Chapter 8
Tribological Properties of Metal Matrix Composites

Metal matrix composite (MMC) materials constitute an important class of materials for tribological applications. In this chapter, we review tribological properties of some MMC with emphasis on the graphite-reinforced materials.

8.1 Introduction

Composite materials are engineered or naturally occurring materials made from two or more constituent components with significantly different physical or chemical properties which remain separate and distinct at the macroscopic or microscopic scale within the finished structure. In the case of two constituent components, one with the highest volume fraction is considered the “matrix,” whereas the other is the “reinforcement” modifying the properties of the matrix. A metal matrix composite (MMC) is composite material with at least two constituent parts, one (the matrix) being a metal. The other material may be a different metal or another material, such as a ceramic or organic compound. When at least three materials are present, it is called a hybrid composite. MMCs are synthesized by dispersing a reinforcing material into a metal matrix. The reinforcement surface can be coated to prevent a chemical reaction with the matrix.

The matrix is the monolithic material into which the reinforcement is embedded, and is completely continuous. This means that there is a path through the matrix to any point in the material, unlike two materials sandwiched together. In typical structural applications, the matrix is usually a lighter metal such as aluminum, magnesium, or titanium, and provides a compliant support for the reinforcement. In high-temperature applications, cobalt and cobalt–nickel alloy matrices are common.

The reinforcement material is embedded into the matrix, usually in the form of particles, fibers, whiskers, or wires. The reinforcement does not always serve a

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purely structural task (reinforcing the compound), but is also used to change physical properties such as wear resistance, friction coefficient, or thermal conductivity. The reinforcement can be either continuous, or discontinuous. Discontinuous MMCs can be isotropic, and can be worked with standard metalworking techniques, such as extrusion, forging, or rolling.

Continuous reinforcement uses monofilament wires or fibers such as carbon fiber or silicon carbide. Because the fibers are embedded into the matrix in a certain direction, the result is an anisotropic structure in which the alignment of the material affects its strength. Discontinuous reinforcement uses “whiskers,” short fibers, or particles. The most common reinforcing materials in this category are alumina and silicon carbide.

There are several methods to synthesize MMCs, which can be classified as solid, liquid, and vapor deposition. Solid state methods include powder blending and consolidation (powder metallurgy) and foil diffusion bonding: Liquid state methods include electroplating, stir casting, squeeze casting, spray deposition, and reactive processing (in the latter, a chemical reaction occurs, with one of the reactants forming the matrix and the other reinforcement).

Carbon-reinforced MMC are widely used for tribological applications. When lamellar solids such as graphite or molybdenum disulphide are applied to sliding surfaces, friction and wear are observed to decrease. The crystal structure of a lamellar solid has sheets or layers weakly bonded with each other but the bonding within the sheet is quite strong These solids are thus strong in compression but weak in shear, and act as solid lubricants as discussed by Bragg (1928) explaining the origin of lubricity in graphite. Graphite, which consists of carbon atoms arranged in a layer-like structure, displays a very low coefficient of friction ranging from 0.1 to 0.2 while sliding on another clean surface, thus suggesting that it can be used as a solid lubricant. In Bragg’s view the layered structure imparts graphite with an inherent quality of lubricity. However, a fourfold increase in friction of graphite and three orders of magnitude increase in wear under vacuum over that in air clearly indicates that the lubricity of graphite is not inherently derived from its structure alone. The environment appears to play a significant role in the lubrication behavior of graphite. In fact, graphite has been found to require the presence of absorbed vapors such as water or hydrocarbons to develop good lubrication properties (Rohatgi et al. 1992).

One of the main difficulties in using graphite as a solid lubricant lies in maintaining a continuous supply of graphite which acts as a solid lubricant between two sliding surfaces; such a continuous supply is more easily maintained in the case of fluid lubricants. An interesting innovation to ensure a supply of graphite between sliding surfaces is to incorporate graphite into the matrix of one of the sliding components forming a composite. Under optimum conditions the metal–graphite composite becomes self-lubricating because of the transfer of the graphite embedded in its matrix to the tribosurfaces and its formation into a thin film which prevents direct contact between the mating surfaces. The success of metal matrix–graphite particle composites depends on the ability of the graphite particles to come out of their embedded state in the matrix and spread evenly in the form of a solid lubricating film over the tribological surface to provide lubrication.

In recent years, considerable work has been done on the metal matrix–graphite particle composites which exhibit low friction, low wear rate, and excellent antiseizing properties. In these composites, graphite presumably imparts improved tribological properties to the composite through the formation of a graphite-rich film on the tribosurface which provides solid lubrication. The formation of the solid lubricating film depends on the matrix characteristics, for example, its deformability helping the process of transfer of graphite to the tribosurface, adhesion of graphite film to the matrix, and the presence of an environment which permits graphite to spread in the form of a film and act as a solid lubricant. In metal matrix–graphite composites, graphite particles are embedded in the matrix, and the formation of a graphite film will take place by transfer of the graphite from the particles embedded in the matrix on to the tribosurfaces during initial periods of sliding. The observed friction and wear behavior will, therefore, have two distinct stages: (a) transient state, while a graphite film is being established, and (b) steady state, when a stable graphite film (in the dynamical sense of being continuously replenished to make up for the wear loss) has formed.

It should be noted that there is a growing family of composites where graphite is present in fiber form. While much of the discussion is on synthetically prepared graphite particle composites, for example, copper–graphite, iron–graphite, silver–graphite, and aluminum–graphite, discussion on tribological properties of cast irons has been included even though they represent iron–graphite mixtures which form during solidification of molten carbon-rich irons and are not generally classified as modern composites. They have been used extensively in antifriction applications and illustrate the mechanism of solid lubrication by graphite. In the second section, the processes for fabrication of composites containing graphite particles are outlined and in the third section the theoretical framework for understanding the tribological behavior of these composites is described. The influence of the matrix alloy composition, the graphite content and its shape and size, and test variables such as contact pressure and sliding velocity on the tribological behavior of MMCs are discussed in the fourth section. The effects of chemical, electrical, and thermal environmental factors on the friction and wear behavior of metal matrix–graphite particle composites are presented in the fifth section. In the sixth section, the process of graphite-rich film formation on the tribosurfaces of these composites is described; this has been critically examined since the superior tribological properties of metal matrix–graphite composites are strongly dependent on the formation of graphite-rich film on tribosurfaces. In the seventh section, selected applications of metal matrix–graphite particle composites and their industrial potential are described. In the eighth section, an attempt is made to give an integrated picture of current understanding of the overall tribological behavior of these composites, highlighting the gaps in knowledge.

Typical microstructures of selected metal matrix–graphite particle composites are shown in Fig. 8.1. The microstructures generally exhibit dark particles of

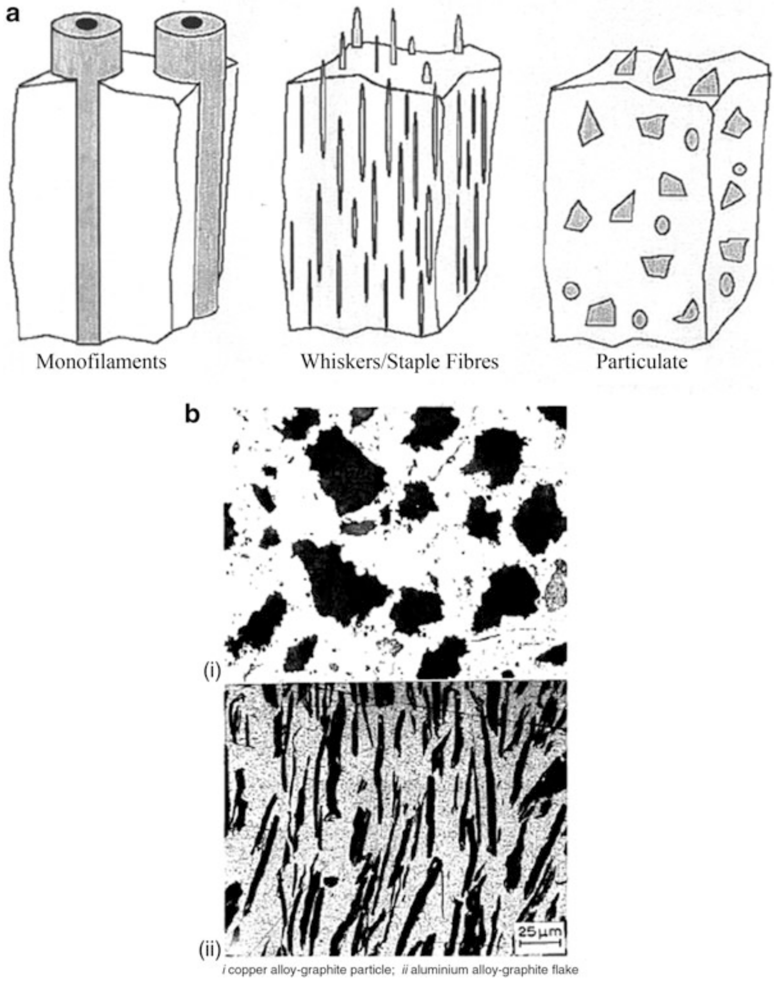


Fig. 8.1 (**a**) Monofilament, whiskers, and particulate reinforcement in composite materials. (**b**) Typical microstructure of MMCs (Al–Si/20 vol% Gr_p (i) and Al-alloy graphite flake (ii))

graphite dispersed in the matrix of light etching matrix phase which is generally the continuous phase. The microstructure of the matrix phase depends on the technique used for processing the composite.

Generally, the processes for synthesis of MMCs containing graphite can be divided into three main categories depending on techniques employed: (a) powder metallurgy, (b) casting metallurgy, and (c) spray deposition. The process used to synthesize the composite appears to have an effect on its tribological properties, because of its influence on matrix microstructures, the distribution of graphite particles, and the bonding between the matrix and the graphite.

8.2 Manufacturing Methods of MMC

8.2.1 Powder Metallurgy

The basic manufacturing in powder metallurgy (PM) includes mixing, compacting, and sintering of mixtures of powders of metals constituting the matrix and graphite powders. The initial process of mixing raw materials is an important first step, since it controls the distribution of particles and porosity in composites both of which influence the tribological behavior. Segregation or clustering of particles is thus a common problem with the present state-of-the-art mixing technology. The reason for segregation is the different flow characteristics of different powders during mixing and the tendency of agglomeration of particles to minimize surface energy (Rack 1988). It has been reported that generally the larger the size of the powders, the better the degree of their distribution. Spherical particles mix better than irregular particles. Density differences also affect the results of mixing. During mixing, light particles tend to stay on the top, while the heavy particles primarily segregate to the bottom.

After the mixing operations, mixtures of powders are pressed in a die at pressures that make the mixtures adhere at contacting points. This process is called compacting. Sintering is closer to the final step in manufacturing and the primary control parameters during this stage are the temperature and atmosphere. The primary problems in fabrication of metal–graphite composites by PM are the presence of oxide films on powder, imperfect distribution of graphite in metal matrices, sweating during liquid phase sintering, and poor strength in solid phase sintering. The tendency of liquid metals to sweat out results from the frequent poor wettability of graphite powders by liquid metal.

The inadequate bonding between the graphite and the matrix at sintering temperatures below the melting point of the metal results in poor strength in the composite. The problem of sweating has been solved by adding a small amount of calcium in the form of calcium–silicon alloy to the powder mixture in iron–graphite systems and the volume fraction of graphite can then be increased to values as high as 90%. The techniques developed to overcome lower strengths include mechanical alloying and hot pressing processes. The mechanical alloying involves repeated fracturing and partial melting of mixtures of constituent powders by high energy compressive impact forces. It has been reported that by sintering the compacts under pressure, the density of composite materials may be increased up to 98% of theoretical density (Rack 1988). Various metals and alloys have been used as matrix material for the synthesis of metal matrix–graphite particle composites, using PM techniques. These include copper and silver. The cost of synthesis of metal matrix–graphite particle composites by powder processes is an order of magnitude higher than the liquid metallurgy processes, and the sizes and shapes which can be produced by PM methods are limited.

8.2.2 Casting

The advantage of casting processes for the synthesis of metal matrix–graphite particle composites is their relatively low cost compared with PM techniques, and the ability to produce large complex shapes. In the casting process, one can either produce graphite particles in situ by precipitation from liquid, according to the equilibrium phase diagram, or one can introduce graphite particles from the outside into the liquid without the restraints of the phase diagram. An example of the phase equilibrium generated composite is cast iron, where graphite precipitates from the molten iron during the solidification of cast iron. Currently, two types of casting methods are employed for synthesizing the nonequilibrium synthetic type of MMCs: (a) impregnation methods whereby a bed of dispersoids is impregnated by liquid metal flowing under a pressure differential, as in squeeze casting and pressure infiltration, and (b) dispersion methods such as stircasting or compocasting where the dispersoids such as the particles or fibers are dispersed in liquid or semisolid alloys by stirring and the resulting slurry is cast. In squeeze casting, liquid metal is forced under high pressure (70–100 MPa) into a bed or a preform of particles or fibers (Cornie et al. 1990). In pressure infiltration, molten alloy is usually forced in under low pressures (<15 MPa) (Cornie et al. 1990). A typical method in this category is pressure infiltration, in which pressurized gas is used to apply pressure on liquid metals and the particles, compacted into a preform or a bed in a tube. The preform or the bed is penetrated by the liquid metal to form a composite. By using this method, the composites can be produced with high volume fraction of dispersoids. The pressure required for infiltration can also be applied by a hydraulic ram in a die casting machine (Heine 1988).

In dispersion processes such as stircasting or compocasting, dispersoid particles are stirred into alloys in molten or semisolid state and the resulting slurry is cast by gravity or pressure die casting. The main advantage of dispersion processes is that the methods can be used to manufacture composite components using conventional foundry type casting processes. The different processes for fabricating cast composites have been reviewed recently by Ray (1990), Zhang (1988), Cornie et al. (1990), and Rohatgi et al. (1986).

8.2.3 Spray Deposition

In this method, liquid metal and dispersoid powders are co-sprayed through an atomizer on a substrate to form billet, disc, tube, strip, or laminated structures. Particles of sizes 5–500 μm have been used with metal flow rates of 0.25–2.5 kg s^{-1} to produce composites with 5–35 vol% particles (Lavernia 1989). Aluminum, iron, nickel, titanium, copper, and cobalt base alloys have been used to produce MMCs by this method (Lavernia 1989; Momoun 1975).

8.3 Theoretical Basis for Understanding Friction and Wear Behavior in Composites

It is well known that even the most carefully prepared real surface is gently undulating and consists of many microscopic and macroscopic asperities. The friction between two mutually contacting solid surfaces arises from the interaction at these discrete points of asperities where actual contact occurs. The basic processes involved in these interactions are (a) adhesion at the contacting points and (b) deformation (either elastic or plastic) of the asperities by the load. The force required to overcome friction will consist of the force required to shear the adhesion bond F_{a}, and the force F_{d} required to deform elastically or plastically the obstructing asperities of the relatively softer material in the path of the asperities of the relatively harder material. If N is the applied normal load on the contacting surface, the coefficient of friction f is given by Bowden et al. (1945)

$$f = \frac{F_{\mathrm{a}} + F_{\mathrm{d}}}{N} = \frac{F_{\mathrm{a}}}{N} + \frac{F_{\mathrm{d}}}{N} = f_{\mathrm{a}} + f_{\mathrm{d}}, \tag{8.1}$$

where f_{a} and f_{d} are, respectively, the coefficients of friction due to adhesion and deformation. The adhesion strength and the resulting friction f_{a} are strongly influenced by the presence of surface films and contaminants. The presence of oxides, absorbed films, and grease prevents intimate contact between the mating surfaces and inhibits the growth of a strong adhesional bond. When a surface consisting of solid lubricants like graphite dispersed in a metallic matrix comes into contact with another surface, a thin film of solid lubricant graphite-rich layer covers the mating surface, reducing the adhesional friction. The nature of this film then governs the adhesional component of friction in graphite-containing MMCs. However, the contribution of deformation to the coefficient of friction is still determined by the mechanical properties of the underlying composites.

8.3.1 Friction and Thin Film Lubrication in Metal Matrix–Graphite Particle Composites

In 1945, Bowden and Tabor (1945), developed a theory for thin film lubrication and the coefficient of friction f was expressed as

$$f = \frac{S_{\mathrm{f}}}{H_{\mathrm{g}}} \tag{8.2}$$

A low shear strength of the film S_{f} on the sliding surface and a relatively high substrate hardness H_{s}, results in a low coefficient of friction compared with that of either the substrate or bulk of film material alone. However, this simple picture cannot explain the detailed friction behavior of a combination of a film and a substrate. Further, the plastic deformation of the film begins to influence the contact area. The shear strength of the lubricating film S_f has to be replaced by S_p, the shear strength of the film under pressure as proposed by Bridgman (1936)

$$S_\mathrm{p} = S_\mathrm{f} + \alpha P, \tag{8.3}$$

where α is a constant of the film material and P is the applied normal pressure. The friction coefficient under these conditions becomes

$$f = \frac{S_\mathrm{f} + \alpha P}{P} = \frac{S_\mathrm{f}}{P} + \alpha. \tag{8.4}$$

At low pressures P, the indentation of the asperities of the mating surface may be confined within the film layer if the film is thick and the load will be supported by the film, resulting in $P = H_\mathrm{f}$, the hardness of the film. If the film is soft, then the coefficient of friction will be higher because of the higher contribution of the first term in (8.4). However, for thin films, the indentation load will be supported by relatively hard substrate material and $P = H_\mathrm{s}$ resulting in a lower value of coefficient of friction. As the normal load increases, the real area of contact will also increase; but, after it becomes equal to the geometrical area of contact, there will be no further increase in this variable. As pressure will increase above this value, the contribution of the first term in 8.4 will reduce, and in the limiting case of very high pressure the coefficient of friction will approach the value of α, a characteristic of the film material. In the case of MMCs before any sliding, the area fraction of tribosurface occupied by graphite is close to the original volume fraction of graphite in the composite if the distribution of graphite particles is uniform, and the planar surface is representative of the volume distributions. However, as the tribosurface is subjected to deformation during sliding, the graphite is squeezed out of the graphite particles in the embedded state, and these are spread during sliding on the tribosurface in the form of a film of solid lubricant. The film of graphite may not cover the entire tribosurface and the coefficient of friction of the composite may be roughly correlated with the extent of film formation on the interface by the rule of mixture

$$f = (1 - A_\mathrm{g})f_\mathrm{m} + A_\mathrm{g} f_\mathrm{g}, \tag{8.5}$$

where f_m and f_g are, respectively, the coefficients of friction in the matrix and in the areas covered by graphite film and A_g the fraction of the interface covered by graphite film. Following (8.1) and (8.4), one may write

$$f_\mathrm{m} = f_\mathrm{am} + f_\mathrm{dm} \tag{8.6}$$

and

$$f_\mathrm{g} = \frac{S_\mathrm{g}}{P} + \alpha, \tag{8.7}$$

where f_{am} and f_{dm} are contributions to the coefficients of friction of the matrix f_{m} due to the process of adhesion and deformation, respectively. S_{g} is the shear strength of graphite and $P = H_{\mathrm{m}}$ the hardness of the matrix. Thus, the coefficient of friction may vary from f_{m} to f_{g} depending on the composition of the composite, and the ability of the solid lubricant phase to spread over the given matrix and counterface.

The formation of a film of solid lubricating graphite takes place during the initial period of sliding of the solid lubricant bearing composites against a counterface. During this period the solid lubricant emerges from the embedded graphite particles and, as wear proceeds, spreads over the sliding surface of the composite and is transferred to the counterface. These processes progress along with continued wear of the film and the matrix. After a given time, the rate of formation of the film in terms of its area and thickness balances the rate of its wear, giving rise to a dynamic steady state characterized by a steady value of friction. The evolution of the graphite film on the tribosurface from its initial transient stage to its dynamical steady state can be characterized by the changing coefficient of friction. During the transient period there will be greater metal–metal asperity interaction; during later stages the film formation will intervene and prevent such metal to metal contact. In the presence of lubricating oil there will be fluid film lubrication preventing direct metal to metal contact, until the running conditions change into a boundary lubrication when the solid lubricant film of graphite will intervene.

8.3.2 Wear in Composites Containing Solid Lubricants

In elastic–plastic materials like composites, wear particles are generated by the following mechanisms (Suh 1977; Suh 1986; Jahanmir et al. 1975; Rigney et al. 1984): (a) adhesion, deformation, and fracture of asperities resulting from repeated single or multiasperity interaction during sliding, (b) ploughing by hard entrapped particles or hard asperities at the sliding surface, and (c) delamination caused by subsurface crack nucleation and propagation. The wear debris generated by these mechanisms forms loose particles, or sometimes transfers to the countersurface by mechanical interlocking or by adhesion on the counterface. In the dynamic steady state of wear, the asperities are continuously reformed, and are removed by asperity deformation and fracture. Ploughing also will contribute to the process of wear and formation and reformation of asperities. When a sample of a given roughness is put to wear, the extent of material removal depends on the size of the asperities. Abrahamson et al. (1975) have shown that the higher is the initial roughness, the more is the material removed in the initial transient period before steady state wear characterized by a wear rate independent of initial roughness sets in. It is therefore obvious that the often omitted data on the initial surface roughness of the samples are very important when reporting results on bulk wear averaging over a period including that of transient state. The initial roughness of the composite will have an important influence on the process of film formation in the transient state.

Wear arising out of the three basic mechanisms (Bowden et al. 1950; Rabinowicz 1966; Sasada 1985) of adhesion, delamination, and abrasion is found to be proportional to the applied normal load W, the sliding distance S, and inversely proportional to the hardness of the wearing body H

$$w = k\frac{WS}{CH}, \tag{8.8}$$

where w is the abraded volume, k the wear constant, and C a geometrical factor equal to 1 for abrasion and 3 for adhesion. The reciprocal of wear constant K is often taken as a measure of the wear resistance of a material. Since both the hardness and the wear constant of a material depend on its microstructure, (8.8) can be simplified as

$$w = kWs, \tag{8.9}$$

where k is called the wear factor and depends on the material and microstructure. The surfaces of pure metals and alloys are often contaminated with oxides and absorbed gases. During sliding at very small loads, the oxide or absorbed layer may not be disturbed and the wear behavior will correspond to that of the contaminated layer. At a still larger load the oxide or absorbed layer may wear out, exposing fresh metallic surface, but the fresh layer may become contaminated again before its next contact with the counterface in some test configuration used in practice. The process of re-forming the oxide or absorbed layer is promoted by higher local temperatures at contact spots. When the conditions of load and sliding velocity are such that the oxide layer wears out during contact and fails to form again before the next contact because the time between successive contacts is insufficient for contaminating the surface again, the wear behavior changes. From mild oxidative wear, the wear becomes severe and metallic. However, this transition will also depend on the test configuration which determines the time between successive contacts.

In mild wear, the worn out particles are very fine (1–10 μm) and the subsurface is not heavily deformed. The coefficient of friction does fluctuate in mild wear. In severe wear, the worn particles are large (~10–100 μm) and metallic, and subsurface is heavily distorted. The coefficient of friction is relatively stable. For a given load the transition from mild to severe wear takes place at a specific sliding velocity; for a given sliding velocity, the transition takes place at a specific load. This transition is quite distinct from time-dependent transition at constant load.

In metal matrix–graphite particle composites, if the composition is such that the tribosurface is partly covered by the graphite film, the change in the nature of wear of the metallic part of the tribosurface will be reflected in the overall wear of the composite. Thus, for low graphite bearing composites one may observe a transition in wear behavior, but this effect will be obliterated when a large part of the tribosurface is covered by graphite films, as is the case in composites containing higher amounts of graphite.

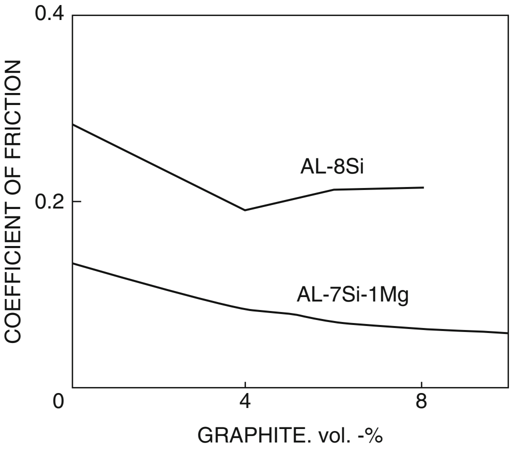
The wear in the graphite film may take place primarily by delamination within the film when the thickness of the film exceeds a critical value. Accumulation of dislocations below the tribosurface may lead to subsurface cracking resulting in delamination (Suh 1986). The softer asperities on graphite are fractured by repeated loading due to asperity interaction and a smooth surface is generated. The nature of the contact changes from asperity–asperity type to asperity–plane contact. The harder asperity induces plastic deformation on the softer surface under repeated loading. This accumulated plastic deformation results in void nucleation below the surface. Any dislocation generated near the surface will move out to the surface because of the image force, leaving a thin surface layer free of dislocations. During sliding there will be two types of stress: (a) tri-axial compressive stress, and (b) shear stress. The former is greater at the surface and opposes nucleation of voids. Thus, the nucleation of voids does not take place on the surface. Below the surface, the compressive stress diminishes and below a certain critical depth it is possible for the shear stress to nucleate voids. If there are second phase particles below the surface, the void nucleation takes place preferentially at the interface of the second phase and the soft material; such voids have been observed even at the interface between the matrix and the graphite particles in the subsurface region in aluminum–graphite particle composites. The voids so nucleated extend and coalesce to form crack exceeding a critical length. This crack is unstable and propagates to the surface generating a thin sheet of soft material as debris of this wear process. This wear process continues to erode the thickness of the soft graphite layer unless its thickness is so small that it is totally free from dislocations and tri-axial compressive stress prevents any void nucleation or resulting delamination in the layer.

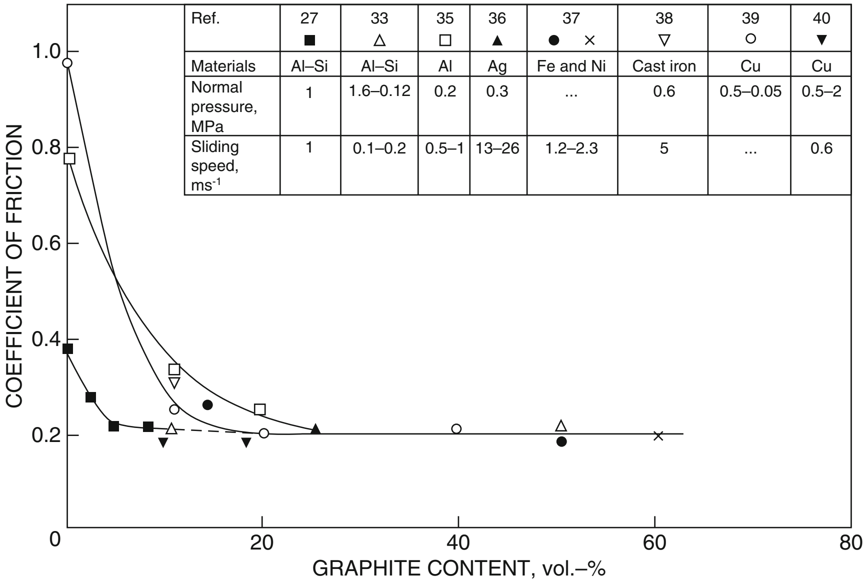
8.4 Friction, Wear, and Seizure Behavior of Graphite Bearing Composites

8.4.1 Friction Characteristics

The particulate composites of graphite and a matrix alloy are characterized by (a) the composition and microstructure of the matrix alloy, (b) the size, volume fraction, and distribution of particles, and (c) the nature of the interface between the matrix and the dispersed graphite. In addition, the composites may have defects such as voids and porosity which, unless accounted for, will result in an erroneous estimate of area of contact and thereby influence wear and friction. In addition, the strength of the composite will reduce with increased porosity content, enhancing wear. An insufficient characterization of composites, particularly in respects of particle size, distribution, and defects, often lead to variations in observed friction as shown in Fig. 8.2, where the friction coefficients of two cast Al–Si alloy–graphite composites, with some variation in matrix composition, are shown (Gibson et al. 1984; Tokisue et al. 1978). The difference in matrix composition cannot explain the doubling of the friction coefficient in one set of alloys compared

Fig. 8.2 Variation of coefficient of friction with graphite content for composites of similar base composition





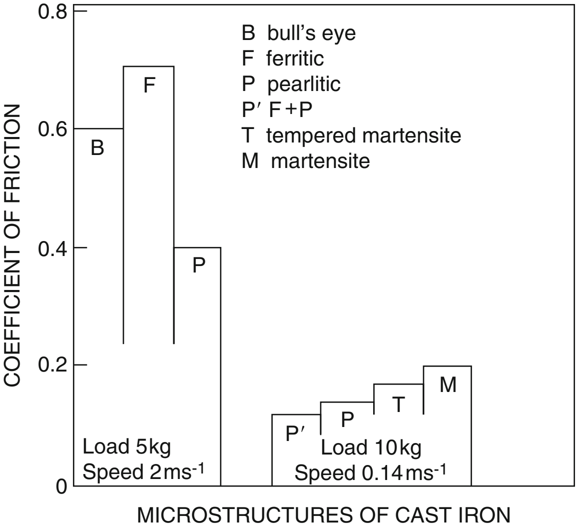
Ref.	27 ■	33 △	35 □	36 ▲	37 ● ×	38 ▽	39 ○	40 ▼
Materials	Al–Si	Al–Si	Al	Ag	Fe and Ni	Cast iron	Cu	Cu
Normal pressure, MPa	1	1.6–0.12	0.2	0.3	...	0.6	0.5–0.05	0.5–2
Sliding speed, ms^{-1}	1	0.1–0.2	0.5–1	13–26	1.2–2.3	5	...	0.6

Fig. 8.3 Variation of coefficient of friction with graphite content for composites with different base alloys

with the coefficient in the other. It is suspected that other contributing factors might have been responsible for this variation but could not be identified during the analysis of this data because of insufficient characterization of the samples; this type of large scatter in the data is endemic to this field of study.

Figure 8.3 shows the coefficient of friction observed in a number of particulate graphite composites with aluminum, copper, iron, nickel, and silver as the matrix (Gibson et al. 1984; Lancaster 1983; Pardee 1967; Dillich et al. 1983; Rybakova et al. 1985; Rohatgi et al. 1990a, b, c, d; Rohatgi et al. 1991; Yuasa et al. 1986;

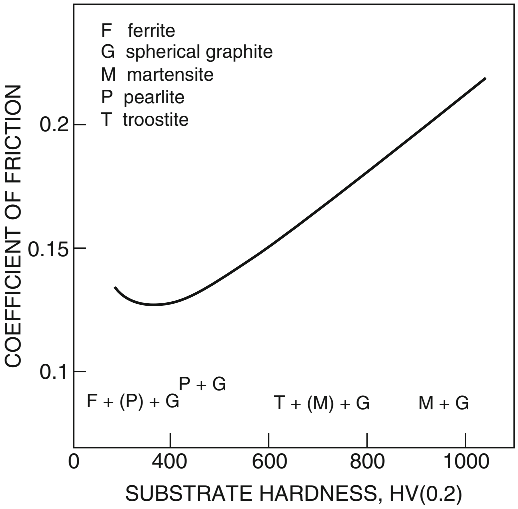
Fig. 8.4 Influence of matrix microstructure on coefficient of friction of gray cast iron



Johnson and Kuhlmann-Wilsdorf 1983a, b; Bowen 1963; Kawamoto et al. 1980; Tsuya 1985; Owen et al. 1987). Results for the coefficient of friction of pearlitic gray cast iron and aluminum–silicon alloy–graphite particle composites have also been included in this figure. The tests were carried out with different loads and sliding velocities. All the composites, with the exception of the silver matrix, were tested against steel, for the conditions indicated in Fig. 8.3. The variation in friction coefficient with graphite content shows that when the graphite content in the composites exceeds 20 vol%, the friction coefficients observed in different composites are virtually independent of the matrix and the graphite content, and appear to attain a constant value close to 0.2. The elemental graphite has a friction coefficient of 0.18 and this increases with the desorption of adsorbed vapors. Thus, it appears that both the mating surfaces, including the graphitic composite and the counterfaces like steel, become completely smeared with graphite, and a friction coefficient close to that of pure graphite against itself is observed, regardless of the matrix. The contribution of the first term in (8.4) and (8.7) to the coefficient of friction f is dependent on the hardness of the substrate or matrix alloy, but it does not appear to make a significant difference in the friction coefficient observed in these composites (Fig. 8.3) containing more than 20 vol% graphite.

The influence of the microstructure and the resulting hardness of gray cast iron on its coefficient of friction as determined by Sugishita and Fujiyoshi (1981a, b) is given in Fig. 8.4. Similar values of coefficients of friction have been reported by Kawamoto et al. (1978) as shown in Fig. 8.5: the increase in friction with hardness of the matrix is contrary to what is expected from (8.4) probably because the cast iron surface will have very little graphite film. A study by Barry and Binkelman (1966) on the friction observed in different substrates covered with a thin film of MoS_2 reveals that for substrates softer than the film material, there is a sharp increase in the coefficient of friction with a decrease in hardness of the substrate; however, for harder substrates the friction becomes independent of the hardness of

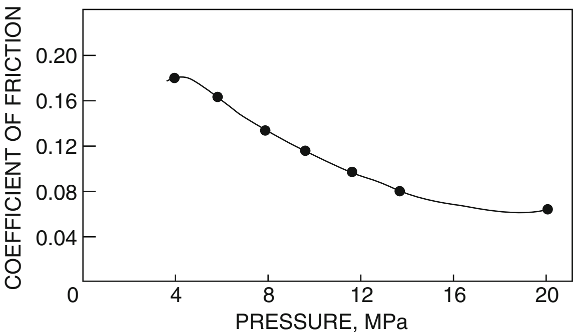
Fig. 8.5 Variation of coefficient of friction with matrix hardness in gray cast iron



the substrate. It appears that the trend of variation of coefficient of friction as given in Fig. 8.4 may have resulted from the process of film formation on the sliding surface. Microscopic examination of the gray cast iron samples shows that a softer matrix leads to a larger area of the sliding surface being covered by graphite films. If there is a supply of graphite on the covered surface, the plastic flow of the surface layer of the matrix appears to help in spreading of graphite into a film. This layer is capable of deforming continuously without much work hardening or fracture because of the absence of dislocations and voids as explained above. The graphite film in gray cast iron is not likely to cover the entire sliding surface because of lower volume fraction of graphite, so the overall coefficient of friction should reflect the friction of the matrix as well. It has been observed that the pearlite matrix results in a lower coefficient of friction than that for ferrite matrix as shown in Fig. 8.5 because of relatively poor adhesion and the higher strength of pearlite. However, the pearlite matrix contains part of the carbon as carbide, thus affecting the amount of graphite available for the process of film formation. Thus, a mixed ferrite–pearlite matrix shows lower friction compared with that in either a ferrite or pearlite matrix alone. The relatively higher friction in martensite or troostite matrix over that in pearlite, indicates that the increase in matrix strength was more than offset by the lowering of the amount of graphite due to carbon in solid solution in iron; in addition, the spreading of graphite with the flow of the surface layer was adversely affected because of the higher hardness of the matrix.

The variation of friction in composites with load was discussed above in the section "Theoretical basis for understanding friction and wear behavior in composites," on the basis of (8.4) and (8.5). If the steady state has been achieved, the contribution of the uncovered matrix on the tribosurface to the overall friction should be governed by (8.5), and f_{m} would be reasonably constant. However, the contribution from the regions of tribosurface which are covered by graphite film

Fig. 8.6 Variation of coefficient of friction with normal pressure for Al–1.5 vol% graphite composite tested at sliding velocity of 1.5 m s^{-1}



may vary with pressure. For lower contact pressures, P in (8.7) is equal to the hardness of the film and thus, f_g should be constant. However, as the pressure increases beyond the point of total contact, P increases till the asperities indent the matrix below, and P is equal to the hardness of the matrix. The friction should thus be constant at lower load, and then reduce with a further increase in pressure. A similar behavior has been observed by Muran and Srnanek (1985) in Al–1.5 vol% graphite composite tested at a sliding velocity of 1.5 m s^{-1} as shown in Fig. 8.6. The agreement between the predicted and the experimentally observed variation of friction with load in the steady state is apparent. But, the absolute values of friction coefficients observed are very low.

8.4.2 Wear Characteristics

The dry wear in composites containing solid lubricant graphite is governed by the nature, thickness, and the spread of the lubricating film on the tribosurface as discussed above in the section.

Figure 8.7 shows the wear volume with sliding distance for different Al alloys, and that for the same alloys containing different amounts of graphite (Kawamoto et al. 1978; Barry et al. 1966; Muran et al. 1985; Suwa et al. 1976; Biswas et al. 1981; Choo et al. 1979; Jha et al. 1989). All investigators, apart from Biswas and Pramila Bai (1981) find that wear decreases when the alloy contains dispersed particles of graphite. However, the absolute values cannot be compared because of different test conditions and poor characterization of the composites. The porosity content and particle size distributions are known to affect wear; however, these microstructural parameters are inadequately reported while describing the wear behavior. This problem becomes more apparent when one considers the variation of wear rate with pressure in Al–Si alloys as shown in Fig. 8.8 (Gibson et al. 1984; Suwa et al. 1976; Choo et al. 1979; Das et al. 1989). The wear rates of the

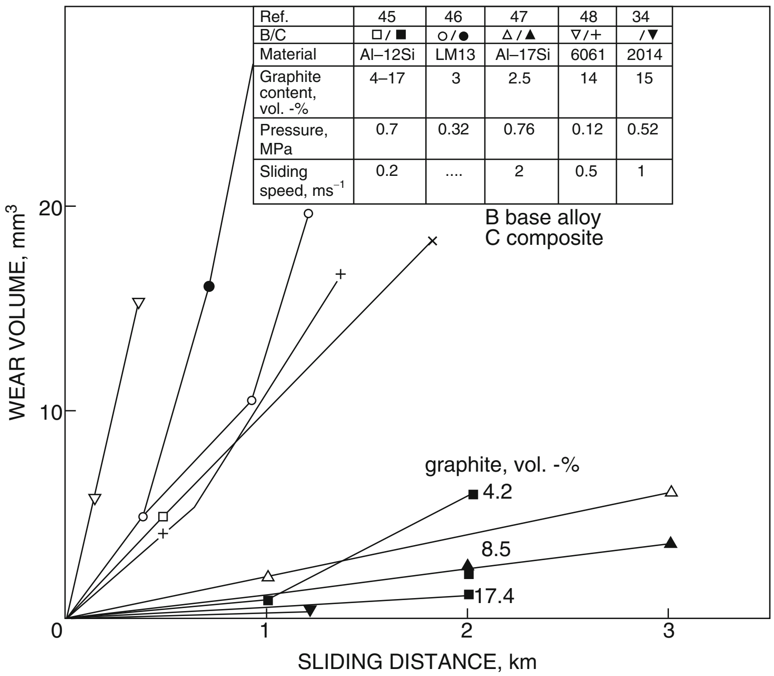


Fig. 8.7 Variation of wear volume with sliding distance for different aluminum alloy–graphite particle composites and corresponding base alloys

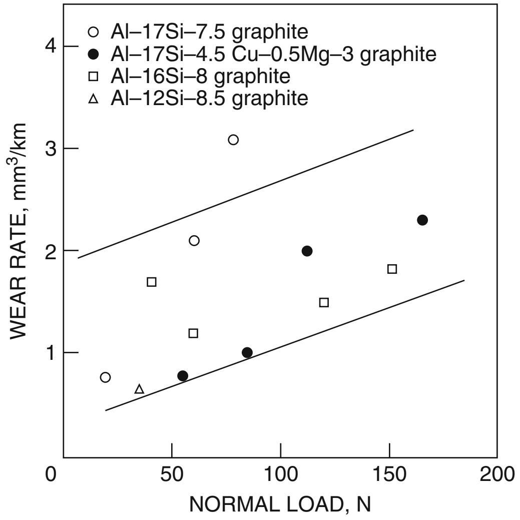
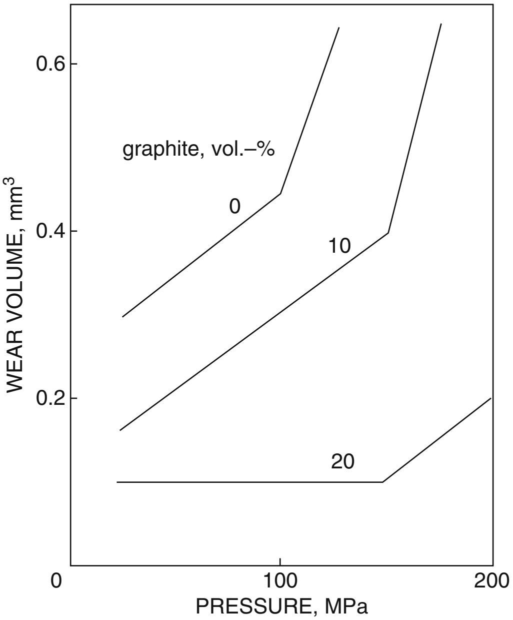


Fig. 8.8 Variation of wear rate with normal load for Al–Si alloy–graphite particle composites

Fig. 8.9 Variation of wear volume with pressure (normal) for copper–graphite particle composites containing 0–20 vol% graphite

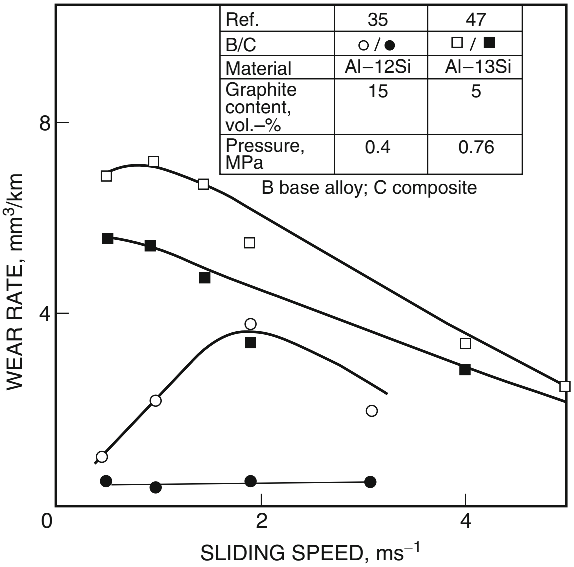


composites investigated by various investigators do not fall on a single curve, but are scattered (within limits) as the normal load increases, even though the base alloys and the graphite contents are similar.

Figure 8.9 shows the variation of wear in copper–graphite composite with contact pressure (Suwa 1986). The critical load for transition from "mild" to "severe" wear increases with increase in the graphite content from 0 to 10%. In addition, the wear both before and after transition is lower the higher the graphite content in the composite. Since the wear rate in Cu–20 vol% graphite composite is so low after transition, compared with the rate of severe wear in the matrix alloy, it is possible that this may merely correspond to instability of the film and not represent severe wear in its true sense. That is the reason for using the terms mild or severe within quotes in the context of composites. If the experiments could have been carried out using greater applied pressures, it is possible that another transition might have occurred.

Figure 8.10 shows the variation of wear with sliding velocity in graphitic composites of Al–Si alloys, and compares it with that of the respective matrix alloys without any graphite (Choo et al. 1979; Yuasa et al. 1986). As the sliding speed increases, the interface temperature also increases resulting in (a) the formation of oxides on the sliding surface, and (b) decrease in flow stress. In addition, there may be microstructural changes such as dissolution of precipitates, which will also be reflected in the wear behavior. In Fig. 8.10, one observes that the composite with only 5 vol% graphite retains more or less the same trend of wear rate with sliding speed as that of the matrix. However, the composite with 15 vol% graphite

Fig. 8.10 Variation of wear rate with sliding speed for Al–Si alloy–graphite particle composites and corresponding base alloys



shows a completely different trend to that of the matrix; this is an indication that the sliding surface might have been largely covered by graphite film so that the wear rate becomes almost unaffected by changes in sliding speed under the given test conditions. When the graphite content is low, the sliding interface is, for the most part, not covered by the graphite-rich film, and the wear characteristics.

Figure 8.11, which shows that the wear rate decreases with increasing graphite content, and levels off once the film of graphite completely covers the sliding surface (Gibson et al. 1984; Suwa et al. 1976; Choo et al. 1979; Das et al. 1989). However, Jha et al. (1989) observed a different trend where wear rate increases with graphite content; their anomalous results may have been caused by porosity as the composite used by them had been prepared by powder techniques.

It is likely that the wear rate may increase when graphite content in the matrix reaches very high values, because of the decrease in strength of the matrix at very high graphite levels and the formation of thick graphite film of thickness exceeding the critical value, which itself can wear by delamination within the film in a manner similar to that of bulk graphite. The reciprocal of the wear constant in (8.8) may be taken as a measure of wear resistance, and it increases with an increase of graphite content for both Al and Cu-base alloys, as shown in Fig. 8.12.

The effect of particle size of graphite on the wear behavior of composites of bronze containing graphite particles is illustrated in Fig. 8.13, where one observes that, for the same sliding distance, wear volume is higher in composites containing finer graphite particles. This effect has been attributed to the plastic flow of matrix alloy to cover the smaller graphite particles effectively so that the sliding surface has very little graphite. The smaller the particle, and the more ductile the matrix, the greater will be the extent to which the particles are covered. If the ductility of the

Fig. 8.11 variation of wear rate with graphite content and Al alloy matrix

Ref.	27 ○	45 ●	47 □	48 ■
Materials	Al–12Si	Al–8Si	Al–13Si	6061PM
Normal pressure, MPa	1	0.7	0.76	0.12
Sliding speed ms^{-1}	1	0.2	2	0.5
Sliding distance, km	1.8	0.5	4	0.25

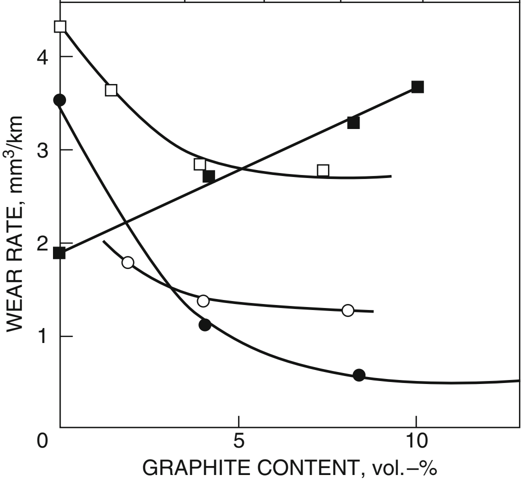
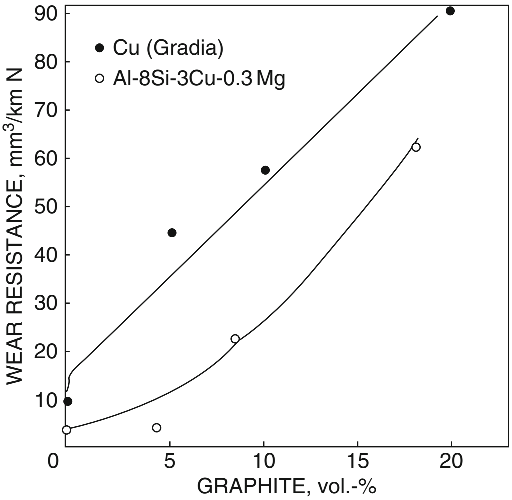


Fig. 8.12 Improvement in wear resistance with graphite content in Al alloy and Cu alloy base composites



matrix is reduced by the addition of phosphorus, the wear reduces because of a decrease in the extent of plastic flow of the matrix on the top of the embedded graphite particles. Sugishita and Fujiyoshi (Sugishita and Fujiyoshi 1981a, b) have observed the same effect in nodular cast iron, where the larger nodule size results in lower wear.

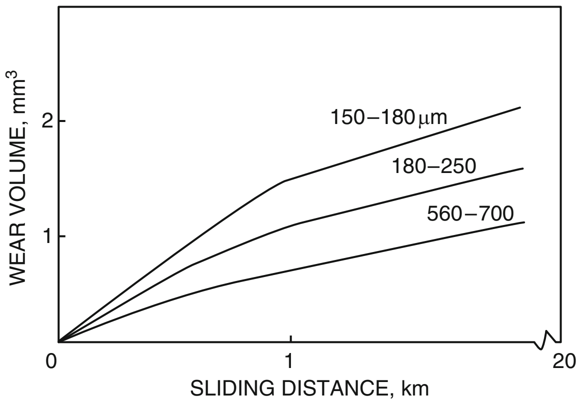


Fig. 8.13 Effect of graphite particle size on variation of wear volume with sliding distance for bronze matrix composites; 4.9 MPa, 0.2 m s^{-1}

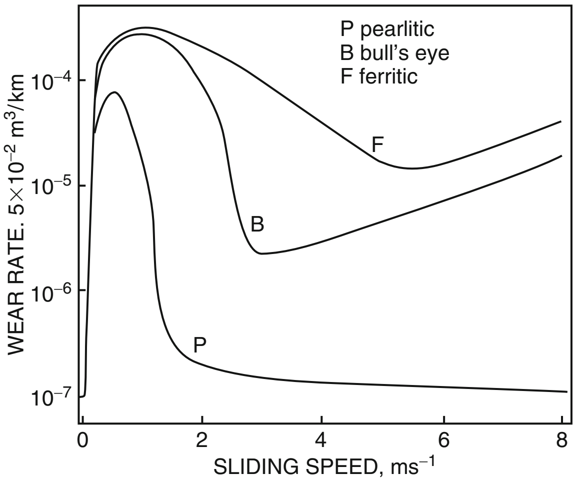
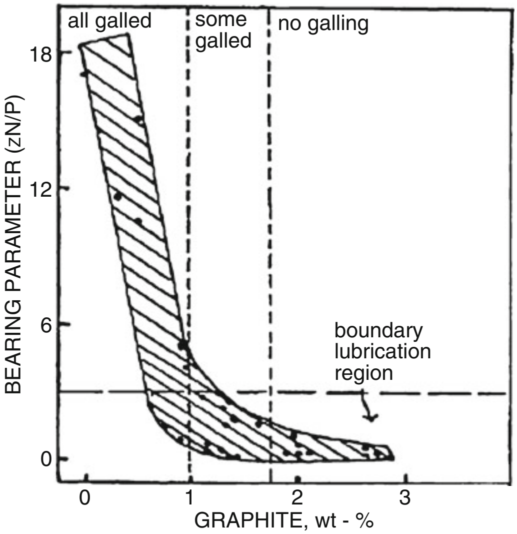


Fig. 8.14 Influence of matrix microstructure on variation of wear rate with sliding speed for spheroidal gray cast iron

Also, a softer matrix over the graphite undergoes larger deformation and results in enhanced removal of metal by fatigue. Kawamoto and Okabayashi have investigated extensively the effect of the matrix on the wear of spheroidal gray cast iron under dry sliding condition as shown in Fig. 8.14. Fully pearlitic matrix shows the lowest wear when compared with that of fully ferritic, and bull's eye structure with free ferrite and pearlite in the ratio of 1:1. Okumoto et al. (1974) have observed that the wear is also dependent on the shape of graphite. Gray cast iron with flake graphite's has inferior wear resistance compared with spheroidal gray cast iron. This may be due to lower matrix strength in gray cast iron containing flake graphite and also, the small transverse dimension of the flake makes it easier for matrix to cover it by plastic flow. Wear rate becomes dependent on the relative orientation of the flakes, the sliding direction, and the flake size.

Fig. 8.15 Variation of bearing parameter with graphite content for Al–Si alloy base composites



8.4.3 Seizure Characteristics

The seizure resistance of a material can be defined as its resistance to welding under pressure during sliding contact (Rohatgi et al. 1980). The seizure of aluminum on aluminum is particularly severe under boundary lubrication, and it sometimes occurs even under full film lubrication because of instabilities in the film (Rohatgi et al. 1980; Smith et al. 1959; Prasad et al. 1987; Rohatgi et al. 1979). Investigations of Badia and Rohatgi (1969) have shown that the seizure resistance of aluminum alloys can be improved significantly by dispersing graphite particles in the matrix of these alloys. Figure 8.15 shows that the minimum bearing parameter *(zN/P)* corresponding to seizure, reduces significantly with graphite content; z is the viscosity of the lubricant, N the rotational speed of shaft, and P the contact pressure. The improvement in seizure resistance could be due to the following factors (Badia 1989): (a) lubrication provided by the graphite film between the mating surfaces, (b) dispersion of fine graphite particles in the debris in lubricating oil and resulting in improved lubrication, and (c) the voids left in the matrix after transfer of graphite to tribosurface, acting as reservoir of lubricant. Rohatgi et al. (1979, 1987) suggest that the improvement in gall resistance is primarily due to the formation of graphite film and that there is an observed minimum graphite content of about 2 wt% required to prevent galling in Al–Si–Ni alloys.

Pai and Rohatgi (1974) have pointed out only 2 wt% graphite can considerably improve the seizure resistance of aluminum base alloys against the same alloy under boundary lubrication conditions. Das and Prasad (1989) have concluded that 3 wt% of graphite in Al–Si–Cu alloys (LM 30) increases the seizure pressure by 2 MPa over that for the base alloy under boundary lubrication, as shown in Fig. 8.16. Rohatgi et al. (1990a, b, c, d) have summarized the results of the seizure behavior in aluminum–graphite composites by using normalized velocity and pressure as shown in Fig. 8.17. It is evident that the seizure resistance of Al alloys

Fig. 8.16 Influence of graphite on pressure variation corresponding to seizure at different sliding speed in Al–17Si–4Cu matrix composites

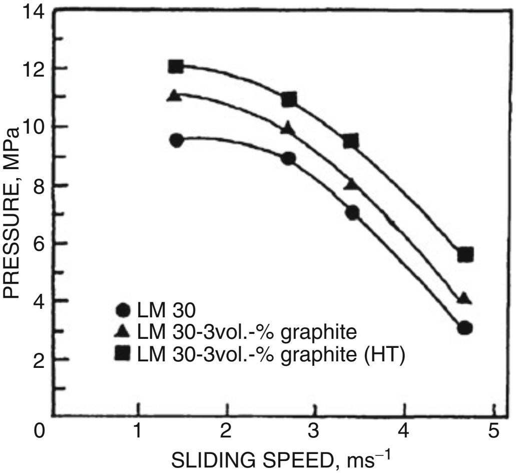
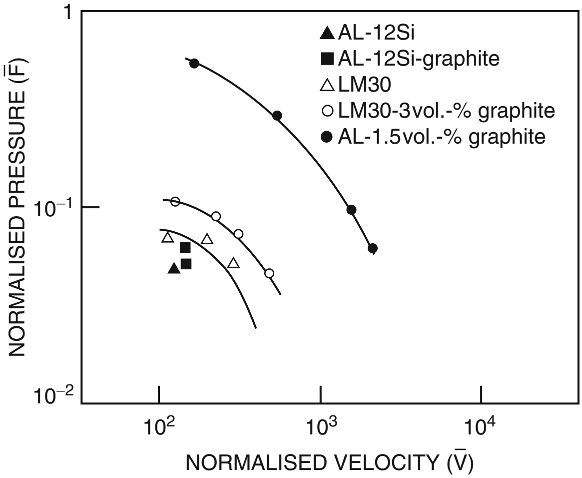


Fig. 8.17 Displacement of seizure boundary by graphite in Al alloy base composites



can be improved by adding graphite particles. This is evidence of graphite interfering with asperity interactions and cold welding. Microstructural studies have revealed that the increase in seizure resistance of aluminum alloys was primarily due to the formation of a graphite film on the tribosurface.

8.5 Effect of Environmental Factors on Friction and Wear

8.5.1 Environmental Conditions and Lubrication

One of the most important factors affecting the tribological properties of metal matrix–graphite particle composites is lubrication provided by the graphite film on

Table 8.1 Effect of environment gas [a]

Gas [b]	Contact drop (V)	Friction coefficient	Energy loss ($J\ cm^{-2}\ m^{-1}$)	Wear in brush ($mm^3\ Mm^{-1}$)
Air	0.00	0.34	2.3	23.3
CO_2	0.03	0.18	1.6	3.2
SF_6	0.18	0.10	1.9	2.2
N_2	0.17	0.06	1.6	1.5
He	0.26	0.06	2.1	1.3
Ar	0.17	0.06	1.5	0.7

Copper ring surface velocity 13 m s^{-1}

Brush loads: 78 A cm^{-2}, 8 N cm^{-2}

Brush bulk temperature range: 67–80°C

[a] SG2 silver–graphite brushes, 75 wt% Ag: 1 cm^2/brush.

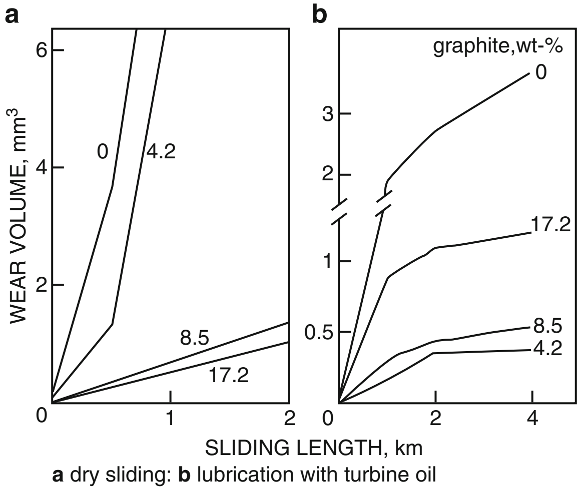
[b] ~10^5 Pa total pressure. Moisture partial pressure 600 Pa

the tribosurface. However, some environmental factors significantly affect the lubrication behavior of graphite. Graphite has a layered structure which allows the material to smear out on both the rubbing surfaces by interlayer slippage (Bryant et al. 1964; Deacon and Goodman 1958). However, Savage (1948) has pointed out that easy slip of one layer of graphite over another occurs readily only in the presence of water vapor or some volatile organic solvents. The importance of environmental condition on the lubrication behavior of MMCs containing graphite have been stressed by Kuhlmann-Wilsdorf et al. (1988a, b), Johnson et al. (1967, 1970, 1982), Tsuya (1985), Casstevens et al. (1978a, b, c), and others (Baker and Hewitt 1936; Johnson and Kuhlmann-Wilsdorf 1983a, b; Lee and Johnson 1978). Lee and Johnson (1978) have investigated the effect of environmental gas on the friction and wear of Ag–25 wt% graphite composite and the results are given in Table 8.1. Brush performance, in terms of desired low energy loss and low wear, is significantly improved in different moist nonoxidizing gas environments compared with that in moist air. A low level of moisture (partial pressure of 600 Pa in 10^5 Pa total pressure) significantly improves the performance of electrical brushes.

The effect of operating temperature on friction has been reported separately for different metal matrices (Bowen 1963). The increase in temperature from 38°C to 540°C increases the value of friction coefficient by about 0.05 only for iron–graphite composites. It is apparent that the lubricity of graphite is largely retained up to about 540°C if the presence of graphite is ensured by preventing oxidation through suitable environmental control. But the easy plastic flow of the matrix material at an elevated temperature may result in a greater coverage of small graphite particles reducing its supply on the tribosurface for film formation and an increase in the coefficient of friction may result.

The effect of lubricant on the wear behavior of composites containing graphite particles is illustrated in Fig. 8.18, where the variation of wear volume with sliding distance is compared for composites based on an Al–Si alloy with different graphite contents under dry sliding and under lubrication with turbine oil (Suwa et al. 1976). The load for lubricated sliding had to be considerably increased (to 10 MPa) before getting a significant amount of wear. Rohatgi et al. (1980, Biswas and Rohatgi

Fig. 8.18 Variation of wear volume with sliding distance for Al–8Si–3Cu–0.3Mg–graphite composites



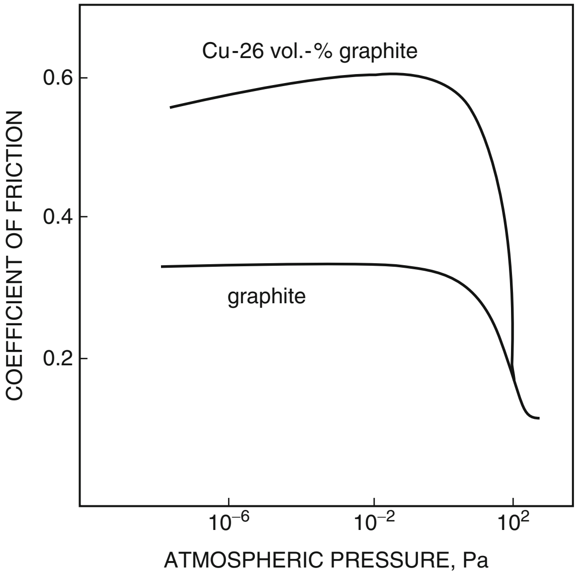
1983) have observed that the graphite film formed on the tribosurface of the composites helps to spread the lubricant oil much more rapidly than that observed in alloys without graphite, resulting in better tribological behavior of the former. It is observed that only a small amount of graphite (~4.2 vol%) reduces the wear volume drastically in the presence of lubricant, but an increase in graphite content above this level results in enhanced wear. This may be a result of higher amounts of graphite in debris getting mixed with the lubricant and contributing to lowering of its mobility which may counteract the contribution of graphite toward lubrication.

The effect of atmospheric pressure on the coefficient of friction of copper–graphite composites is shown in Fig. 8.19. A marked increase in coefficient of friction is observed in the composite when the atmospheric pressure is reduced from 100 to 0.01 Pa. A similar increase in coefficient of friction is observed in graphite itself presumably because of desorption of gases from graphite resulting in loss of its lubricity. Desorption of gases from the surface of matrix alloy will also contribute to a change in coefficient of friction of a composite under reduced pressure.

8.5.2 *Wear in Electrical Contacts*

Several composites have been designed for use in electrical contacts by combining constituents which impart excellent wear resistance with constituents which have high electrical conductivity (Clauss 1972; Pardee 1967; Dillich and Kuhlmann-Wilsdorf 1983; Johnson and Kuhlmann-Wilsdorf 1983a, b; Kuhlmann-Wilsdorf et al. 1988a, b; Johnson and Schreurs 1982; Johnson and Moberly 1967; Johnson and Mckinney 1970; Casstevens et al. 1978a, b, c; Baker and Hewitt 1936; Lee and Johnson 1978; Johnson and Taylor 1980; Jones 1957; Teraoka 1983) and ability to

Fig. 8.19 Effect of reduced atmospheric pressure on coefficient of friction of graphite and copper–graphite composite



suppress arc erosion. The most widely used composites in this field include copper base–graphite composites (considered to be inexpensive) and silver base–graphite composites with very low bulk and contact resistance (Kuhlmann-Wilsdorf et al. 1988a, b). The electrical contacts wear under sliding during flow of current, which complicates the friction and wear behavior compared with that under purely mechanical sliding conditions. The amount of materials removed under sliding electrical contact is the sum of contributions from purely mechanical wear in the absence of current arc erosion and an increment of mechanical wear resulting from softening of the matrix by local heating as a result of arcing (Jones 1957).

Various workers have reported (Kuhlmann-Wilsdorf et al. 1988a, b; Johnson and Schreurs 1982; Lee and Johnson 1978) that in silver–graphite systems, the wear rate of composites increased with an increase of current density at both low and high temperatures, as shown in Fig. 8.20. The figure shows that when there is a transition in the mode of sliding wear with temperature the current density for the same wear is considerably higher while sliding at higher temperatures, compared with that observed during sliding at ambient temperature. The coefficient of friction decreases with the current density, as shown in Fig. 8.21, both in air and in a CO_2 atmosphere.

The effect of sliding velocity on wear seems a little complex. Teraoka (1983) has reported that for pantographs with contact strips made of copper–graphite composites, the wear rate decreases as the sliding velocity is increased from 6.9 to 27 m s^{-1}. The opposite result has been reported by Casstevens et al. (1978a, b, c) for copper–lead–graphite composites under high sliding speeds of 750 m s^{-1} and by Johnson and Kuhlmann-Wilsdorf (1983a, b) for silver–graphite composites tested under speeds of 13 and 26 m s^{-1}.

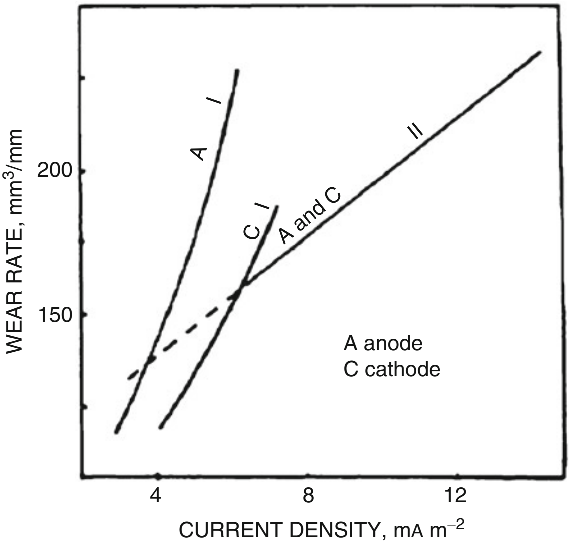


Fig. 8.20 Variation of wear rate with current density at ambient and elevated temperatures; I is observed below 100°C, but II is observed at elevated temperatures, above 100°C

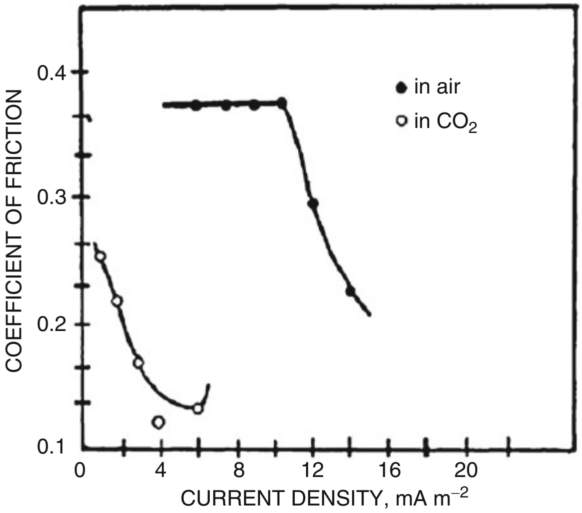


Fig. 8.21 Reduction in coefficient of friction of Ag–25 vol% graphite composite with current density in air and CO_2 atmosphere

The arc erosion tests carried out in copper–graphite composites (Jones 1957) indicate an increase in erosion with arc current. The erosion rate of the copper–graphite composite is also higher than that of the base alloy, as shown in Fig. 8.22. However, Marshall (1966) has suggested that the wear of the brush resulted mainly from mechanical factors rather than the electrical current.

Different contact pairs also affect the results, and Teraoka (1983) has reported that the different rail car bases affected the wear results of pantograph contact strips. Similar results have been reported by Lee and Johnson (1978).

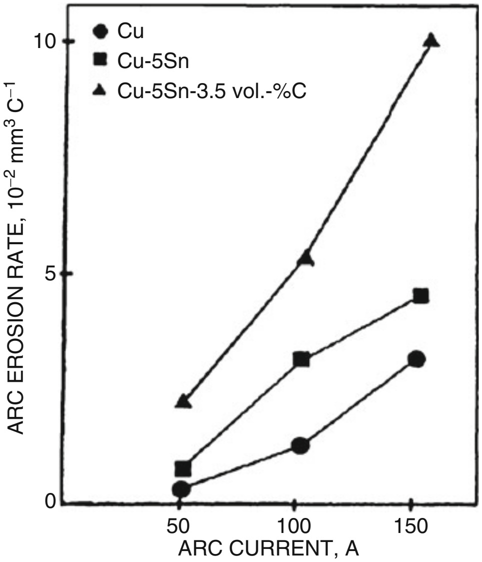


Fig. 8.22 Variation of rate of arc erosion with arc current for bronze–graphite composite, bronze, and copper

The wear mechanism in electrical contacts of composites is complex and depends on the composition of the composites, the contact pairs, the current and voltage levels, the sliding speed, the testing environments, and the contact pressure. Some insights into mechanisms have been provided by Kuhlmann-Wilsdorf and co-workers (Kuhlmann-Wilsdorf et al. 1988a, b; Johnson and Schreurs 1982; Lee and Johnson 1978; Kuhlmann-Wilsdorf 1987) and these are discussed in the next section.

8.5.3 Film Formation

During sliding contact of various materials with graphite particle composites, it has been observed that graphite film forms on the sliding surfaces reducing the extent of direct metal–metal contact as observed from the microstructure of aluminum–-graphite composites, before and after tribodeformation, as shown in Fig. 8.23. When the surface of a graphite particle composite is polished, there is plastic flow of the metal at the surface layer that tends to mask the graphite particles, restricting their transfer to the tribosurface. The friction coefficient and wear rates of such surfaces are high until the metallic layer masking the graphite particles partially wears away and the normal load squeezes out the graphite on the sliding surface. These graphite particles sheared on the sliding surface and eventually joined to form a continuous layer or a film. The process of masking of the graphite particles by the plastic flow in the surface layer of matrix alloy as shown in Fig. 8.23 for aluminum–graphite composites (Rohatgi et al. 1990a, b, c, d) is particularly effective in cases of fine particles of graphite. This process interferes very effectively with film formation by restricting the supply of graphite to the tribosurface,

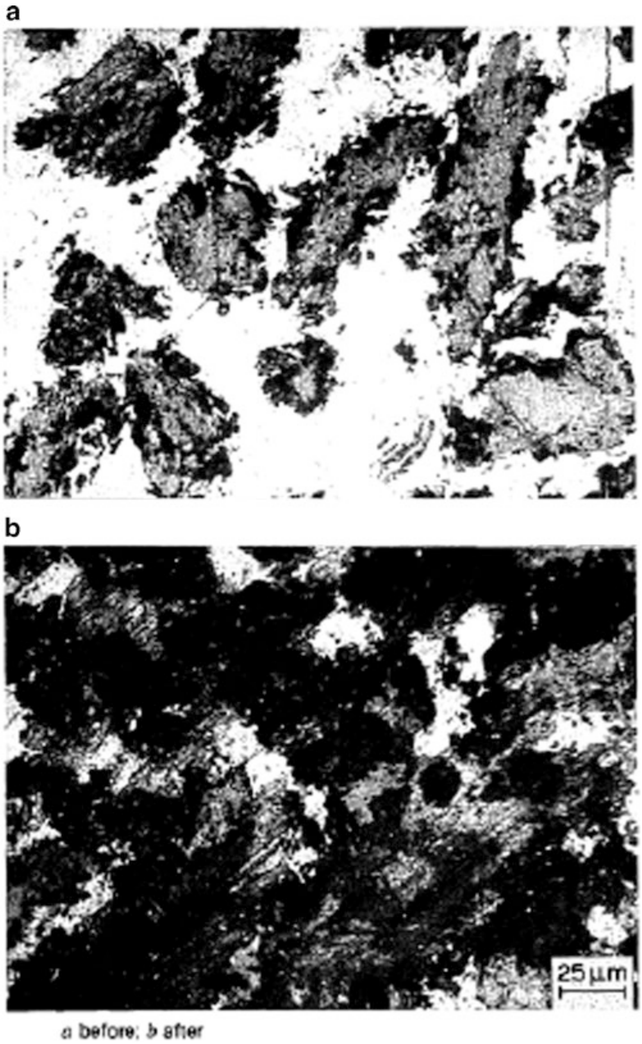


Fig. 8.23 Effect of sliding of microstructure of aluminum–graphite composite (**a**) before; (**b**) after

resulting in higher wear as shown in Fig. 8.13. However, if there is partial metal coverage over the graphite particles the graphite can still be squeezed out, as observed by Sugishita and Fujiyoshi (1981a, b) for nodular gray cast iron.

Rohatgi et al. (1990a, b, c, d) have analyzed the sliding surface of Al–10 vol% graphite by Auger spectroscopy, and established that the major elements on the tribosurface are carbon, oxygen, and aluminum as shown in Fig. 8.24. The surface is covered by graphite to the extent of 30%, which is a clear indication of smearing. However, the thickness of the film is not uniform as seen from the three-dimensional carbon distribution map shown in Fig. 8.25 (Rohatgi et al. 1990a, b, c, d).

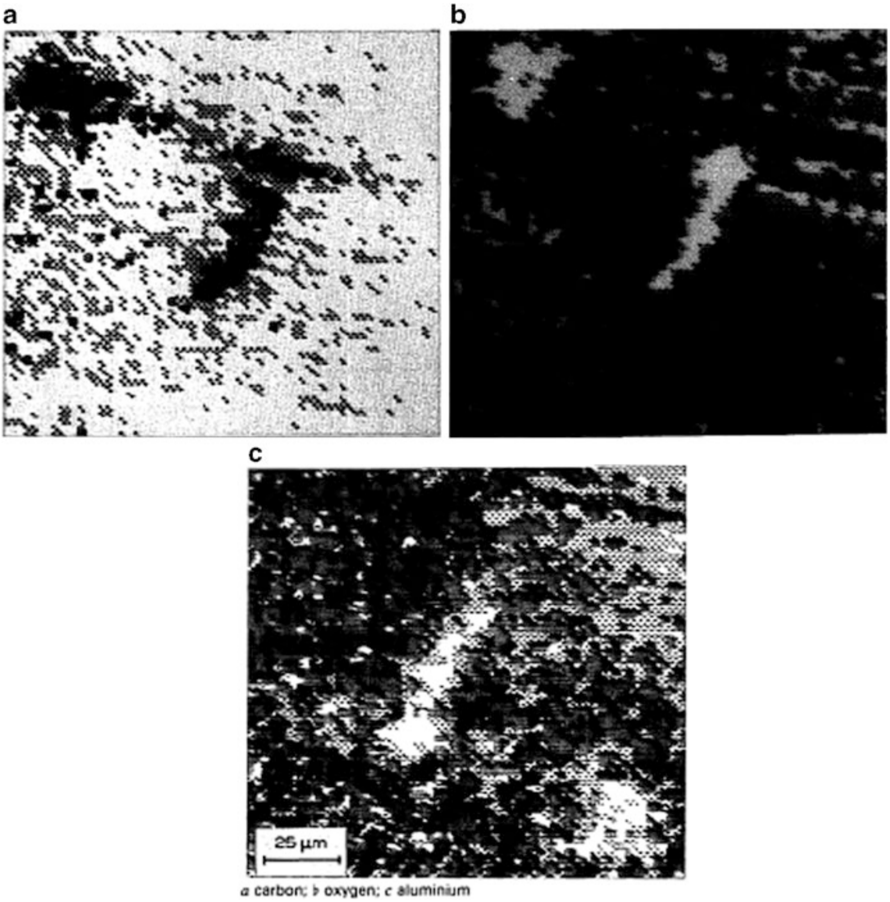


Fig. 8.24 Distribution of (**a**) C, (**b**) O, and (**c**) Al on tribosurface of Al–10 vol% graphite composite as determined by Auger spectroscopy

The film is generally 10–20-nm thick, but there are places where the thickness is relatively large. The phenomenon of film formation has also been reported in other composites containing solid lubricants such as MoS_2 (Tsuya and Takagi 1964) and Pb (Mohan et al. 1990).

Ruff and Peterson (1990) have observed similar film formation in copper-intercalated ($NiCl_2$)-graphite composites both on the wear test pins and on the counterface of steel. The films are patchy in distribution and nonuniform in thickness. Surface profilometry indicates an average thickness of about 1.1 µm but some film patches are as thick as 10 µm. However, the film distribution on the tribosurface and the thickness would depend on test conditions as well as the matrix characteristics. Ruff and Peterson (1990) have also observed that the wear debris is preferentially collected at the entrance edge of the recessed graphite region and the

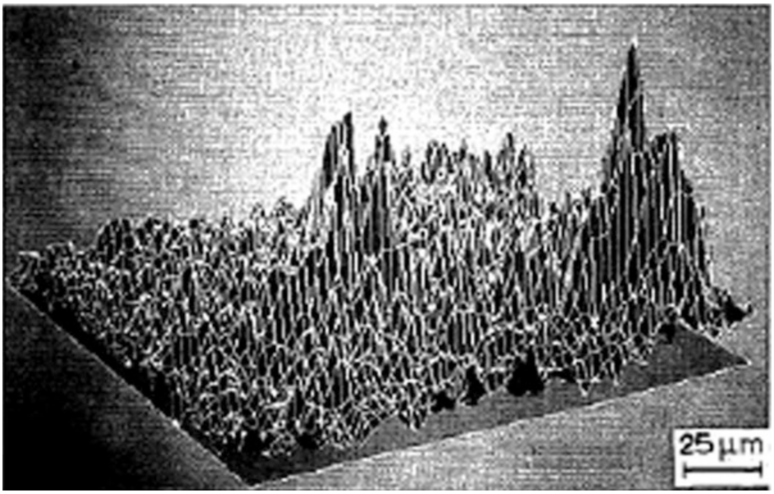


Fig. 8.25 Intensity distribution of carbon in an area on tribosurface

graphite film is formed at the exit edge. Various workers (Bryant et al. 1964; Deacon and Goodman 1958; Baker and Hewitt 1936; Kuhlmann-Wilsdorf 1987; Kuhlmann-Wilsdorf et al. 1988a, b) have observed a change in the mechanism of wear with temperature in silver–graphite and copper–graphite particle composites. At relatively lower temperatures of below 100°C, they assume a layer of moisture in graphite which permits easy shear on the basal plane of graphite. However, at higher temperatures, the moisture is desorbed resulting in the rise of critical resolved shear stress of graphite to a level above that of the matrix alloy or counterface. The graphite will not spread in the form of films because shear will take place in the softer material and the mechanism of wear will be predominantly that for metal–metal sliding.

8.6 Industrial Applications

Metal matrix–graphite particle composites combines the strength, hardness, and abrasion resistance of the matrix alloy with the natural lubricity and machinability of graphite. The matrix alloy may also be chosen to impart good electrical and thermal conductivity to the composite. The dry coefficient of friction of the composites against polished steel shafts is in the range 0.2–0.25 when the graphite content of the composite exceeds about 20 vol%; when submerged in water, petrol, and most other liquids the coefficient of friction drops to a fraction of the value for running dry (Clauss 1972; Kauffman 1980). Table 8.2 summarizes a few important applications of metal matrix–graphite composites.

Table 8.2 Tribological application of metal matrix–graphite composites

Composite	Applications
Copper–graphite	Plane bearing for trucks, cranes, bulldozers, and automotives: drive shafts, bearings, stoker chain, screw conveyor, roller conveyor and roller bearings; spherical bushings for automotive transmission; slider for electric cars, overhead railways, dams and flood gates; slide bushing for discharge valves in hydraulic turbines; electrical contacts and brushes
Al–Si alloy–graphite (Silgraph)	Piston and liner in two stroke and four stroke engines in passenger and racing cars tested by Ferrari, Alfa Romeo, and Hiromotors
Al alloy–graphite	Cylinder block, journal bearings, connecting rods and pins, fan bushings, and internal combustion engines
Mg alloy–graphite	Pistons, structural applications in space
Silver–graphite	Electrical contacts and brushes, bushing in chemical solutions that attack other lubricants and metallic bushings
Babbitt metal–graphite	Medium load and medium speed application in pump and stoker bushings, thrust washers, rotating seal rings
Cadmium–graphite	Current carrying bushings and electrical contacts

Copper–graphite composites can be used up to a temperature of 370°C in oxidizing atmosphere and a temperature of 925°C in submerged conditions or under nonoxidizing atmospheres. These composites are quite suitable for high load and slow speed applications such as in stoker bushings, drying oven conveyor bushings, high temperature stirring shafts and agitators, and current carrying bushings. A number of other applications have been conceived by Hitachi Ltd particularly for cast copper–graphite composites called Gradia (Suwa 1986). It has been suggested that a slider made of Cu–10–20 vol% graphite composite can result in very low wear if used for trolley wire contact (Suwa et al. 1976). A slider made of cast copper–graphite has resulted in lower wear compared with that made of sintered copper–graphite composite as shown in Fig. 8.26. Copper–graphite composite electrical brushes are distinguished from carbon electrical brushes by their very low resistivity and high current carrying capacity, and are therefore suitable for applications such as automotive starter brushes which require low and stable resistance and ability to carry high current instantaneously as the starter commences. Graphite when dispersed in copper base alloys imparts excellent machinability by breaking the chips and providing lubrication at chip/tool interface. Graphite has, therefore, the potential to act as a substitute for lead which is a potential health hazard in copper base alloys particularly when applied for plumbing, and bearings.

Silver–graphite composite brushes are marked by very low noise level, low and stable contact resistance, low friction, and high conductivity. In modern inertial energy storage devices (homopolar motor generators), a large amount of energy is stored and the energy is delivered in the form of low voltage, high current pulses. Silver–graphite or copper–graphite brushes are suitable for such systems. Silver–graphite brushes suppress radio interference noise level and are useful for slip rings, segmented rings, and other applications where special requirements justify the high cost.

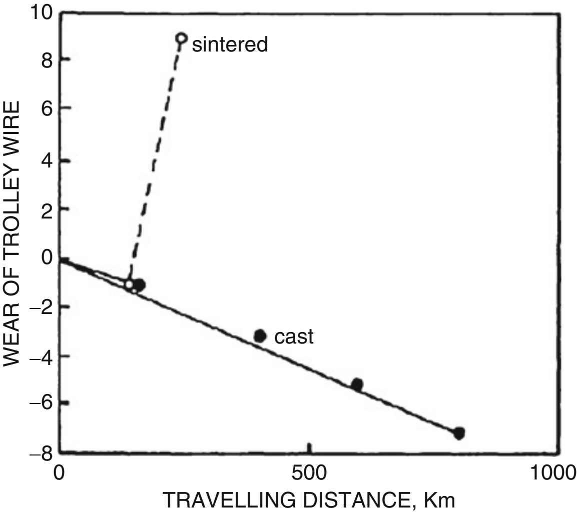


Fig. 8.26 Comparison of wear by trolley wire of sliders made of sintered copper–graphite and cast copper–graphite composite

Much of the early work on metal matrix–graphite particles composites was done using powder metallurgy which is expensive and limited in the sizes that can be produced. Cast aluminum–graphite composites for antifriction applications were developed beginning in 1966. The cast aluminum–graphite alloys have a unique structure, in which graphite particles are in the interdendrite regions and the alloys have been reported to have superior tribological properties compared with similar alloys prepared by PM techniques (Hitachi). These alloys have been cast into tribological components using sand casting, gravity die casting, centrifugal casting, and pressure die casting.

Cast aluminum–graphite particle composites exhibited lower friction coefficients and wear rates and ability to run under boundary lubrication conditions when tests were run with samples submerged in oil in a Hohman wear tester. The composites with over 2 vo1% graphite were able to attain bearing parameters and friction coefficients characteristic of boundary lubrication without galling when they were either self-mated or were running against other aluminum alloys without any graphite (Badia and Rohatgi 1969; Badia 1989).

Microscopic and ESCA examination showed that a graphite film had formed on the sample containing over 2 vo1% graphite particles. In addition, the subsurface had deformed extensively under shear and contributed to the formation of the film of graphite which apparently imparted the antiseizing properties.

Composites were tested as cylindrical sleeve bearings against steel shafts in lubricated conditions and they exhibited a performance superior to that of copper alloy bearings, including phosphor bronze. The bearings of aluminum–graphite were successfully tried out as a replacement for bronze bearings in machine tools, electric fans, water pumps, and in diesel engines at the small end of the connecting rod. Gorbunov et al. (1974) have reported successful use of aluminum– graphite bearings as a replacement for copper alloy bearings in marine diesel engines.

Pistons of aluminum–graphite particle composites when tested in a 3.7-kW diesel engine resulted in reduced wear of the piston and the rings, reduced loss of frictional horsepower, and freedom from seizing under adverse lubrication conditions. The specific fuel consumption decreased. The use of pistons and liners of Al–Si eutectic alloy–graphite particle composite alloys lead to similar results in 0.4 kW petrol engines (Kirshnan et al. 1983; Kirshnan et al. 1981).

Associated Engineering Co., in Italy dispersed 4 vo1% graphite particles in Al–18Si alloy. This composite was wear tested against Al–11.48Si alloy in heated oil in a wear testing rig and it was shown that graphite improved scuffing resistance by a factor of two (Bruni and Iguera 1978; Rohatgi 1991). Further evaluation was made of liners of these alloys in two stroke and four stroke engines for Ferrari, Hiromotors, and Alfa Romeo for passenger and racing car applications. They found that the power generated was improved by 10%, there was no scuffing well beyond the 5-min limit along with no friction marks, and negligible wear was observed. When the tests were run in a four-stroke engine (Alfa Romeo 1300 cc), no liner wear was found and the pistons were in good conditions with no signs of scuffing.

8.7 Development of New Graphite Reinforced MMC Materials

The friction and wear behavior of composites containing graphite particles depend critically on the ability of the graphite to leave its embedded state and smear out in the form of a self-lubricating film separating the matrix and the counterface. The tentative mechanism of film formation as it is understood at present is shown schematically in Fig. 8.27. When a composite surface makes the initial sliding contact with the counterface, the graphite particles are in the embedded state, and the matrix interacts directly with the counterface, resulting in plastic flow of the matrix at the tribosurface and in the subsurface region. The cavities containing graphite particles in the subsurface region deform, and the graphite particles are squeezed out. However, the concurrent plastic flow of matrix alloy tries to smear the matrix alloy over graphite particles. The former process transfers graphite to the tribosurface whereas the latter restricts it. The relative magnitudes of these two processes will depend on the strength, ductility, deformation behavior, and the stress state of the matrix, the smallest dimension of the particle, and its orientation with respect to the sliding direction. The importance of these processes accompanying particle transfer is manifested in the observed effects of particle size and orientation of flake particles on the friction and wear of composites containing graphite. However, no systematic investigation has been directed as yet to understand these two processes and identify the important variables. Nonetheless, it is established that it is the persistence of the self-lubricating graphite-rich layer on the tribosurfaces of metal matrix–graphite particle composites which results in lower coefficient of friction, lower wear rate, and increased seizure resistance.

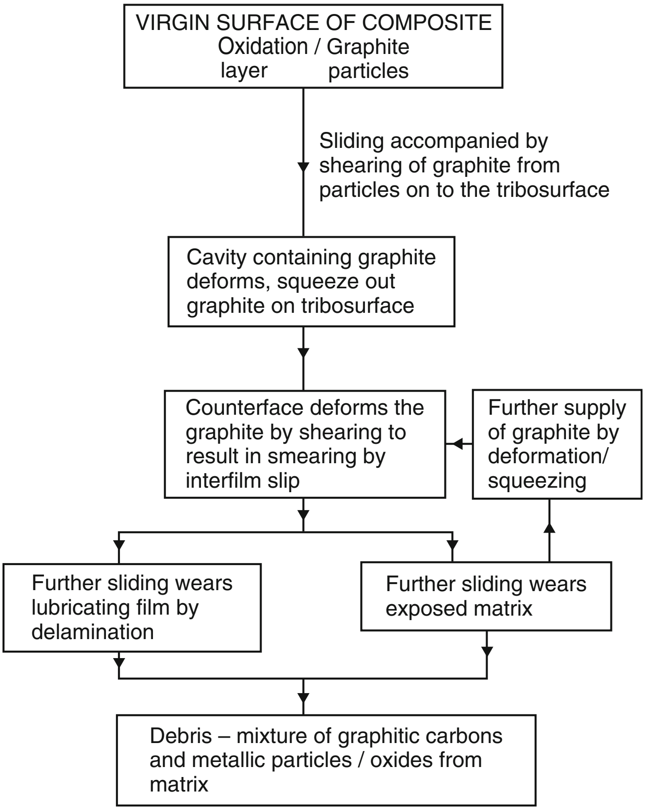


Fig. 8.27 Stage in wear process in metal matrix–graphite particle composites

Once the graphite particles are on the tribosurface, the shear stresses induced by sliding cause slip on the basal plane of graphite if its critical resolved shear stress (CRSS) is lower than those of the matrix and counterface. In addition, one of the interfaces between the graphite and matrix, or the counterface, should be so strong that it does not shear on sliding, and basal slip of graphite takes place in preference to debonding of graphite. It is well known that the CRSS of graphite is lowered by adsorbed moisture and gases. If the temperature is above the desorption temperature, the CRSS of graphite will be very high and the mechanism of wear may change depending on the matrix and the counterface. For a given matrix and counterface, the CRSS of graphite can be varied with appropriate intercalations and its impact on friction and wear behavior should be systematically investigated in the future.

The extent of film formation will depend on the supply of graphite on the tribosurface and the test conditions of load and sliding velocity. The supply of graphite will also depend on the nature of the matrix and its composition.

It is observed that above 20 vol% of graphite in a composite, the friction coefficient is more or less independent of the matrix. This is probably indicative of near complete elimination of direct matrix–counterface interaction. While the variation of wear with sliding velocity is similar to matrix alloy in Al-base composites containing 5 vol% graphite, the trend is completely changed in composites with 15 vol% graphite; this needs further investigation. There has been no investigation as yet on the variation in the extent of film formation with composition in a given composite system. The extent of film formation can be characterized by profilometry as it has been done by Ruff and Peterson (1990) or by sputter etching and XPS as employed by Rohatgi et al. (1990a, b, c, d). The influence of test parameters on the film formation should also be investigated in selected metal matrix graphite particle composites with a given graphite content, to illustrate the effect of matrix composition.

The friction behavior of a composite will clearly have two distinct stages from the time the sliding starts (Rohatgi et al. 1990a, b, c, d) (a) the transient stage during which film formation is taking place (this could include films on composite component as well as on the counterface), and (b) steady state (dynamical) when the extent of coverage by graphite film on both the rubbing surfaces has become more or less constant and the amount of wear in the film is being replenished by new graphite supplied to the tribosurface. These characteristics of friction behavior have been broadly reflected in high initial values of friction, and its reduction to a steady value during sliding; however, detailed investigations are required to correlate test parameters to the process of evolution of film to steady states. The study of the transient state is important, since during this period high friction coefficients can occur and seizing and galling can also take place.

The wear of a composite will be high in the transient state, but will decrease considerably in the steady state depending on the composition of the alloy. There may be several transitions in the wear mechanisms when the test parameters are varied. If the composite has a lower graphite content, there will be direct interaction between the metallic matrix and the counterface in the steady state, and a transition from oxidative mild wear to metallic severe wear should be observed. In addition, if the supply of graphite on the tribosurface becomes large because of composition or test conditions, the thickness of built up graphite film will take it beyond the critical thickness for the initiation of extensive delamination wear within the graphite film itself. These different regimes of wear in metal matrix–graphite composites should be identified by careful analysis of the debris and may be represented in a wear map similar to that proposed by Ashby and co-workers for metals and alloys (Rohatgi et al. 1990a, b, c, d). It is also necessary to make long-term wear tests to determine the overall life of the graphite rich film and its ability to be replenished by graphite in the matrix. There are very limited data available on the *P*–*V* limits of metal matrix–graphite particle composites and these need to be studied at higher speeds/loads. Table 8.3 summarizes the present state of knowledge and suggests some directions for future investigation on the tribological behavior of composites containing graphite.

Table 8.3 Present state of knowledge and suggested future work on tribocharacteristics of metal matrix–graphite particle composites

Broad aspect	Indicator variables	Characteristic behavior	Present state of knowledge	Suggested future work
1. *Intrinsic characteristics*				
Tribological behavior	Coefficient of friction, wear, and bulk wear	Variation with pressure, sliding speed, and volume % and size of graphite	Limited scattered data available for very few systems including Al, Cu, Fe, Ag base	Establish minimum amount of graphite significantly to change the friction and wear; and optimum amount of graphite for minimum friction and wear
Mechanism of transfer of embedded lubricant to the tribosurface and mechanism of film formation	Graphite distribution (area and thickness) on tribosurfaces; graphite content of debris	Variation with composition volume % of graphite, pressure, and sliding speed	Limited microscopic observations on tribosurfaces after film formation available for very few systems	Establish total mass balance involving transfer, delamination process (slip/shear), and compacting; role of counterface, recycling process
Nature of film	Composition, structure, orientation, particle size, adhesion, and microhardness of film, chemical nature of debris	Variation with pressure, sliding speed, matrix structure	Limited recent data available on very few systems	Determine: film composition (NMR, EMP, EDAX), film structure (XRD, LEED, SR), film orientation (XRD, LEED), film microhardness, film thickness (ESCA, Auger profile, RBS) for selected systems
Effect of matrix on film formation	Graphite distribution on the sliding interface; nature and deformation of subsurface	Variation with different matrix alloys for given experimental conditions	No systematic information available	Establish relation between the film and plastically deforming layer of matrix. Examine film matrix interface using ESCA profile, laser Raman, and RBS. Examine subsurface area using sections vertical to tribosurface
Development of models to explain observed tribological behavior	Graphite distribution	Variation of friction and wear	Very scanty evidence of some of the mechanisms proposed	Schematic description of process of film formation and failure, development of models and equations

(continued)

Table 8.3 (continued)

Broad aspect	Indicator variables	Characteristic behavior	Present state of knowledge	Suggested future work
Role of counterface made of different materials on film formation and graphite	Graphite distribution and debris composition	Variation with counterface of Cu, Al, steel, cast iron	Practically no information available	Relation between extent of film formation and the role of sliding counterface
2. *Extrinsic interactions*				
Effect of chemical nature of environment	Coefficient of friction, wear rate, and extent of chemical reactions	Variation of friction and wear with different gas environments; inert gases N_2, Ar, He: reacting gases O_2, H_2O	Only limited data on a few selected systems. No understanding	Tribological behavior of composites under different environmental conditions, interaction between graphite, matrix, and environments during sliding wear
Effect of atmospheric pressure	Coefficient of friction, wear rate	Variation with pressure	Limited data on only one system. No understanding	Tribological behavior of composites under vacuum and high pressure
Effect of environmental temperature	Coefficient of friction, wear rate, and extent of oxidation	Variation of friction and wear with temperature	Limited data on very few systems. No understanding	Tribological behavior of composites under different temperatures, oxidation layer effect

8.8 The Role of Solid Lubricants

8.8.1 General Considerations

Some key features as explained by Erdemir (2001) on solid lubricants are the following:

1. When there is a sliding interface that is present, the low friction is due to the fact that they can shear much more easily than liquid-type lubricants.
2. They can withstand very high pressures.
3. They are not dependent on temperature compared to liquid-type lubricants which are capable of turning into the solid state at low temperatures and becoming oxidized at high temperatures.
4. They also show some insensitivity toward harsh chemical environments compared to liquids.

However, a major concern about solid lubricants is the fact that they are prone to getting oxidized at high temperatures in an oxygen-rich environment. Once they get oxidized, the chemical structure of the compound gets altered to the point where it may have adverse effects on the friction and wear properties of the material under consideration. Furthermore, this oxidation process can occur gradually over time and thus becomes harder to restore the lubricant. Another disadvantage that is seen when considering a solid lubricant is the fact that they are not very good conductors of heat. Therefore, finding a way for dissipating the heat produced at the sliding interface is a challenge.

In this way, it is seen that solid lubricants can be used for many demanding industrial applications where using liquid-based lubricants may not help. However, the key idea when using solid lubricants is that their properties are significantly affected by surrounding environmental conditions. One particular solid lubricant may work well in a certain instance of temperature and pressure, but may work adversely in other situations. The main point is focusing on exactly what type of solid lubricant needs to be selected, to work in a given setting.

8.8.2 Nanoparticle and Microparticle Lubricants

Recently, there have been advances into the micro and nanotechnology arenas, where nanoparticles have been added to the matrix and/or to the lubricating oil. The primary method is to disperse solid particles within the metal matrix to help in its self-lubricating ability. A good example of this method can be seen in the case of porous bearings in which microparticle lubricants in the form of additives (Erdemir 2001) like hexagonal Born Nitride (h-BN) are incorporated as shown by Pawlak et al. (2009). The sizes of the particles were of the order of 1–2 μm. The results from experimental testing of these self-lubricating bearings with h-BN as additive showed that there was a definite decrease in overall friction coefficient compared to that of engine oil alone. Their reasoning behind this is that the h-BN lasts for a longer time in the matrix and is “gradually released” to the area of surface interaction. Therefore, it is practical to try to add microparticles into the matrix alloy for greater reduction in friction. An even better approach is to use the nanoparticle-sized h-BN into the composite because that will have an even better chance to propagate itself into the area of surface interaction. These will be more efficient as a solid lubricant than the micron-sized h-BN.

One of the main difficulties as explained by Hernandez-Battez (2010) regarding nanoparticles (Hernandez-Battez 2010) is that they are very hard to synthesize. Despite this fact, there are many applications where the addition of nanoparticles to lubricants or to materials may help greatly in reducing friction and wear.

Rapoport et al. (2005) have used nanoparticles of WS_2 and MoS_2 to create structures that are used as solid lubricants in composite materials. They were found to act as very good solid lubricants especially when under high normal stresses. This obviously had a great advantage over liquid-type lubricants, which would escape out of the rubbing interface and thus have no lubricating effect.

8.8.3 Graphene and Diamond Carbon Additives

Carbon in its various forms, have generated a lot of interest recently among researchers and scientists to see what possible tribological properties they exhibit to help in the reduction of friction coefficients and wear rates. Erdemir (2004) indicates the fact that carbon has many “exotic” structures like fullerenes, nanotubes and the like to provide low friction coefficients. The major type of carbon film that has seen the greatest use and research work done on is the DLC films or the Diamond-like Carbon films. This is basically an amorphous carbon state with different types of carbon–carbon bonds, specifically sp^3 hybridized carbon atom bonds. It possesses the same qualities like diamond in that it is very hard and stiff and at the same time has very low friction coefficient and so is very smooth. It is used in mechanical parts that experience a lot of abrasive wear such as common milling tools, and certain drilling tools as well. It is also used in bearing materials and engine parts to reduce the sliding and rolling wear produced. It also has high chemical inertness and does not corrode easily. Such a material no doubt enjoys many uses in industry today. Graphene is basically graphite at the atomic level, and is composed of sheets that have formed a honey-comb like lattice structure. It is also seeing some use in creating self-lubricating materials or coatings with graphene-based oxides. However, the main difficulty here is that it is very difficult to synthesize and so is seeing limited use in industry.

There are many materials which when used in conjunction with others contribute toward the reduction of the adverse tribological effects associated with friction and wear. The solid lubricants or additives (which may be in the form of a MMC) described above are much superior to their liquid counterparts. In general, the materials that would assist in this process are those with a layered structure. This is because the materials would easily shear between the moving parts and form a lubricating layer between the two interacting surfaces. This makes graphite a very good example of this type of solid lubricant. As mentioned before the only key point here is the amount of graphite that is needed to be added on to the MMC to enable the part to work efficiently and at the same time not weakening its mechanical properties as a result of the addition. In conclusion, different forms of graphite including graphene, DLC, and possibly nano-sized particles including h-BN are promising additions to the materials that can help reduce overall friction and wear by providing self-lubrication.

8.9 Summary

Although a qualitative picture on friction and wear behavior of metal matrix–graphite particle composites is emerging, the quantitative understanding of their tribological behavior is far from satisfactory. A theoretical basis to predict the tribological behavior of MMCs does not exist; the experimental measurements of friction, wear, and seizure behavior, coupled with macroscopic observations of tribosurface and subsurface have been used to develop tentative mechanistic models. Even the experimental literature suffers from lack of standardization; test conditions used by different investigators are not clearly indicated and are quite different, and only a correlation of results in terms of broad trends is possible. Frequently, the materials characteristics of the composites such as the porosity content, size, and shape of graphite have not been adequately reported making the assessment of results extremely difficult. Despite these problems, the following significant conclusions emerge:

1. The coefficient of friction and wear rate of most of the metal matrix–graphite particle composites investigated to date reduce significantly with increase in the graphite content. The absolute values of friction coefficients and their variation with graphite content depend on the specific matrix composition up to a critical volume level of about 20 vol%. Above 20 vol% of graphite, the values of the coefficient of friction of different MMCs appear to converge to a value around 0.2, which is close to the friction coefficient of pure graphite, regardless of the matrix composition.
2. The variation of wear rate of metal matrix–graphite particle composites with sliding velocity is similar to that of the matrix alloys in composites containing graphite contents below 10 vol%; however, in composites containing above 10 vol% graphite, wear becomes almost insensitive to changes in sliding velocity.
3. The wear rate in metal matrix–graphite particle composites is significantly lower than that in the corresponding matrix alloys under identical load conditions. The wear rate in MMCs with less than 10 vol% graphite increases with normal load.

4. In gray cast iron where graphite precipitates in situ from the liquid phase, the coefficient of friction depends on the matrix, i.e., whether it is ferritic, pearlitic, or martensitic.
5. When the graphite content is below the critical level, the extent of coverage of tribosurface by solid lubricating film increases with the graphite content of the matrix. For composites containing graphite in excess of the critical amount above which the friction coefficient approaches a constant value regardless of the matrix, the sliding surface is completely covered with a graphite solid lubricating film.
6. Once the entire surface is covered by the graphite solid lubricating film, the wear rate does not significantly change with graphite content until the thickness of the graphite film becomes large enough to cause its own wear by delamination.
7. The extent of spread of the graphite film depends on the matrix material and environment, and limited observations with selected composites suggest that the graphite film probably does not form readily under high vacuum, and the friction under these conditions is quite high. Selected metal matrix–graphite particle composites continue to exhibit improved tribological behavior up to 540°C suggesting that the process of graphite film formation is not yet adversely affected.
8. The process of graphite film formation on the tribosurface of a composite containing graphite is still not very clear. The detailed mechanisms are likely to be revealed through a study of wear behavior during the initial transient period during which the graphite film forms. The existence of a critical thickness of the film as predicted by delamination theory may also be verified for composites by direct measurements. The nature of spreading and thickness buildup in the graphite film and its relation to matrix characteristics and alloying should also be investigated in the future for a complete understanding of wear behavior of graphite.
9. The thickness of the graphite film formed on the tribosurface of Al-10 vol% graphite composite is generally of the order of 10–20 nm but at places the film is much thicker. In intercalated graphite, the film is patchy and the thickness is of the order of micrometers. The thickness of the film may depend on the matrix, graphite content, and the test conditions.
10. The gall resistance of aluminum–graphite composite is higher than that of the base alloy. At >2 vol% graphite, the aluminum–graphite composites are able to run under boundary lubrication when they are self-mated, or run against steel.
11. In view of these superior tribological properties of composites containing graphite compared with those in the base alloys, there have already been several applications of these materials. Silver–graphite and copper–graphite composites have been employed in electrical brushes for several years. Iron–graphite composites and cast irons have been used in several mechanical components subjected to wear.
12. Cast aluminum–graphite particle composites have been developed which exhibit reduced friction, wear, and enhanced antiseizing characteristics under boundary lubrication conditions.

Metal matrix–graphite particle composites have been successfully employed by Associated Engineering in racing cars exhibiting reduced wear and friction. These alloys have also been tried as pistons and liners in petrol and diesel engines leading to reduced frictional losses and wear, and enhanced resistance to seizing compared with those observed for standard aluminum alloys or cast iron. The aluminum–-graphite composite has proved to be a better bearing material at lower cost in comparison with phosphor bronzes and leaded bronzes in machine tool and connecting rod bearings.