3. SOLID LUBRICATION

Materials developed for friction and wear mitigation are commonly known as tribological materials. These materials must primarily meet mechanical and physical properties such as strength, stiffness, fatigue life, thermal expansion and, damping, in addition to tribological properties. Friction and wear reduction is achieved by introducing a shear-accommodating layer between the contacting surfaces. The intricate regions where liquid lubrication is not possible, such as high temperature applications, vacuum or in conditions where liquids cannot be introduced, solid lubricants is the most promising solution [9].

Solid lubrication was considered as an art only a half century ago but now it has emerged as an integral part of research discipline in the area of materials science and engineering. The functioning of solid lubricants on a surface is similar as that of liquid lubricants. The former shears easily and facilitates the tribological behavior between the sliding surfaces.

3.1 Fundamentals of solid lubrication

The theory as given by Bowden and Tabor [10] presented friction force (F) as a product of the real contact area and the shear strength of the lubricant material, $A_r.\tau$ (Fig. 2). Thus, the friction coefficient can be expressed as

$$\mu = \frac{F}{L} = \frac{A_r \cdot \tau}{L} = \frac{\tau}{P_H} = \frac{\tau}{P_H} + \alpha \tag{1}$$

where L is the normal load, P_H is the mean hertz pressure, τ is the interfacial shear strength, a ''velocity accommodation parameter'', which is a property of the interface and the constant α is the pressure dependence of the shear strength, which is the lowest possible friction coefficient for a given friction pair. According to Eq. 1, the friction coefficient is the ratio of frictional force to the applied normal force or can be termed as the ratio of shear strength to pressure.

Any hard material with a soft skin provides low coefficient of friction by reducing τ and increasing P_H. The Bowden and Tabor concept is schematically illustrated for the soft metal versus hard metal contacts as shown in Fig. 2.

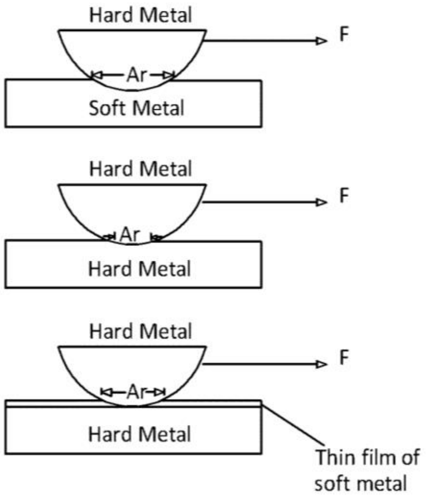

Fig. 2. Friction behaviour between Soft and hard metal [10].

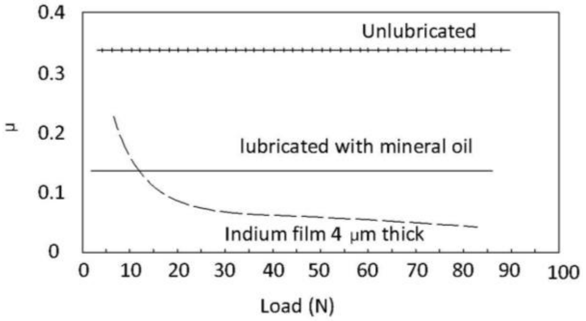

Fig. 3. Coefficient of friction of indium coated and uncoated steel [10].

The figure shows the behavior of friction force with metal substrate hardness. The shear strength and contact area changes with the hardness and, for the substrate covered with thin film of some soft metal, friction is relatively less. They validated their model by demonstrating that indium metal can act as a solid lubricant when applied as a thin film on a much harder steel substrate as shown in Fig. 3. It also shows the dependency of friction on the applied load. Friction coefficient is independent of load in case of unlubricated steel and steel with oil whereas, same does not hold good for third curve, where friction coefficient decreased with the increase in load.

3.2 Solid lubricants

Solid lubricants are a class of solid materials which are used to reduce friction and wear of the rubbing parts by preventing direct contact between their surfaces under different loads.

Table 1. Solid lubricants .

Classification	Key examples	COF
Lamellar solids	MoS_2	0.002-0.25
	WS_2	0.01-0.2
	hBN	0.150-0.7
	Graphite	0.07-0.5
	Graphite fluoride	0.05-0.15
	H_3BO_3	0.02-0.2
	GaSe, GaS, SnSe	0.15-0.25
Soft metals	Ag	0.2-0.35
	Pb	0.15-0.2
	Au	0.2-0.3
	In	0.15-0.25
	Sn	0.2
Mixed oxides	$CuO\text{-}Re_2O_7$	0.3-0.1
	$CuO\text{-}MoO_3$	0.35-0.2
	$PbO\text{-}B_2O_3$	0.2-0.1
	$CoO\text{-}MoO_3$	0.47-0.2
	$Cs_2O\text{-}MoO_3$	0.18
	$NiO\text{-}MoO_3$	0.3-0.2
	$Cs_2O\text{-}SiO_2$	0.1
Single oxides	B_2O_3	0.15-0.6
	Re_2O_7	0.2
	MoO_3	0.2
	TiO_2 (sub-stoichiometric)	0.1
	ZnO	0.1-0.6
Halides & sulfates or alkaline earth metals	CaF_2, BaF_2, SrF_2 $CaSO_4$, $BaSO_4$, $SrSO_4$	0.2-0.4 0.15-0.2
Carbon-based solids	Diamond	0.02-1
	Diamond-like-carbon	0.003-0.5
	Glassy carbon	0.15
	Hollow carbon nanotubes	-
	Fullerenes	0.15
	Carbon-carbon & carbon-graphite-based composites	0.05-0.3
Organic materials/polymers	Zinc steraite	0.1-0.2
	Waxes	0.2-0.4
	Soaps	0.15-0.25
	PTFE	0.04-0.15
Bulk or thick-film(>50 μm) composites	Metal-, polymer-, & ceramic-matrix composites consisting of graphite, WS_2, MoS_2, Ag, CaF_2, & BaF_2	0.05-0.04
Thin-film (<50 μm) composites	Electroplated Ni & Cr films consisting of PTFE, graphite, diamond, B_4C, etc., particles aslubricants.	0.1-0.5 0.05-0.15

Lubricants can be used in various forms to achieve the set of objectives, such as free-flowing powders, additives in oils, greases and sometimes as a key ingredient in certain anti-friction coatings or anti-seize pastes. A solid lubricant levels the valleys and peaks of surface asperities and adheres to the substrate. Under extreme operating conditions, the solid lubricants tend to deliver efficient boundary lubrication, thus improving friction and minimizing the wear.

Dry and clean lubrication, resistance to contamination, protection against corrosion, lubrication at various conditions and temperatures, etc. are some of the significant characteristics of solid lubricants due to which such lubrication is frequently being adopted [11-12]. The solid lubricants with their classification and coefficient of friction (COF) are as shown in Table 1 [13].

In comparison to fluid films used for hydrodynamic lubrication, the boundary films created by solid lubricants are capable of maintaining a uniform thickness irrespective of speed, temperature and load [14]. Also, a film formed by a solid lubricant may exhibit significant load bearing capacity and easy shearing capability [15]. Various different methods are used to apply these solids to sliding surfaces such as magnetron sputtering, ion-beam-assisted deposition, pulse laser deposition, ion-beam mixing, etc**.** [16-17], where as some are formed by vapor phase deposition molecular grafting, sulfurizing etc. [18-19].

4. CLASSIFICATION OF SOLID LUBRICANTS

Solid Lubricants are classified as:

- Inorganic lubricants
- Soft metals
- Chain structured Organic lubricants
- High temperature solid lubricants

4.1 Inorganic lubricants

The crystal lattice of these materials has a layered structure which consists of several thin parallel planes with hexagonal rings in each plane. Every atom in the plane is strongly bonded to the other atoms and the planes are bonded to each other by weak Vander Waals forces which causes the sliding movement of the parallel planes. This weak bonding between the planes determines their low shear strength and thus, the lubricating properties of the material. Inorganic materials such as molybdenum disulfide, graphite, hexagonal boron nitride, etc., offer excellent lubrication due to their lamellar structure [20-25].

Various sulfides, selenides, tellurides, monochalcenides, chlorides of cadmium, cobalt, lead, cerium, zirconium, etc. also belong to this category of lubricants [26-28].

4.2 Soft metals

Soft metals such as lead (Pb), tin (Sn), bismuth (Bi), indium (In), cadmium (Cd), silver (Ag), polyimide, etc. are used as solid lubricants because of their low shear strength, plasticity, rapid recovery and recrystallization characteristics. These metals have multiple slip planes in their crystal structure and do not work-harden during sliding [29-30].

The combination of properties as offered by soft metals are not found in other lubricants, for example, silver possesses softness along with oxidation resistance, electrical and thermal conductivity, good film forming tendency and a relatively high melting point. Lubrication at room temperature is best offered by Pb, In and, Sn than, Ag, Pt, Au, etc. which offer lubrication at high temperatures [31-32].

4.3 Chain structured organic lubricants

The molecular structure of these materials consists of long-chain molecules parallel to each other. The weak bonding strength between the molecules results in sliding past one other at low shear stresses but the strength of the molecules along the chains is high. Due to anisotropic mechanical properties and strong bonding between the atoms within a molecule, they provide good lubrication characteristics e.g., Polytetrafluoroethylene (PTFE) and polychlorofluoroethylene [33]. They have certain temperature and pressure limits which makes their use restricted to certain applications [34].

4.4 High temperature solid lubricants

Majority of the solid lubricants (lamellar solids) loose their lubrication characteristic at temperatures above 500 °C in open air and thus, such lubricants cannot be used in high temperature applications. The oxides formed at the interfaces of some of the metals and ceramics during sliding, dominate the wear and friction behavior of these interfaces at elevated temperatures [35]. Some oxides and sulfates because of their shearing capability at elevated temperature may be used as lubricants [36-37].

Some soft metals along with fluorides and oxide based solid lubricants also show better performance at elevated temperature such as silver (Ag), gold (Au), calcium fluoride (CaF_2), barium fluoride (BaF_2), lead oxide (PbO), Copper Oxide(CuO), Molybdenum trioxide (MoO_3) and, boron oxide (B_2O_3) [38-41]. These lubricants control their lubricity at higher temperatures due to their ability to soften and resist oxidation [42-44]. Composite lubricants have been developed which exhibit the tribological behavior over a wider range of temperatures. Composite nano films comprising of lead oxide/molybdenum disulfide (PbO/MoS_2), Molybdenum trioxide/Silver Oxide (MoO_3/Ag_2O) and zinc oxide/tungsten disulfide (ZnO/WS_2) show better performance, both at room and elevated temperatures [45-47]. The triological properties of some of the chemically modified oils were also enhanced by adding nano particles of WS_2, CuO, TiO_2 etc. [48-49]. Oxides of Titanium and Zirconium also exhibited a profound wear resistance [50].

At room as well as elevated temperatures, MoS_2 and a compound called Lead Molybdate ($PbMoO_4$) behaves as a lubricant [51]. A significant potential is there for tailoring film compositions to act as a lubricant over extended temperature ranges. The tribological behavior of a solid lubricant formed by combining Antimony trisulfide(Sb_2S_3) with MoS_2 shows improved performance at higher temperatures. This is due to low shear strength and presence of more sulfur content in antimony sulfide (Sb_2S_3) [52]. Copper Molybdates such as Cu3Mo2O9 and CuMoO4 synthesized from the mixture of CuO and MoO3 powders exhibited low friction and wear over a temperature range of 0-700 ^oC [53].

The composites developed using both low temperature and a high temperature lubricant has shown good tribological properties over a wide temperature range [54-55]. Ternary compounds such as A_xVO_4, A_xMoO_4 and

A_xSO_4(A=Ba, Sr and Ag) have also been confirmed as high temperature lubricants. Recently $Ba_xSr_{1-x}SO_4$ (x=0.25, 0.5, 0.75) was declared as a new solid lubricant at high temperatures [56-57].

Table 2. High temperature solid Lubricants.

Type of solid lubricant	Highest operating temperature in service (^0C)	Remarks
MgO/Mo/Fe	500	Self-Lubricating bearing material used in gas turbines.
CdO/Graphite	500	Soft CdO acts as a binder.
Ni/BaF_2/CaF_2	535	Bearing material. Abrasion rate of this mixed lubricant decreases as temperature increases.
Na silicate/ Graphite	535	Na silicate acts as a binder.
Metal sulphides, selenides and tellurides of group IVb, Vb, VIb and VIII elements	535	Vacuum Lubricants.
MoS_2/Graphite /Na Silicate/PbS/B_2O_3	650	Base: Nickel alloys
Ni/Cr blends with eutectic mixtures of fluorides	650	Pressure-produced Ni/Cr blends impregnated with 40 % eutectic mixture of fluorides.
Fluoro-chlorinated hydrocarbons	650	Lubricating coatings formed by chemical reactions with bearing surfaces.
PbO/Pb silicate	675	Sprayed as water paste on bearing surfaces and baked at 995 ^0C.
CaF_2	>675 under certain conditions	Chemically stable in hot oxidizing and reducing atmosphere; low vapor pressure, low solubility in water, ready cleavage of crystals.
MoO_3, Pb molybdate, K molybdate, Na tungstate, B_2O_3, Ag	700	All these substances protect bearings at high temperatures from serious abrasion and display low friction coefficients. Unsuitable at low temperatures e.g., optimum temp for silver is 315 to 975 ^0C
CaF_2+LiF blends	(In hydrogen) 815 (in air)615 (in liquid sodium)535	Sprayed as water paste on Cr/Ni alloys and baked under hydrogen cover. Good thermal and chemical stability.
Graphite/B_2O_3 /Silver halides	815	Silver halides are efficient high temperature lubricants but highly abrasive at normal temperatures.
Graphite/$CrCl_3$	1,000	Friction coefficient decreases with increasing temperature.

Lubricating material in the form of tribo-logical pads have been developed and tested by researchers and the results confirmed the reduction of friction within tribo-mechanical systems such as piston -cylinder liner [58].

The operating temperature and application areas of some of the high temperature solid lubricants are as shown in Table 2 [34].

5. FERROUS BASED SELF - LUBRICATING COMPOSITES

As discussed in the sections above, it is clear that a wide variety of solid lubricants are available. However, only some of the solid lubricants have been used frequently with ferrous based composites, as discussed below.

5.1 Graphite

Graphite is an allotropic form of carbon and is a crystalline solid of black-grey color with metallic luster. Its structure corresponds to a stacking of planes of carbon atoms bonded to each other by covalent bonds and these are arranged in hexagonal planes wherein, these different planes are bonded by Vander Waals weak forces. These weak forces facilitate the slip of the planes with respect to each other by the application of mechanical forces. This property of being easily sheared along the planes is what makes graphite a solid lubricant. It lubricates as long as moisture is available and functions as a lubricant up to 700 °C. Due to the requirement of moisture, graphite however, does not function as a lubricant in vacuum [59]. The coefficient of friction remains low at room temperature but above 90 ^oC, it increases and further at around 400-500 ^oC, the friction coefficient again decreases due to the oxidation of metal in contact with graphite. Fig. 4 shows the change in friction coefficient of graphite over the temperature range. It has been observed that coefficient of friction can be reduced over a range of temperature by mixing some salts with graphite such as cadmium oxide as shown in Fig. 4.

The coefficient of friction of graphite below 100 °C is 0.1. Up to 230 °C (450 °F), it varies from 0.1 to 0.4 due to desorption of water and is of the order of 0.2 above 218 °C(425 °F) due to interaction of graphite with oxides product of substrate. Maximum operating temperature of graphite is about 450 °C and above this temperature range, graphite begins to oxidize at an appreciable rate. However, when mixed with cadmium oxide the mixture works well up to a temperature of 1000 °F with low values of coefficient of friction [59].

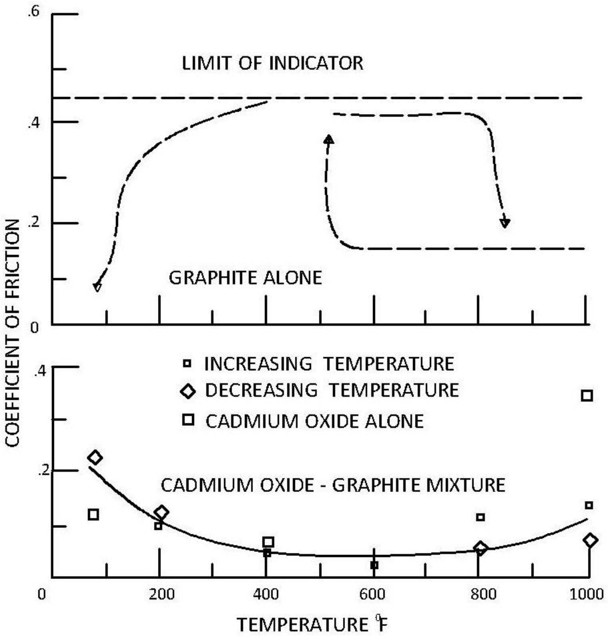

Fig. 4. Variation of friction of graphite [22].

Graphite mostly is used as a component of base compositions in Fe-C, Fe-Cu-C, Fe-C-Ni composites, etc. Thus role of graphite in the composition is to bring changes in the microstructure and to lubricate. It also prevents the swelling caused in the sintered composites due to the addition of copper in Fe-Cu alloys. Graphite has shown 30–50 % decrease in wear loss along with decrease in friction values at various sliding speeds when compared to titanium oxide and boric acid under extreme boundary lubrication regimes [60].

With increase in graphite content from 0.5 to 2 %, the microstructure of iron based composite undergoes a change from ferrite and pearlite to pearlite and a small amount of ferrite and cementite (Fe_3C). The increase in temperature results in more uniform sintered microstructure and the hardness thus improves due to the formation of cementite and lattice distortion of the ferrite. The density of the composites sintered at 1100 °C is higher than that sintered at 600 °C for higher percentages of graphite. At constant sintering temperature, the degree of superheat increases with an increase in the graphite content which results in the growth of austenite grain [61].

Graphite is being used in most of the ferrous based composites, as it helps in the development of various phases which causes improvement in the wear and friction characteristics. One such composite i.e., Fe-C-Ni was developed via powder metallurgy followed by various heat treatment processes such as quenching, tempering and, inter-critical annealing. The presence of various hard phases improved wear resistance in annealed specimens [62]. Iron copper tin (Fe-Cu-Sn) alloys can be used with graphite and talc as solid lubricants. The mechanical properties of Fe-Cu-Sn-C alloys sintered at temperatures ranging from 1000-1150 °C are comparable to that of wrought bronze alloys. The graphite results in poor mechanical and tribological properties at a sintering temperature of 850 °C due to incomplete diffusion. However, on increasing temperature from 850 °C to 1150 °C, the tribological properties improve at moderate and high loads [63].

Graphene is a single, tightly packed layer of carbon atoms bonded together in a hexagonal honeycomb lattice. It is a noval and an emerging lubricant with great characterstics. Easy shearing capability, high strength and chemical inertness makes grapheme suitable for tribological applications. Iron surface is the most stable surface for grapheme as it easily adsorbs on iron surface, thus enhancing tribological properties. It can be used both at micro and nano scales [64-65].

5.2 Molybdenum Disulfide (MoS_2)

MoS_2 exists naturally in the form of thin solid veins within granite. It has a hexagonal crystalline structure and easily shears at the interface between the layers comprising of sulfur molecules and is effective in high-vacuum conditions. The maximum temperature to which it can actively participate is 400 °C (752 °F) as it oxidizes gradually in atmospheres up to 300 °C (600 °F). In an oxygen free and dry atmosphere, it can function as a lubricant even up to 700 °C (1300 °F). Molybdenum trioxide (MoO_3) and sulfur dioxide are its oxidation products. MoS_2 is hydroscopic in nature and thus causes friction problems in standard atmosphere. It greatly influences the density of high speed steel powder by a combined reactive and super solidus sintering process [66]. The addition of

MoS_2 to iron, graphite and copper (Fe-C-Cu) composition via compaction and sintering enhances compressibility of the composite and thus increases density. The tribological properties improve at 3 wt% addition of MoS_2 but brittle phases present at 5 % results in high friction and wear [67]. MoS_2 in different amounts was added to iron, copper (Fe-Cu) composition using induction hot pressing sintering method. Hardness and anti compressive strength improves with 8 wt% MoS_2. The coefficient of friction and wear rate against hardened steel counter-face material decreases with the addition of 8 wt% MoS_2 at all temperatures due to the formation of solid solution of Fe-Mo and sulfides [68] as shown in Fig. 5a and Fig. 5b.

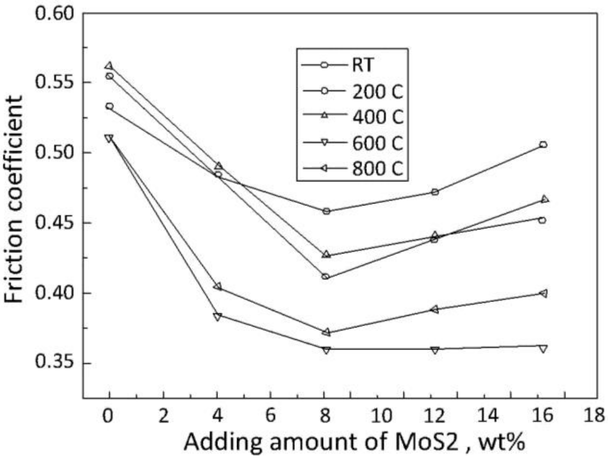

Fig. 5a. Friction coefficient of MoS_2 [68].

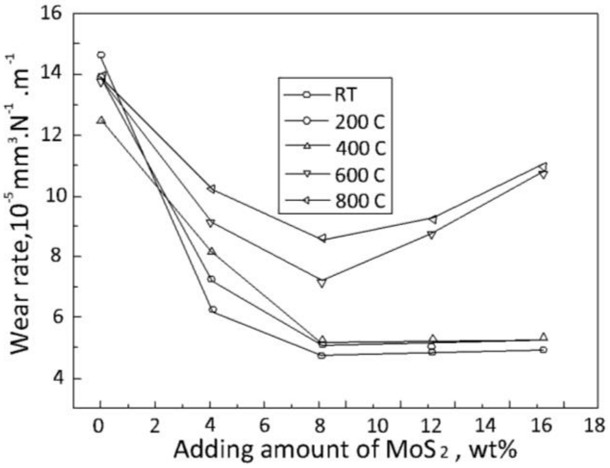

Fig. 5b. Wear rate of MoS_2 [68].

The properties of the composite beyond 8% MoS_2 deteriorates and high wear rate was observed at 600 °C due to the abrasion cause by the hard intermetallic phases which results in ploughing of soft films. The compressibility and density of the Fe-C-Cu-Ni compacts improves and the coefficient of friction along with wear loss decreases with addition of MoS_2. This is due to the increase in hardness and strength as secondary sulfide phases form in the as-sintered compacts. The worn out surfaces MoS_2 added samples were smooth when compared to that of the base composition [69]. Sintered steels with Fe-Cu-C-Ni and Fe-Cu-C as base composition with varying additions of MoS_2 shows high coefficient of friction and low wear rate of MoS_2 in comparison to the respective base compositions [70].

Solid lubricants have also been tried with steels in order to enhance their tribological behavior such as, austenitic stainless steels which are more prone to wear and galling because of their relative softness [71]. 316L stainless steel with different quantities of MoS_2 fabricated via powder metallurgy shows better tribological properties but at the cost of tensile strength. It is due to the fact that bonding between steel particles weakens when content of MoS_2 is increased [72].

Various other sulfides can also be used such as Zinc Sulphide (ZnS), Tungsten Disulphide (WS_2), etc. The antifriction properties of iron based sintered materials with C, Cu and ZnS as additives have been investigated. The findings revealed that the load carrying capacity of Fe-C composite increases by introducing Cu and ZnS and the composite with 1.5 % C, 2 % Cu and 8-10 % ZnS by weight exhibited best antifriction property [73].

The layered structures of WS_2 and CaF_2 as combined lubricants were used on steel and titanium nitrate (TiN) substrates and the films formed were found to perform lubrication up to 500°C. The interaction of CaF_2 and WS_2 led to the formation of calcium sulfate ($CaSO_4$), which acted as an excellent lubricant. $CaSO_4$ is a better high temperature lubricant as it is easily deformable, thus leading to the formation of layer on the substrate and provide lubrication [74].

Nano particles of MoS_2 are also amongst the most common lubricant additives, due to their strong interlayer covalent bonding and weak Vander Waals forces between its molecular layers. The stability of the lubrication film and load carrying capacity of nano MoS_2 particles is more pronounced than most of the nano lubricants [75-77].

5.3 Hexagonal Boron Nitride (h-BN)

Hexagonal Boron Nitride is very similar to Graphite in properties. The firm binding of electrons by nitrogen makes h-BN superior to graphite. It has high thermal conductivity, low thermal expansion, good thermal shock resistance, high electrical resistance and low dielectric constant. h-BN is also non toxic, easy to machine, non-abrasive and lubricious. It is chemically inert and is non-wetted by most molten metal's [78].

Among the existing solid lubricants, h-BN nitride has the highest temperature resistance in air and can be permanently used to an approximate temperature of 900 °C, as other solid lubricants will suffer from oxidation at much lower temperatures. The coefficient of friction of boron nitride remains virtually unchanged over a wide temperature range. In case of Fe-h-BN composites, ferritic grain size decreases with increase in h-BN content and there is maximum internal friction at 4 % of h-BN with no deterioration in the mechanical properties [79].

h-BN when used a solid lubricant with 316 steel and sintered at a temperature of 1250 °C, transformed into a boride liquid phase which deteriorated the lubricating film resulting in an increase in the value of coefficient of friction of the composites. It was observed that specific wear rate and coefficient of friction were relatively lower in compositions with 20 vol% of h-BN at a sintering temperature of 1200 °C [80].

Fe-SiC-h-BN composites were tried with different amounts of h-BN, and the authors observed an improvement in scuffing resistance with the increased addition of solid lubricant. However, the mechanical properties were adversely affected due to the spreading of lubricant around iron particles [81].

5.4 Fluorides

Lubrication at higher temperatures is of great concern for the researchers. Calcium fluoride (CaF_2) and barium fluoride (BaF_2) have played a promising role in lubrication at and above 530°C (1000°F) temperatures. These are mostly being used as a lubricating material in metal/fluoride composites.

Fluoride has been used as a lubricant either by coating, infiltration, powder metallurgy, etc. The calcium fluoride acts as a solid lubricant due to its adhesiveness along with various components of adhesive forces such as intermolecular, coulomb and electrical components [82]. Aluminum, barium, calcium and magnesium fluoride were investigated for their thermal stability in different atmospheres at temperatures ranging from 100 to 1100 °C so that they might be used as a solid lubricant at elevated temperatures. The thermal stability of barium, calcium and magnesium fluorides in air and hydrogen at temperatures of 500–1000 °C is higher than that of zinc sulfide. Zinc sulfide fully decomposes in air at 500 °C and in hydrogen and water vapor at 900 °C [83].

Hardness of CaF_2 and BaF_2 (Table 3) was investigated over a temperature range of 25 to 670 °C and it was found that fluoride eutectic was a good high temperature lubricant which undergoes brittle to ductile transition at about 400 to 500 °C [84].

Table 3. Hardness (Vickers) of CaF_2 and BaF_2

Temp\Lubricant	CaF_2(Kg/mm^2)	BaF_2(Kg/mm^2)
0 °C	170	83
670 °C	13	9

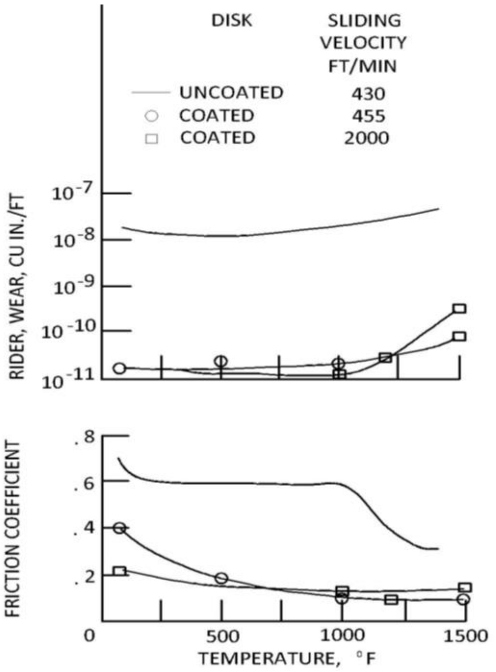

Fig. 6. Wear and Friction of fused fluoride [85].

Figure 6 shows wear properties of fused fluoride coatings of the composition with 38 % CaF_2 and 62 % BaF_2 in air along with wear and friction of uncoated specimen. Fluoride show effective lubrication in liquid sodium and air up to 1200° F and, in hydrogen up to 1500° F [85]. High temperature wear behavior of self lubricating sintered steels with CaF_2, MnS and TiC as additives was investigated and findings revelaed that TiC increased wear resistance whereas CaF_2 and MnS improved self - lubricating properties [86].

In case of Fe-W-CaF_2 composites, there is an increase in the hardness values due to intensive grain refinement and formation of intermetallics such as bcc solid solution of tungsten in Fe, fcc solid solution of tungsten in Fe, iron oxides, and synthesized iron tungstate (Fe_7W_6), etc. These films formed prevented the mechanical contact of the rubbing surfaces and thus lubricates. With increase in the working pressure and at high velocities, the coefficient friction coefficient was found to increase with a significant decrease in wear rate [87].

Mechanical properties of sintered iron base composite with molybdenum(Mo) and calcium fluoride(CaF_2) was investigated and increase in the mechanical properties were observed at high temperatures due to high concentration of CaF_2 [88]. CaF_2 exhibits least wear and friction among zinc, iron sulfides, boron nitride, calcium and, barium fluorides with sintered iron base materials. However, due to the increase in temperature, the resistance to shear deformation of CaF_2 decreases [89]. At high temperatures, ternary lubricants such as $Ba_{0.25}$ $Sr_{0.75}$ SO_4 also exhibited a great improvement in the tribological properties of Fe_3Al alloys [90].

6. CONCLUSION

The use of iron based composites has revolutionized the application areas of metal matrix composites due to its economical and technical reasons. It has been widely used with C, Cu and Ni, etc. to prepare composites with improved mechanical and tribological properties. Solid lubricants such as graphite, molybdenum disulfide, boron nitride, fluorides etc. have been used with iron based composites to increase tribological properties without deteriorating mechanical properties.

High temperature self-lubricating composites have been developed using fluorides as they retain their lubricating properties at such temperatures whereas other lubricants such as graphite, sulfides etc. are only suitable for low temperature applications. The researchers are trying to develop composite material that meets both low as well as high temperature lubrication requirement. This is being achieved by trying various combinations of lubricants which comprises of room temperature lubricant along with high temperature lubricant. The intermetallics formed out of such combinations were found to be more effective in increasing tribological properties.

7. FUTURE SCOPE

There is a scope for the development of Ferrous based self lubricating composites which perform efficiently at both room and high temperature. Moreover, most of the high temperature lubricants such as fluorides, halides etc. have not been tried with many ferrous based matrices, which paves a way to the development of new self lubricating composites. The composites developed therein, can be investigated at room temperature in order to know their behaviour at room temperature as well. Apart from this, hybrid lubricants comprising of low temperature and high temperature solid lubricant may be incorporated in Ferrous based matrices to enhance tribological properties of the resulting composites.

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