
Literature Review

Previous chapter discussed the importance of C/C and C/C-SiC composites for tribological applications. The detailed literature review regarding tribological behaviour of C/C and C/C-SiC composites will be discussed in this chapter.

2.1. Carbon Fibers

Carbon fibres are used to provide strength and stiffness to C/C and C/C-SiC composites. Carbon fibers have been described as the fibers which contain at least 92% of carbon. These fibers are heat treated at a temperature of 1000 °C – 1500 °C during the processing stage. Carbon fibers are polycrystalline and are generally in non-graphitic stage. They possess a long-range order of carbon atoms in planar hexagonal networks, but the order in third direction is not significant. The basic structures of graphite and carbon fibers are shown in Fig. 2.1 and Fig. 2.2 respectively.

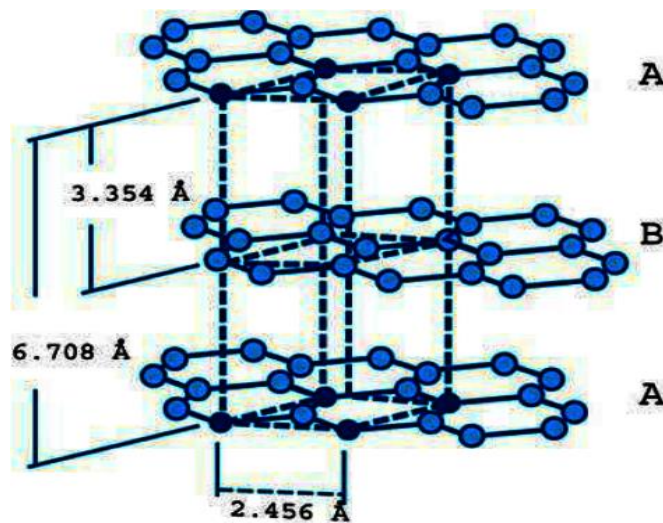


Fig. 2.1. Crystal Structure of Graphite [22].

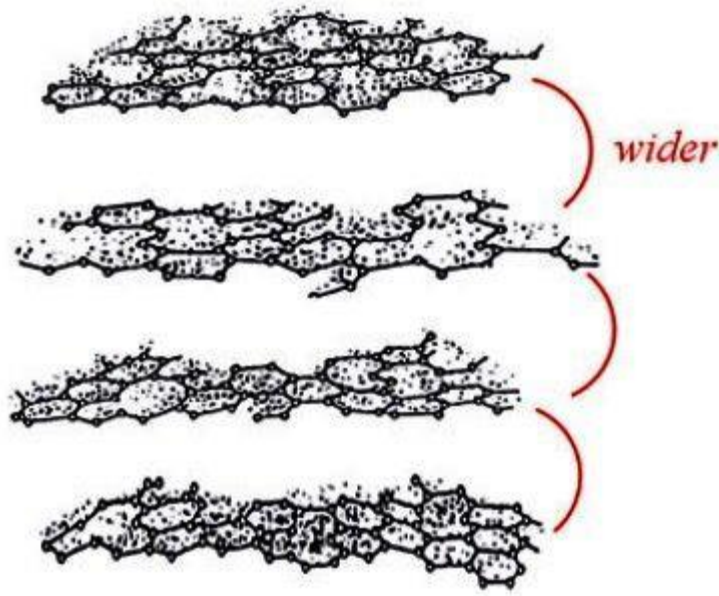


Fig. 2.2. Crystal Structure of Carbon Fibre [23].

The structure of carbon fibres is not homogeneous. They consist of stacks of turbostratic layers and the distance between different layers is more than that in graphite. The basic structural unit of carbon fibres could either irregularly or haphazardly split, tilt, twist and fold. A thousand of carbon fibres are twisted together to form a yarn [23].

The properties and the range of applications of carbon fibres depend upon its precursors. Several kinds of precursors have been investigated to produce carbon fibers [24]. The basic characteristics the precursor of carbon fibre should possess are, (i) high carbon yield, (ii) easy conversion to carbon fibre, and (iii) cost effective processing. Based on these basic characteristics, four types of precursors are generally used which are as follows:

- (i) **Acrylic Precursors:-** These precursors are based on acrylonitrile (AN) monomer with at least 85 wt% of it. Polyacrylonitrile (PAN) is the most widely used acrylic precursor.

- (ii) **Cellulose Precursors:-** The carbon yield of cellulose precursors is approximately 25-30% however, it contain 44.4% carbon.
- (iii) **Pitch based Precursors:-** The carbon yield of pitch based precursors is 85%. The modulus of pitch based carbon fibres is high due to high graphitic content. However, the compressive strength and transverse properties of pitch based carbon fibres are low as compared to PAN based carbon fibres.
- (iv) Phenolic resins and Vinylidene chloride have also been used for the manufacture of carbon fibres but their usage for commercial manufacturing of carbon fibres was not found satisfactory.

Carbon fibres can be reinforced in polymer as well as ceramic matrices. As discussed in the last chapter, carbon fibres reinforced ceramic matrix composites are used for extreme environmental conditions. Among carbon fibers reinforced CMCs, C/C and C/C-SiC composites are used for brake disks of aircrafts and high speed cars. The tribological behaviour of C/C and C/C-SiC composites and the factors affecting it are discussed in the next sections.

2.2. Tribological Behaviour of C/C composites

C/C composites have many common properties of polymer composites, which lead to appear in the group of monolithic materials. As discussed in the last chapter, C/C composites exhibit unique properties such as ability to withstand high temperature, high specific heat, high specific strength, self-lubricating capability (abrasive wear decreases due to self-lubricating property), low thermal expansion coefficient, high stiffness and toughness, and outstanding refractory properties. The thermal shock properties of C/C composites are better than several

other friction materials. Due to lightweight and better mechanical properties, these composites are replacing many metallic parts of the aeronautical structures. C/C composites have excellent tribological properties, especially at high temperature and useful for aircraft's brake applications [25-27]. However, wear of C/C composites depends upon humidity adsorbed on the surface of C/C composites which decreases the coefficient of friction. At lower landing energy, the influence of humidity is quite large because the temperature does not reach the critical value for the complete evaporation of adsorbed species. Humidity has less effect in high energy braking conditions due to evaporation of adsorbed species. In aircraft brakes, C/C composites have to carry three functions simultaneously, that is, producing friction, transferring mechanical load, and absorbing kinetic energy [28-30]. When used in aircraft brakes, C/C composites have long service life, low noise, and smooth operation as compared to the other materials that are used in aircraft brakes [31, 32]. For long service life of C/C composites, these composites need to be protected against oxidation either by matrix modification with silicon, zirconium, hafnium, etc. or by multilayer oxidation protection coatings consisting SiC, silica, zircon, etc. [8] C/C composites show increase in strength with temperature in contrast to metals and ceramics which show decrease in strength with temperature as shown in Fig. 1.1.

2.2.1. Processing of C/C composites

C/C composites are generally manufactured through chemical vapor deposition (CVD) technique with the impregnation of resin or pitch or the process combining both. [16] These composites can also be manufactured by solid pyrolysis using thermosetting resins, or pitch route using liquid infiltration carbonization route. [8] The first step in the fabrication of C/C composites involves the fabrication of a three-dimensional-reinforced or multidimensional

porous carbon fiber preforms with desired architecture or porous carbon–carbon skeleton with carbon fibers and a carbonaceous matrix followed by their densification. Densification can be achieved through chemical vapor infiltration in which the porous fibrous structure is heated to a temperature of 1000–1400°C, and the hydrocarbon gases are made to infiltrate into it and made to crack therein. Ideally, the gas should infiltrate into the pores and then crack, but these gases crack at the outer surface and block the passage and causes closed pores. Thus to have dense composites, the surfaces are grounded and components are re-infiltrated. Due to the slow nature of CVD process, it takes months to obtain dense carbon–carbon composites. Porous carbon–carbon composites can also be impregnated with liquid phase pitch/phenolic resin. This is followed by carbonization and after that heat treated at high temperature, that is, 1000–2700°C. Pitch/resin matrix can be pyrolyzed under normal pressure or high pressure. A new approach has been involved in which the composites are heat treated to high temperature after certain impregnation/ normal pressure carbonization cycles and after that re-impregnated again. Due to this heat treatment at high pressure, pores open up for further infiltration. Generally not a single processing route is followed, but a combination of different processing routes is followed. This can be the fabrication of host composites by pitch or resin route and then densification and pores sealing by CVD.

2.2.2. Carbon–Carbon composites as braking material

Friction brakes decelerate a vehicle by transforming the kinetic energy of the vehicle into heat and dissipate that heat into surroundings. The brakes which are used in automotive braking system are generally made of steel or gray cast iron and coupled with polymer composite pads. [17] These materials are used in braking system with moderate loads and limited capability to withstand temperature. These materials have relatively high and stable

coefficient of friction, low wear rate, and are quiet during operation.[18] However, heavy vehicles require more power for braking than conventional braking system. To accommodate that C/C composites came into picture which can provide more friction and can operate at high temperature. [19, 20]

Fig. 2.3 shows the variation in friction coefficient and wear rate with elastic modulus of carbon fibers and graphitization temperature. Elastic modulus of carbon fibers increases with the increase in graphitization temperature. Many accidents are caused by trucks when their brakes get overheated while descending a hill and are unable to stop. For example, a 20-ton truck stops at a distance of nearly 80 m using cast iron brakes after a descend of 5 km at 10% incline with 60 km/h velocity. [21] This stopping distance can be reduced to 25 m using carbon-carbon brakes.

Nowadays commercial aircrafts such as Airbus — 319, Boeing — 767 to Boeing — 777; MD-11, military aircraft such as the F-15 to F-22, and joint strike fighter such as Mirage 2000 use C/C brakes. [33-35] C/C composites should have capacity to dissipate an extreme

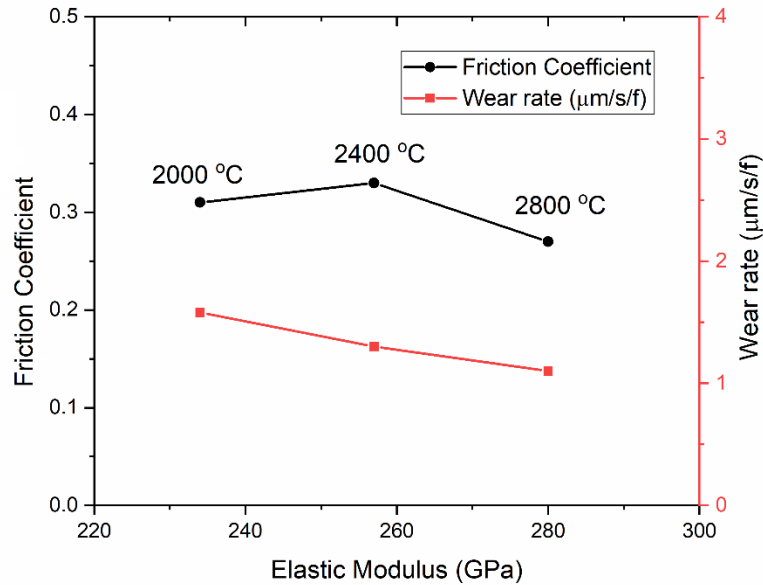


Fig. 2.3. Variation of friction coefficient and wear rate with elastic modulus of carbon fibres in the frictional surface [20].

ablation heat of 20,000 kcal/kg to be used as aircraft brakes. These types of high-speed brakes require 4500 J/cm² of kinetic energy per unit area of sliding surfaces to be converted into heat in approximately 30 s. The thermal cycling leads to cracking of uncoated C/C composite which leads to accelerated wear and oxidation. [36]

2.2.3. Wear and friction behavior of C/C composites

C/C composites are used in the field of aeronautics. [37, 38] However, wear of sliding surfaces of these materials usually occurs at extreme conditions of temperature where lubricants are either ineffective or undesirable. [9, 39, 40] At elevated temperatures, wear loss and oxidation loss both contribute to the weight loss of C/C composites. [36]

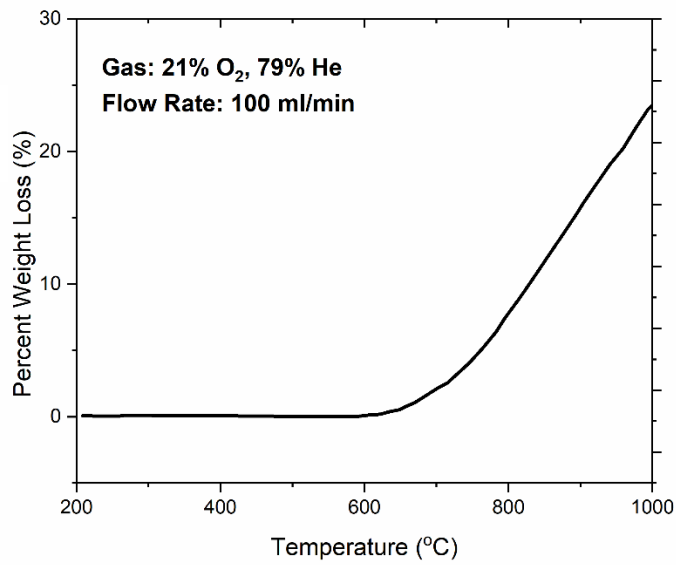


Fig. 2.4. Variation of percent weight loss of C/C composite sample with temperature in a gas mixture consisting of 79% He and 21% O₂ [36]

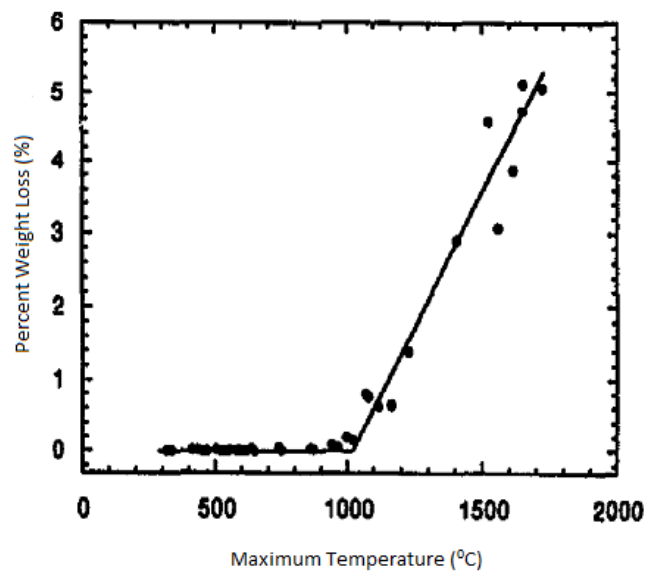


Fig. 2.5. Variation of percent weight loss of C/C composites (with oxidation-inhibitor) with maximum specimen temperature [36]

Fig 2.4 and 2.5 show the percent weight loss of C/C composite with and without oxidation. Wear in C/C composites is mostly because of oxidation of carbon fiber and carbon matrix. It can be observed from Fig. 2.4 that weight loss abruptly increased beyond 650 °C with increase in temperature (as the time elapsed) which was attributed to the rapid desorption of chemisorbed oxygen in the form of CO₂. Due to oxidation, abrasive wear may also increase.[41] The addition of oxidation inhibitor reduced the wear loss, but the failure of oxidation inhibitor at 1050 °C increased the wear loss afterward. C/C composite friction materials absorb a large amount of kinetic energy in the form of heat during braking. The temperature on the sliding surfaces can reach as high as 1000°C under severe braking conditions.[42] This energy is absorbed in very short interval of 15–18 s due to which there is very high rate of heat generation on the sliding surfaces and steep thermal gradients of more than 1000°C across the friction pads of brake material. [21] C/C composites can withstand this much temperature for frictional applications, but its susceptibility to oxidation limits its lifetime. Some researchers have investigated the wear of C/C composites under the representative aircraft braking conditions.[43-46] They found that the oxidation in the subsurface is the predominant wear mechanism in C/C composites due to high interfacial temperature of the friction material. Thus, most of the wear studies of C/C composites are concentrated on oxidative mass loss of the composites at elevated temperature. The temperature rise in the C/C composites is related to the braking pressure.[47] Xiong et al. [47] plotted the temperature, friction coefficient, linear wear rate, and mass loss for two samples, that is, sample A (smooth laminar carbon) and sample B (a high-textured rough laminar carbon). The results of their investigation are shown in Fig. 2.6. It is clear that temperature of worn surface of sample with a high-textured rough laminar carbon, that is

sample B, is lower than that of sample with smooth laminar carbon, i.e. sample A. Thus, oxidation loss for sample B will be very less as compared to sample A which helps in retaining of coefficient of friction and proper wear rates at higher braking pressure.

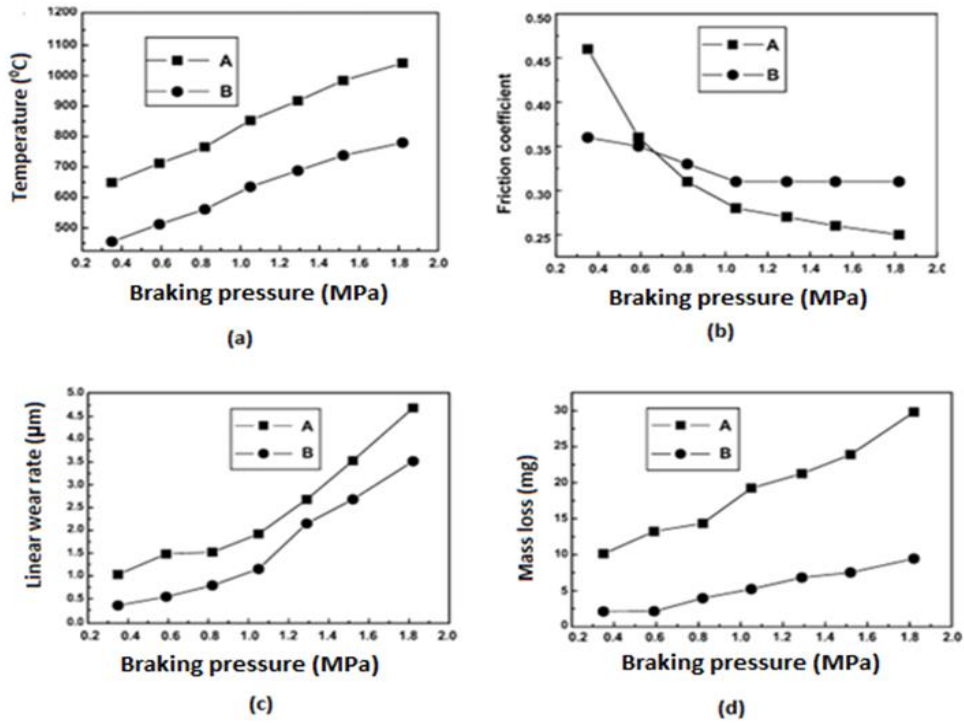


Fig. 2.6. Friction and wear properties of the two samples at various braking pressures: (a) temperature; (b) friction coefficient; (c) linear wear rate;(d) mass loss [47].

2.2.3.1. Effect of nanoadditives on friction and wear performance

Policandriotes and Filip [41] studied the effects of selected nanoadditives on the friction and wear performance of carbon-carbon aircraft brake composites. According to them, the desired properties of C/C composites for aircraft brake applications need modification, which are decreased wear from oxidation and abrasion and stable consistent friction performance at the required energies. The average coefficient of friction stabilizes after the addition of nanoadditives in C/C composites. Fig. 2.7 shows the variation in friction coefficient with different types of nanoadditives.

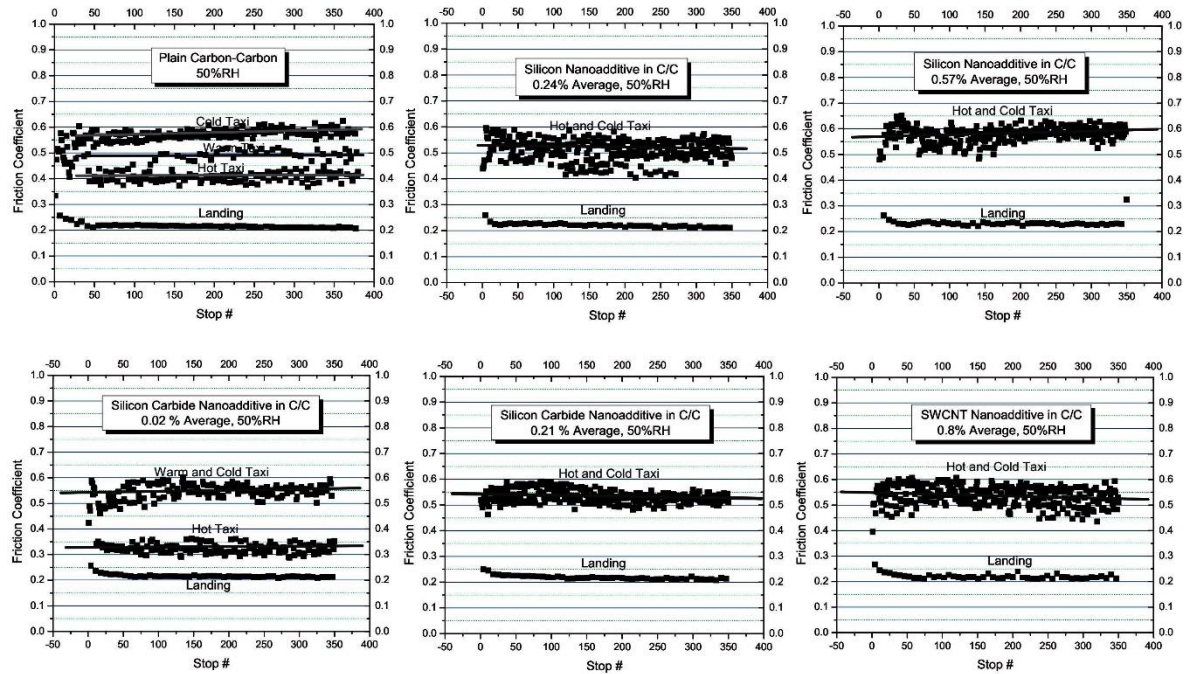


Fig. 2.7. Comparison of the engagement conditions for each of the nanoadditive samples to the baseline plain C/C composite [41].

The open porosity in C/C composites is so small for the penetration of micrometer-sized particles, so nano-sized particles are chosen for additives in C/C composites. The addition of Si and SiC nanoadditives in C/C composites reduces total wear when used in concentrations below 0.25% for Si and 0.2% for SiC in C/C composites. Si and SiC nanoadditives are inexpensive in nature, thus provides a quick solution for the reduction in wear in C/C composites. Nanoadditives form carbides and oxides at the surface of the composites, thus reduces the oxidative wear but sometimes increases the abrasive wear depending upon the concentration of nanoadditives.

Audi discussed the method of infiltration of nanoparticles in carbon–ceramic brake disks in its patent US 7419700B2. [48] This method was developed to reduce the penetration of moisture in open porosity. Nanoparticles can be incorporated into the friction layer by impregnating a resin mixed with nanoparticles into the bulk fiber support structure. [49]

2.2.3.2. Effect of friction film on wear and coefficient of friction

There is formation of uniform friction film on the worn surfaces of C/C composites under various braking conditions. [50] Both types of friction films (particulate type and film type) can coexist on the worn surface of C/C composites, but dominant type of friction film depends on the energy of braking. [51] Wear loss increases and friction coefficient decreases with the increase in brake pressure. [47, 52-54] The formation and disruption of friction film leads to variation in friction and wear with brake pressure and brake speed. [55, 56] The compaction of wear debris to form complete friction film, and its disruption also varies with the sliding time (several mechanisms are involved). This leads to the variation in the friction coefficient and temperature with time, as shown in Fig. 2.8 (a). Furthermore, as the brake energy increases (due to increase in braking pressure/sliding speed), temperature of the worn surfaces increases which results in the rapid desorption of water vapor and oxygen from the worn surface. [53] Fig. 2.8 (b) shows the maximum temperature rise on the worn surface as a function of brake pressure.

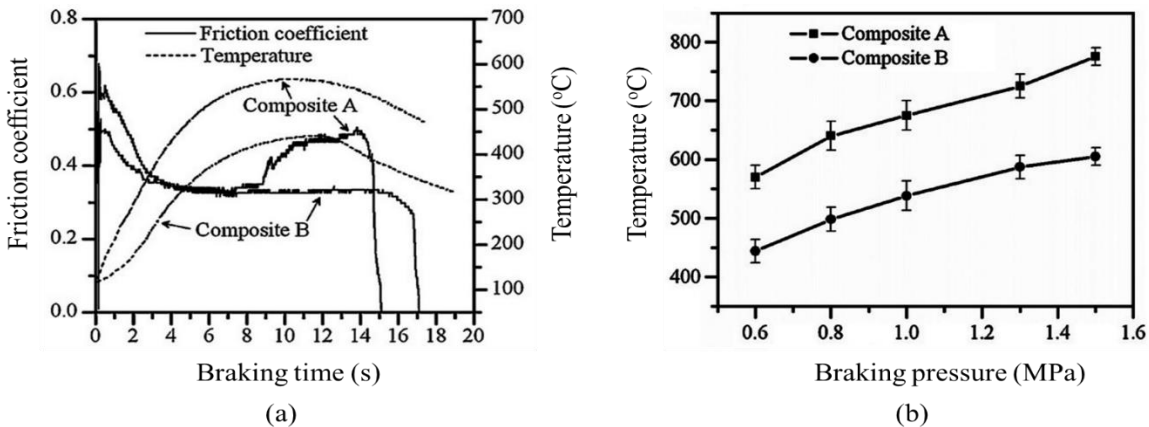


Fig. 2.8. Variation of (a) friction coefficient and temperature with braking time at braking pressure of 0.6 MPa and brake speed of 25 m/s, and (b) maximum temperature with brake pressure at brake speed of 25 m/s [53].

In Fig. 2.8 (b), the composites A and B specifies C/C composites with PAN based carbon fibers, and xylene as matrix precursor. However, the Composite A was densified at 900-1000 °C for 25 h, whereas the Composite B was densified at 1000-1100 °C for 18 h. The resulting densities of Composite A and Composite B were 1.71 g/cm³ and 1.72 g/cm³.

There is a formation of rough, powdery friction film and thick uncompleted worn surfaces of C/C composites. A large amount of particulate-type and flake-type wear debris gets detached from the contacting surfaces and eject out. These morphological variations in friction film and wear debris lead to increase in wear and friction and the unstable braking behavior. When the brake speed increases from a certain level, the carbon matrix and wear debris convert into a smooth and completed friction film due to very high braking energy which results in decrease in average friction coefficient and increase in braking stability and linear and mass wear. Fig. 2.9 shows the variation in friction coefficient with braking speed (Composites A and B are same as described for Fig. 2.8 (b)).

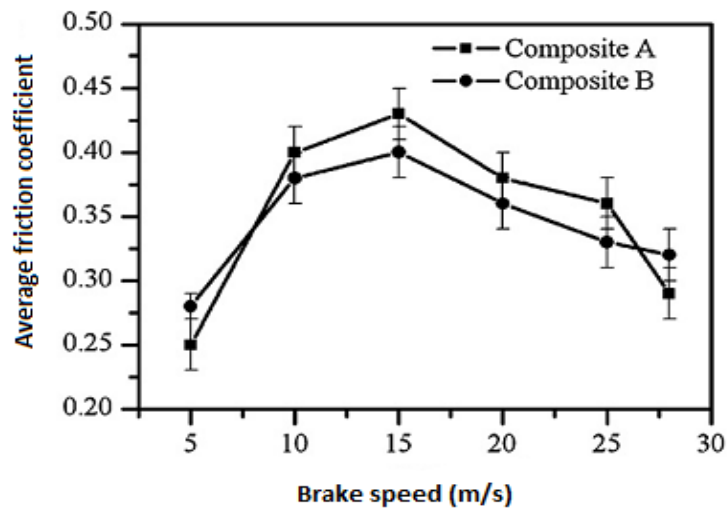


Fig. 2.9. Variation of average friction coefficient with brake speed at the brake pressure of 0.6 MPa [53].

2.2.3.3. Short time oxidation behaviour

The temperature of C/C composites instantly reaches 1000°C while braking and subsequently comes back to room temperature. These conditions of temperature variation and reuse leads to short-time oxidation of C/C composites. This short-time oxidation behavior affects the properties of C/C composites, especially mechanical properties. [57] The performance of C/C composites does not only depend on the structure of carbon fiber and carbon matrix, but also depend on the interface between them. Many researchers have showed that C/C composites preferentially oxidize from the fiber matrix interfacial zone. De-bonding of fiber matrix interface provides rapid oxidation channels and results in drastic oxidation of C/C composites. [58] Thus, mechanical properties and oxidation resistance of C/C composites can be improved by modifying the fiber matrix interface. [59] Carbon nanofibers (CNFs) which are grown in situ can improve the oxidation resistance of C/C composites at low temperature. [60]

2.2.3.4 Effect of in situ grown carbon nanofibres (CNF) on oxidation behaviour

Lu and Xiao [59] studied the oxidation behavior of C/C and in situ grown CNF-C/C composites. They found that up to about 600°C, the mass loss percentage of both C/C composites and CNF-C/C composites is almost zero, but above 600°C it is more for C/C composites than CNF-C/C composites. The result of their study is shown in Fig. 2.10.

From Fig. 10, it is clear that CNFs grown in situ can slow down the oxidation rate at low temperature but has a little influence on the oxidation behavior at high temperature.

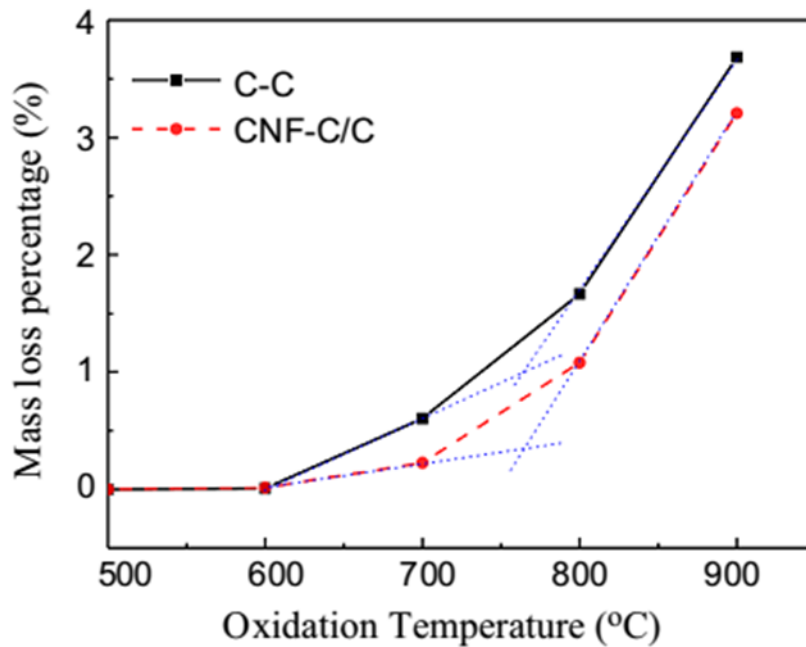


Fig. 2.10. Variation of percentage of wear loss with oxidation temperature of C/C and CNF-C/C composite. [59]

2.2.3.5. Effect of functionally graded coating on oxidation

Ceramic coatings can also be used to prevent C/C composites from oxidation in air at elevated temperatures.[61-63]

But the mismatch of CTE (coefficient of thermal expansion) between the coating and the substrate (C/C composites) leads to cracking of coating at elevated temperatures, and diffusion of oxygen occurs from cracks and oxidation of substrate takes place. Thus to prevent diffusion of oxygen, multilayer coatings or functionally graded coatings are used either to seal the cracks of coating or alleviate the stress which is responsible for the cracking of the coating. [63-68] Fig. 2.11 shows the residual mass percentage of different coatings

with oxidation time. However, bonding between coating and C/C composite should be strong enough to sustain severe thermal cycling.

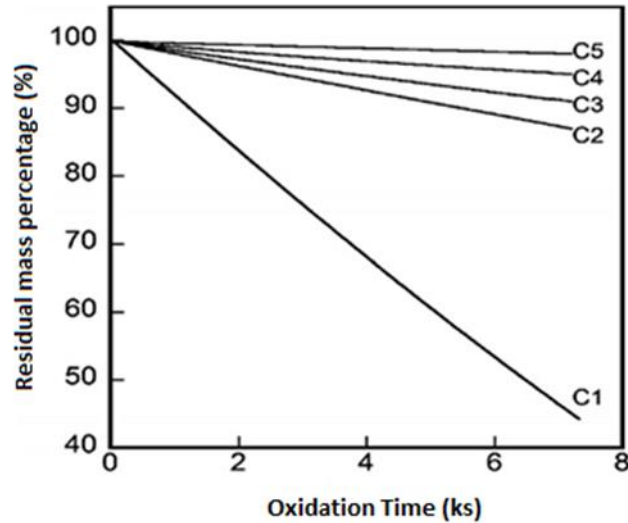


Fig. 2.11. Variation of residual mass percentage with oxidation time at 1200 °C in air (C1; SiC coating, C2; CNT–SiC coating, C3; CNT–PyC5–SiC coating, C4; CNT–PyC10–SiC coating, C5; CNT–PyC15–SiC coating) [63].

Incorporating CNTs in the coating system can enhance the bonding strength between C/C composite and SiC coating and can suppress the cracking in coating. [63] Thus for many multilayer coating systems, SiC coating is used as an internal buffer layer.

2.2.3.6 Effect of ultra high temperature ceramic coating on oxidation behaviour

Ultra-high temperature ceramics have attracted many intentions for coating system due to their high melting temperatures (>3000 °C), high hardness, high thermal and electrical conductivity, high thermal shock and oxidation resistance and excellent chemical stability. [69-75] The typical ultra-high temperature ceramics coating which are attracting attention

these years are tantalum carbide (TaC) and tantalum diboride (TaB₂). [76-81] Xuanru Ren et al. [69] investigated the effect of SiC and TaB₂-TaC-SiC coating on oxidative weight loss of C/C composites at 1773 K temperature. The results of their investigation are given in Fig. 12.

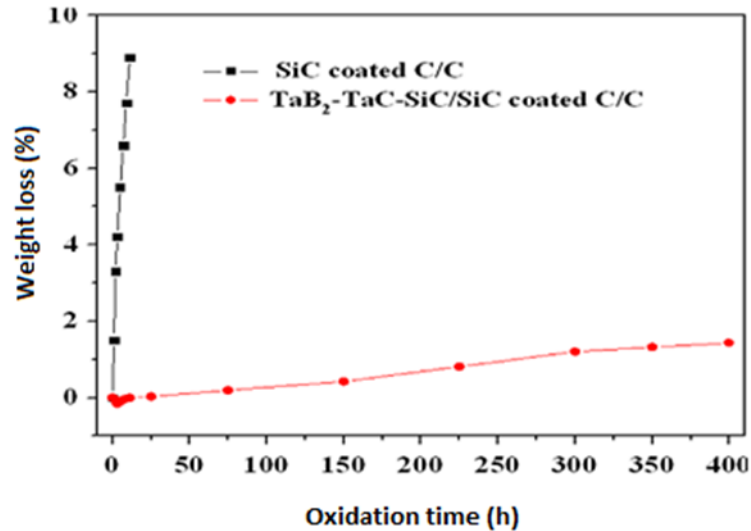


Fig. 2.12. Variation of percentage weight loss with oxidation time of coated C/C composites in air at 1773 K [69].

From Fig. 2.12, it is clear that oxidative weight loss in case of SiC coated C/C composites is more and rapid as compared to TaB₂-TaC-SiC coated C/C composites. This shows the effectiveness of ultra-high temperature coatings on C/C composites.

2.2.3.7 Effect of SiC coating on oxidative wear

SiC coating is used extensively for C/C composites due to its good compatibility with C/C composites [9, 62, 82] Fig. 2.13 shows the variation of friction coefficient of two different types of SiC coating with time.

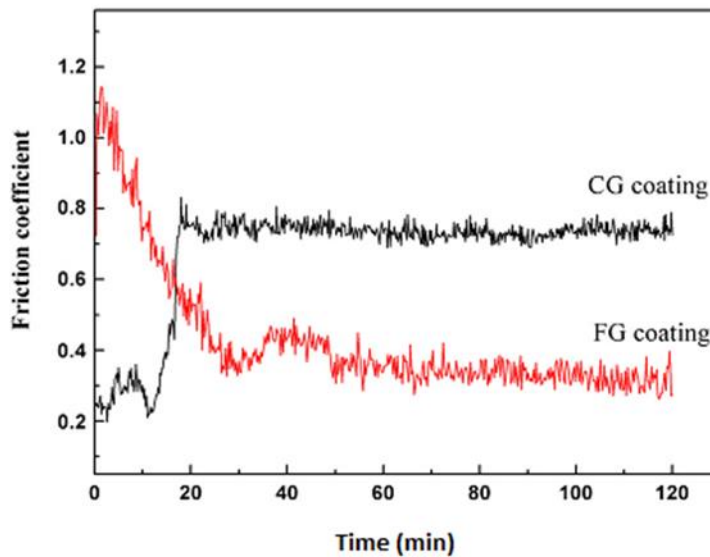


Fig. 2.13. Variation of friction coefficient with sliding time for the CG coating (SiC coating without Ti powder) and the FG coating (SiC coating with small amounts of Ti powder) at 600 °C [9].

SiC coating is able to protect C/C composites from oxidative wear for more than 310 h at 1773 K [83]. The specific wear rate of SiC ceramics is very small at room temperature and almost independent of sliding speed [84]. However, wear resistant SiC coating fails due to grains pullout and brittle fracture at high temperature friction contacts [85]. If grains are refined, grain refinement leads to decrease in flaw size which leads to increase in stress required to failure [86] according to Hall- Petch relation and Archard equation. [87-89]

2.2.3.8 Effect of wet and corrosive environment on friction

C/C composites are best suited for aircraft braking applications but are not frequently used in wet and corrosive environments because of degraded tribological performance in adverse environments. [11, 90] Thus carbon fibre reinforced SiC matrix composites fabricated by

liquid silicon infiltration are used in wet and high speed braking field conditions. [91-93] But liquid silicon reacts with carbon fibres also and damages the fibres. This may reduce the strength of carbon fibres and makes it brittle. However some amount of silicon doesn't react with carbon and remains in free state. This free silicon increases adhesive friction and leads to instability. Thus tribological performance of C/C-SiC composites can be modified by adding ceramic fillers (such as SiC, B₄C etc.) in it. [94] Fig. 2.14 shows the braking curves of some ceramic filler modified C/C composites with small and large sized SiC (1 μm, 5 μm) and B₄C (1.5 μm, 5 μm) particles.

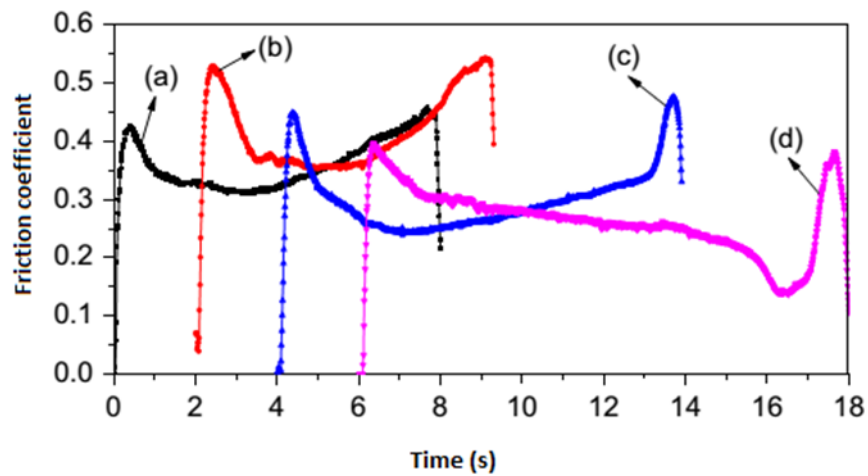
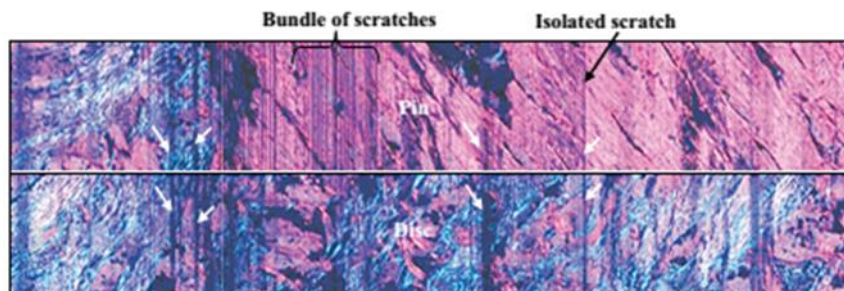


Fig. 2.14. Variation of friction coefficient with time of ceramic filler modified C/C composites at 25 m/s: (a) CCSSF (C/C composite with small-sized SiC filler, 1 μm), (b) CCSBF (C/C composite with small-sized B₄C filler, 1.5 μm), (c) CCLSF (C/C composite with large-sized SiC filler, 5 μm), and (d) CCLBF (C/C composite with large-sized B₄C filler, 5 μm) [94].

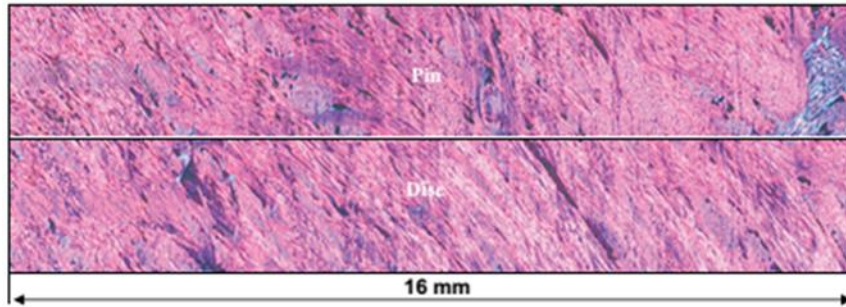
Due to high specific heat of ceramic filler, it can reduce the maximum temperature in the braking process and can increase the rate of carbon matrix graphitization. [95, 96]

2.2.3.9 Characterization of surface grooves induced by friction of C/C composites

Various experiments have been performed to have a better understanding of mechanisms which governs the wear of C/C composites during friction. This includes sliding speed and pressure and temperature during braking [55, 97], interaction with gases during friction [98, 99], third body interaction [100] and their characteristics [101, 102], and the damage caused by friction to the worn surface. [103-105] At low temperature friction, the wear rate and coefficient of friction is high and the rubbing surfaces are rough. [106] The grooves formed on the surfaces of C/C composites at low temperature are of large amplitude (up to 20 μm) and it indicates that at low temperature the predominant wear mechanism is abrasive wear. At high temperature friction, the wear rate (due to friction contacts) and coefficient of friction is low and the surfaces are smooth. The radial profiles of the friction track of both opposing discs after friction at low and high temperature are shown in Fig. 2.15 (a) and 2.15 (b).



(a)



(b)

Fig. 2.15. Radial profiles of the friction track of both opposing discs after friction at (a) low temperature and (b) high temperature (OM images taken between crossed polarizers with addition of a retarder plate) [106]

The grooves are of smaller amplitude because smaller size particles are present due to detachment of smaller size particles at high temperature friction contacts in C/C composites. [98]

2.2.3.10 Effect of carbonization rate

Carbonization rate at the time of fabrication also effects the tribological behaviour of C/C composites [107]. Carbonization is a very time and energy consuming step due to low carbonization rate. Carbonization rate is kept low due to some adverse effects of fast carbonization rate i.e. shrinkage, cracking, thermal stresses due to carbonization, etc. To reduce the carbonization time, the effect of fast carbonization rate on polyacrylonitrile (PAN)/ phenolic-based C/C composite was studied [107]. The wear of PAN/phenolic-based C/C composites carbonized at the rate of 10000C/min is inferior to that prepared with slow carbonization rate. But after post treatment, wear performance and coefficient of friction were found superior. The amount of change depends on the type of post treatment [96].

2.2.4. Wear and friction behavior of C/C-SiC composites

As discussed in the last chapter, the introduction of silicon carbide (SiC) to the matrix of C/C composite leads to the application at high temperature and leads to improvement in tribological properties due to chemical stability and hardness of SiC and self - lubricating action of carbon. The mechanical properties of carbon - carbon silicon carbide (C/C-SiC) composites are not affected at high temperature [91, 92]. C/C - SiC have lower density (about 2.0 g/cm^3), longer service life, higher thermal shock resistance as compared to traditional braking materials. When the weight content of silicon carbide is higher than 20% in the C/C – SiC composite, the composite shows lower sensibility to surroundings and temperature [108].

Research is going on C/C–SiC composites. Several industries and institutions are working on C/C–SiC composites to investigate C/C–SiC composites as friction materials for brake disks and brake pads. [35, 109, 110] In early 1990s, Krenkel et al. investigated C/C - SiC composites for high performance automobile applications [111]. Till now, C/C – SiC have been applied to Porsche, Ferrari and Daimler Chrysler [112]. Various reports on the self - friction of C/C – SiC composites shows that friction performance and stability of composite improves with the reduction of porosity and increase in carbon content [113-115].

C/C composites show extremely unsuitable tribological behaviour in adverse environments. Thus C/C composites are rarely been used in wet and corrosive environments [11, 90]. However C/C – SiC composites can be used as braking material in the wet and high speed braking conditions [91-93].

2.2.4.1. Processing of C/C – SiC composites

Properties of C/C – SiC composites depends on several factors such as type, amount and microstructure of matrix and fibres and their interface as well [116]. Thus the properties of C/C – SiC composites greatly depends on the manufacturing method. The manufacturing methods of carbon fibre reinforced silicon carbide composites mainly differ in the way in which the SiC matrix is built up. Currently three processes are used for the manufacturing of carbon fibre reinforced SiC matrix composites i.e. Chemical vapour infiltration (CVI), Liquid polymer infiltration (LPI), also called polymer infiltration and pyrolysis (PIP) and melt infiltration (MI) or Liquid silicon infiltration (LSI). CVI and LPI processes are expensive due to high material costs caused by fibre coatings. CVI and LPI are also time taking processes and their production cycle times can go from several weeks to months. Thus in the late 1980s, cost efficient and less time consuming process was developed i.e. MI/LSI process, which opened new application fields for carbon fibre reinforced ceramic matrix composites [117].

In MI/LSI process porous carbon/carbon composites are impregnated by molten silicon and carbon reacts with silicon to form silicon carbide. Firstly, a CFRP (carbon fibre reinforced plastic) preform is made by common techniques like resin transfer moulding (RTM), autoclave technique or warm pressing. The use of as received carbon fibres (without any coating) leads to strong fibre/matrix bonding in CFRP composite. The extent of fibre/matrix bonding in CFRP composite is measured in terms of interlaminar shear strengths (ILSS) which typically lies in the range of 40 – 50 MPa for bi-directionally reinforced CFRP composite which are used as preform for LSI process [118]. In the second step, the CFRP composites are pyrolyzed in inert gas atmosphere (N₂) at temperatures between 900 °C to

1650 °C which transforms the polymer matrix into a highly porous C/C preform. As the pyrolysis temperature is increased, shrinkage stresses generate which locally exceeds the tensile strength of matrix and leads to cracking. It was observed by using thermo-optical analysis that in case of bi-directionally reinforced CFRP composites, first fibre/matrix debonding occur beyond 505 °C [119]. This debonding results in the segmentation of the fibre tows and leads to a translaminar microcrack pattern with dense C/C segments [118]. In the last step, the fibre preform having porosity is infiltrated by molten silicon at temperature beyond the melting point of silicon i.e. 1415 °C, mostly applying only capillary forces. Typically the operating temperature is in the range of 1600 °C.

Critical parameters which are to be considered in the processing of C/C – SiC composites by LSI technique are low melt viscosity, the good wetting of fibre reinforcement, high chemical reactivity and the anomaly of silicon during the phase transition (density change of silicon is approximately 8%).

After infiltration, the molten silicon fills the cracks within some minutes. The dense carbon matrix shields the fibre bundles from highly reactive silicon and a layer of silicon carbide is formed around the segments. Thus only a small amount of carbon fibres are converted and damaged. If carbon fibres are thermally treated before implementation in the polymer matrix, the active surface groups are de-activated which leads to reduced fibre/matrix bonding. Thus pyrolysis results in carbon fibre tows without any segmentation and liquid silicon can react with most of the carbon fibres and can damage most of the carbon fibres. Thus load bearing capacity of composites is reduced and fracture behaviour of composites is similar to monolithic ceramics [14, 120].

Many manufacturers have developed different C/C – SiC composites which are characterized by low porosities (lower than 6%), high fibre volume contents (higher than 30%) and moderate mechanical properties.

2.2.4.2. Tribological behaviour of C/C – SiC composites

In case of high speed braking systems, approximately 4500 J/cm² of kinetic energy per unit area of sliding surfaces is required to be converted into heat in approximately 30 seconds. Although C/C composites may serve the purpose, the thermal cycling leads to cracking of uncoated C/C composite which leads to accelerated wear and oxidation [36]. Thus, high wear rate, poor oxidation resistance and relatively low friction coefficient of C/C composites are considered as fatal weaknesses to be applied in high speed braking systems. To overcome these limitations, C/C–SiC composites were developed. The main requirements of high performance brake materials (as discussed in chapter 1), i.e., stable friction coefficient (dynamic and static), low wear rate for increased life, low weight, low life cycle costs, and high degree of freedom in the structural design (for internal cooling ducts, attachments) are efficiently met by the C/C–SiC composites. The effect of service environment on the performance of C/C–SiC composites is also less as compared to C/C composites. Therefore in recent years, C/C – SiC composites were developed as high performance brake materials following metallic materials and C/C composites [121].

The C/C–SiC composites could be effectively used in the wheel brake disks of airplanes and high speed trains. In case of airplanes, brake disks are enclosed in a braking environment, whereas brake disks are exposed to ambient conditions in case of high speed trains. The exposure to ambient conditions may result in oxidation and corrosion of brake disks due to their interaction with snow and rain.

The incorporation of SiC in the composite matrix results in increase in coefficient of friction but wear rate also increases due to abrasive action of silicon carbide [91]. SiC generally damages by fatigue. Carbon fibres get loose by repeated flexion due to debonding of SiC grains. It was observed that the effect of SiC is less when it is deposited by CVI [122]. The presence of free Si in the composite matrix has a great influence on the third body morphology. Adhesive friction also comes into play due to the presence of free silicon and there is increase in coefficient of friction and decrease in wear. The adhesive component of friction increases due to presence of free silicon as silicon is less hard than silicon carbide due to which free silicon is subjected to plastic deformation which increases adhesion [91].

Fig. 2.16 shows emergency brake system and internally ventilated brake disk for passenger cars made of C/C-SiC composite. It can be observed that C/C-SiC composite brake disk is comprised of at least two parts, i.e., friction ring and metallic pot. Thus assembling two parts results in weight saving of about 50% as compared to one-part casted iron brake disks. There should be flow of heat from outer region to the centre of the composite to prevent the overheating of the friction surface (outer region). The overheating may leads to the exposure of the parts nearby the brake periphery (e.g. tyres, braking fluid etc) to high temperature (due to radiation effect) and hence may damage them. Furthermore, the high temperature of the friction surface may reduce the coefficient of friction to an unacceptable value. Thus C/C-SiC composites should have high transverse thermal conductivities. To meet the essential requirements, C/C-SiC composites should be modified in their composition and microstructure. Increase in silicon carbide content of the composite lead to increase in the transverse thermal conductivity of the C/C-SiC composites [92]. However, low carbon

content and increase in the silicon carbide content leads to decrease in damage tolerance of the composite and also influences the mechanical properties of the composite.

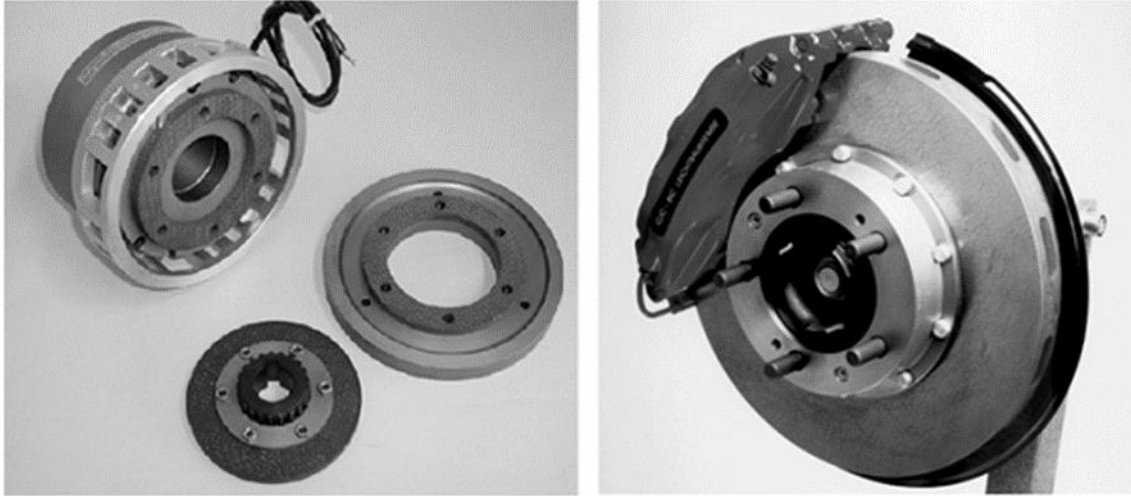


Fig. 2.16. Emergency brake system (left) and internally ventilated brake disk for passenger cars (right), made of C/C-SiC composite [123]

High SiC content is mainly required in the outer region of the disk. Two approaches has been suggested to fulfil the requirement of high silicon carbide content in the outer region [118] which are as follows:

- Gradual increase of SiC from centre to the outer region (i.e. friction surface);
- Homogeneous C/C – SiC composites with Si – SiC coating on the outer region.

These two approaches successfully meet the requirements but due to high coefficient of thermal expansion of ceramic rich surface than C/C – SiC substrate, tensile stresses develop in the surface during cooling after processing leads to micro cracking of the surface. Braking heats up the surface. Thus cracks get narrower as outer region expands more than substrate.

Normally the cracks formed runs throughout the thickness but stops in the ductile core region. Thus breakage of fibres do not occur.

In disk brakes, material of pad also influences the tribological properties of C/C – SiC composites. The composition of pad material influences the coefficient of friction. Even slight change in the composition of pad material can change the coefficient of friction. Results of most of the tests and pad material’s composition are confidential and not published. Some results are shown in Figs. 2.17 and 2.18.

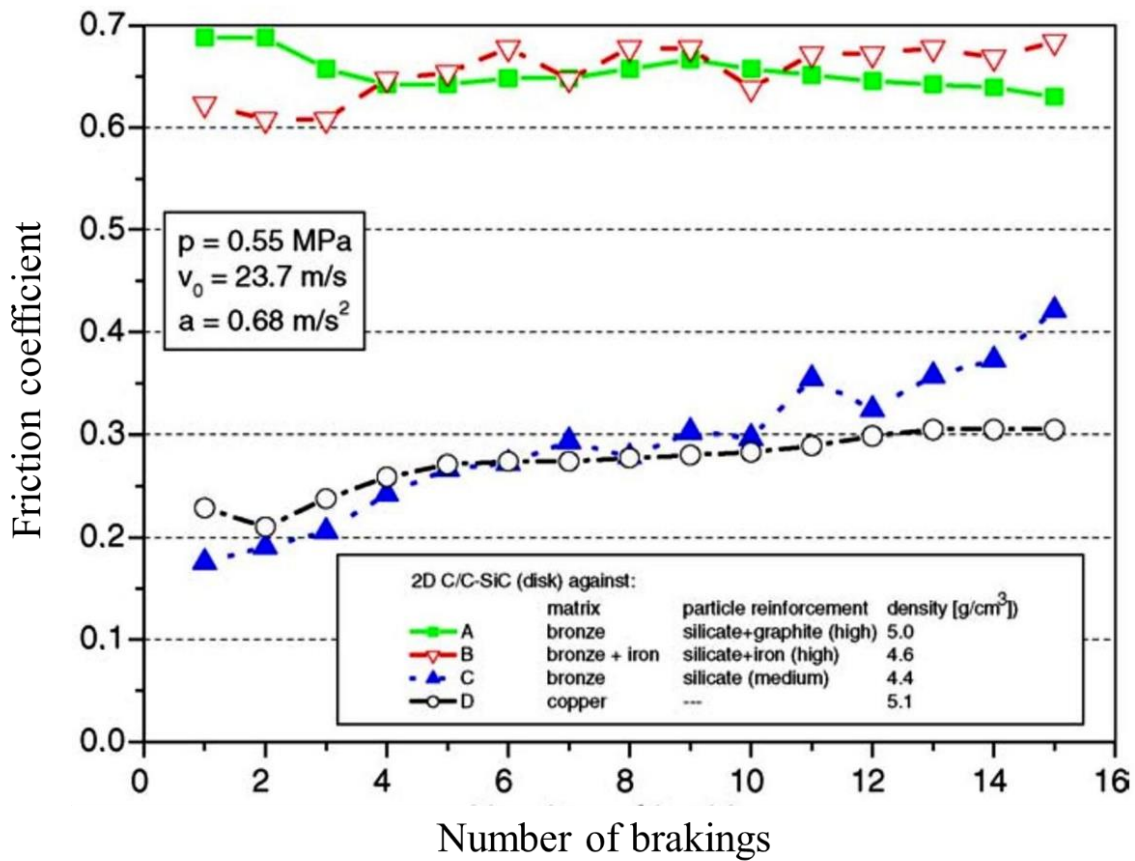


Fig. 2.17. Variation of friction coefficient with number of brakings under the Influence of the pad material on the frictional behaviour of 2D reinforced C/C–SiC brake disks [118].

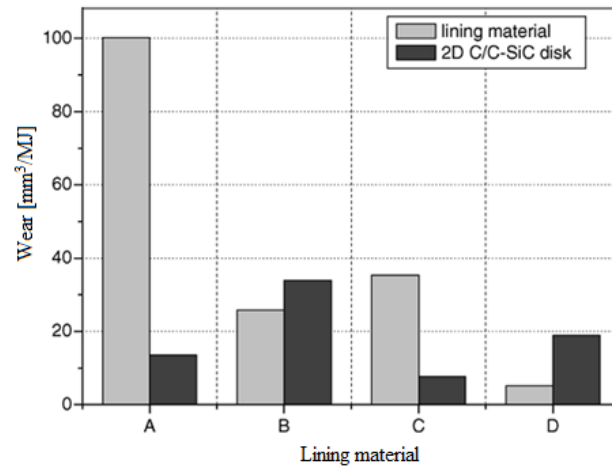


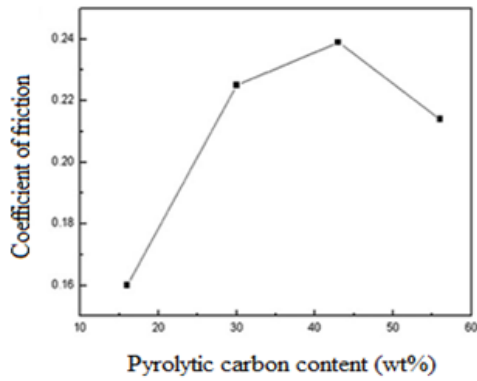
Fig. 2.18. Variation of wear rates of C/C–SiC brake disks in combination with commercial lining materials (material’s composition see Fig. 2.17) [118]

There are so many factors which affect the tribological performance of C/C – SiC composites. Some of them are described here.

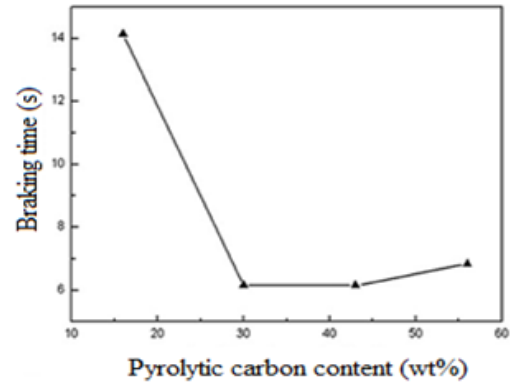
2.2.4.3 Effect of pyrolytic carbon content on tribological properties of C/C- SiC composites

The amount of pyrolytic carbon in matrix has great effect on its final performance because C/C – SiC composite is manufactured from porous C/C preform.

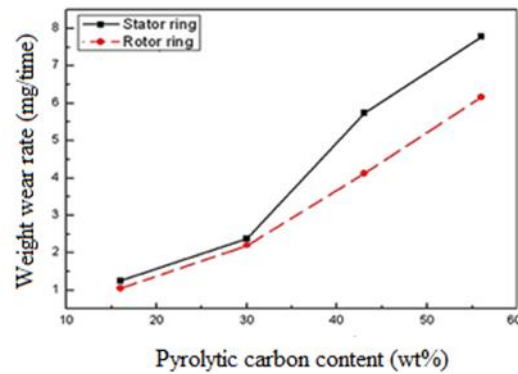
The variation of friction properties with the weight percentage of pyrolytic carbon is shown in Fig. 2.19. It is shown that coefficient of friction increases as weight percentage of pyrolytic carbon increases up to some extent. After that coefficient of friction decreases. Braking time decreases very rapidly with increase in pyrolytic carbon content but after some extent it becomes almost constant.



(a)



(b)



(c)

Fig. 2.19. Dependence of friction properties of C/C - SiC composites on the content of pyrolytic carbon in matrix. (a) Average friction coefficient; (b) braking time; (c) weight wear rate [124]

During braking, superficial hardness can increase the coefficient of friction by enhancing the ploughing effect [115]. Superficial hardness decreases with increase in pyrolytic carbon content which results in increase in coefficient of friction because friction surface gets softer and hard SiC asperities may pierce with ease [124].

2.2.4.4. Effect of porosity and SiC contents on the tribological properties of C/C–SiC composites

C/C – SiC composites can be fabricated by various methods i.e. CVI, PIP, LSI and so on [125, 126]. Each fabrication method has its advantages and drawbacks. The densification is very slow in case of CVI and PIP. Materials fabricated by CVI and PIP contains some residual porosity. However materials fabricated by LSI process display poor mechanical properties [126] and contains some free silicon which affects the frictional properties [113].

Porosity and SiC content decreases with increase in the initial preform density. Fig. 2.20 shows the curves of friction coefficient for samples from different methods.

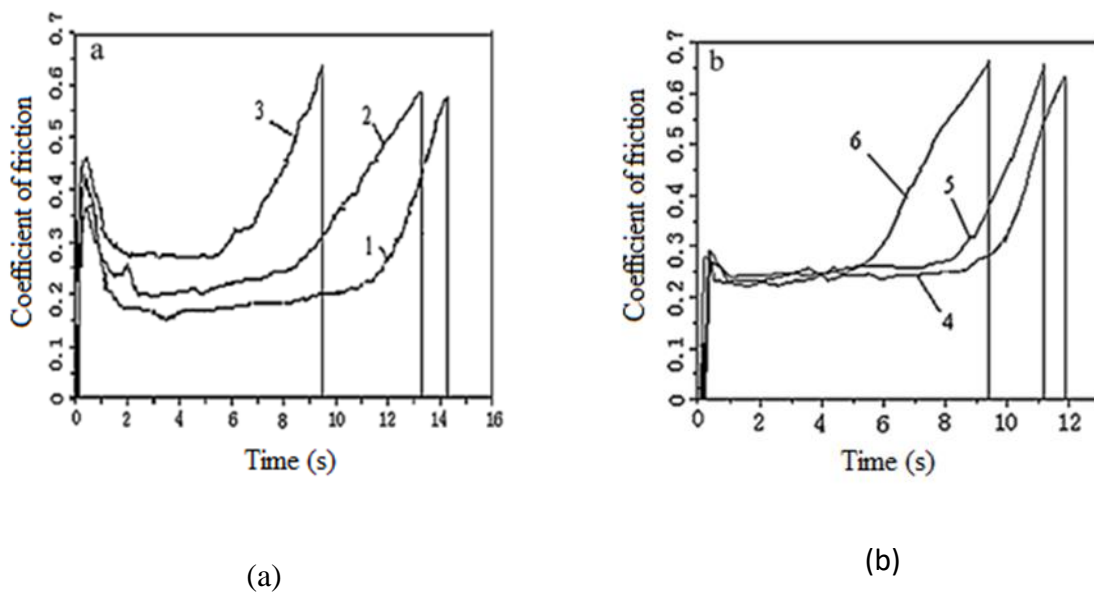


Fig. 2.20. Variation of friction coefficient with time for samples from different methods

(a) PIP; (b) CVI (*details of samples 1, 2, 3, 4, 5 and 6 are given in Fig. 2.21*) [127]

As braking starts, there is sudden pressure on the surface of brakes and first part of the curves in Fig. 2.20 is fluctuating. However due to embedment of grains, there is generation of new abrasive particles which leads to rapid increase of friction [127]. The friction coefficient may reduce due to pulverization of some of the abrasive particles which acts as friction film. There is competition between abrasive action and lubrication action which tend to change the curve (Fig. 2.20) smoothly. Temperature rise in the material lead to the decomposition of the material which leads to increase in the coefficient of friction [114, 127].

Due to high rigidity, abrasion resistance, corrosion resistance, high thermal conductivity of SiC, it has a great influence on the tribological properties of C/C – SiC composites. Due to abrasive nature of SiC particles, it enhances the coefficient of friction. However when the content of SiC is very high, it acts as lubricant and may reduce the coefficient of friction [128, 129]. High porosity may stunt the formation of SiC framework and spur the formation of abrasive film which result in the deterioration of tribological properties [127, 128] (Results can be analysed from Fig. 2.21 and Fig. 2.22 through comparison). Fig. 2.21 shows the percent porosity as the weight percentage of silicon carbide varies.

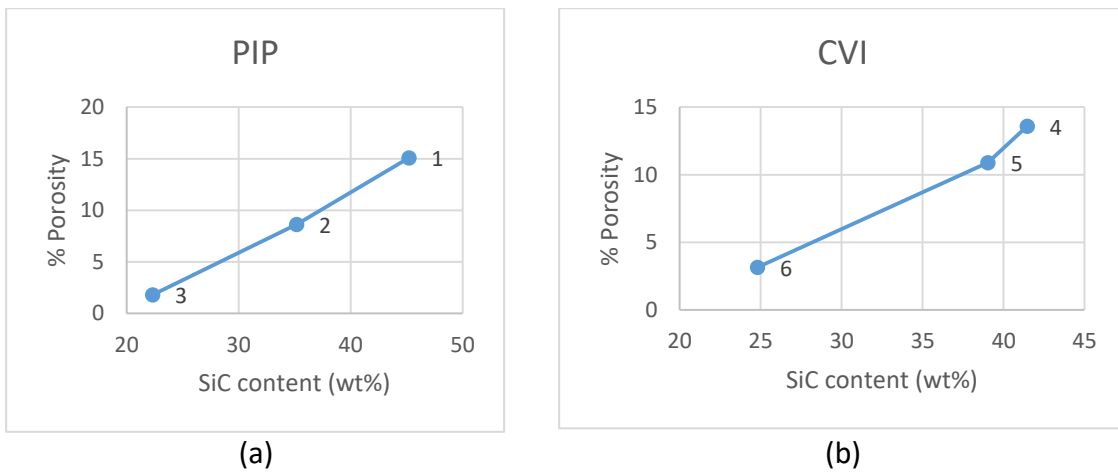


Fig. 2.21. Variation of percent porosity with weight percentage of SiC content (a) PIP; (b) CVI (Reproduced from data given in ref. [127])

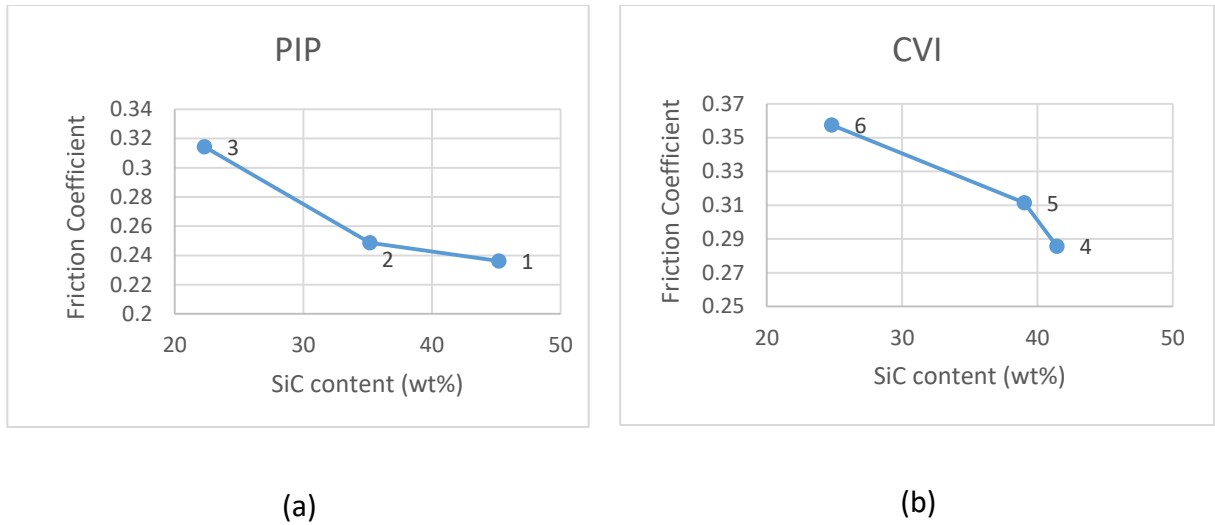


Fig. 2.22. Variation of friction coefficient with weight percentage of SiC content for different samples (a) PIP; (b) CVI (Reproduced from data given in [127])

Fig 2.22 shows the variation of coefficient of friction with the variation of weight percent of silicon. Coefficient of friction decreases with increase in SiC content for both fabrication techniques. However coefficient of friction is more in case CVI fabrication technique than PIP fabrication technique.

C/C – SiC composites have high porosity due to which it possess high wear rate. This is attributed to the fact that due to higher porosity, SiC particles framework doesn't easily form and the hard SiC particles plough and microcut the friction surface results in grain abrasion [113].

2.2.4.5. Effect of braking pressure and braking speed on tribological properties

In brake disk, kinetic energy is converted into heat energy at the time of braking. Braking energy increases as the speed of braking increases.

Fig 2.23 shows the effect of braking pressure and braking speed on the average friction coefficient of C/SiC brake materials. The carbon fibre, pyrolytic carbon, and SiC are brittle in nature. At low braking speed, the impact and shear forces between the asperities are small and the asperities cannot be completely sheared [13]. However when braking speed increases, braking energy increases and so many asperities creates brittle fracture. So due to brittle fracture, there is formation of many new asperities and little debris which results in increase in co-efficient of friction. When the braking speed is high enough to cut the asperities, many asperities shear and pulverizes by impact and shear action between asperities and a lot of debris forms. The debris formed fills the gap between peaks and valleys which decreases the ploughing effect. Due to increase in braking speed, more and more debris forms which forms a continuous film on the surface results in decrease of coefficient of friction and friction resistance. Fig 2.24 shows the schematic illustration of the debris filled and the friction film on the surface [130].

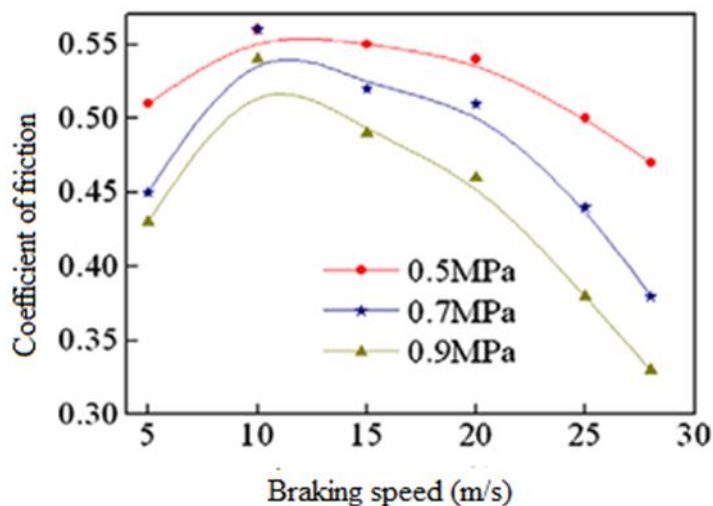


Fig. 2.23. The effect of braking pressure and braking speed on the average friction coefficient of C/SiC brake materials [13].

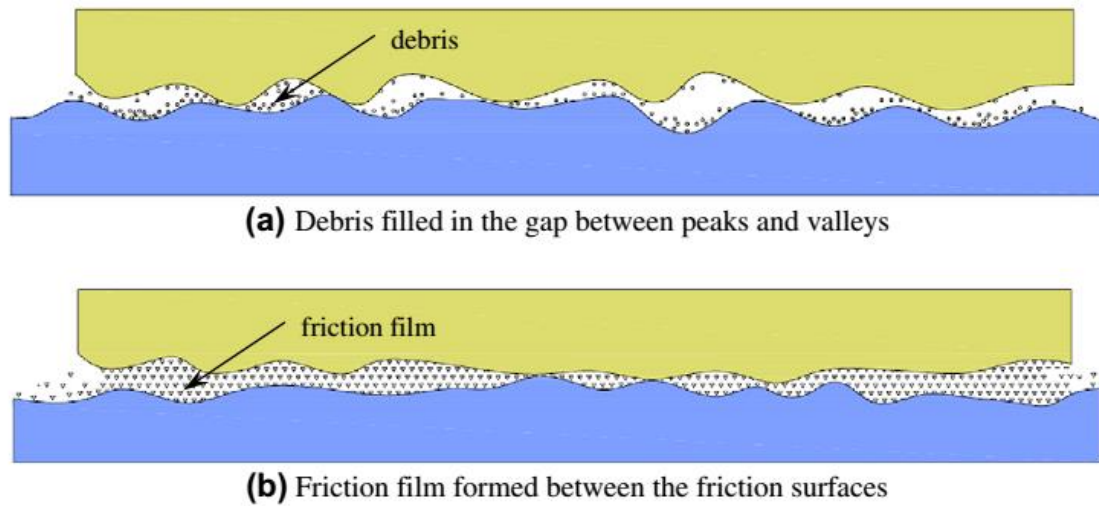


Fig. 2.24. Schematic illustration of the debris filled and the friction film formed [130].

When braking speed increases, wear rate increases due to increase in impact and shear force between asperities and ploughing action between asperities. Temperature also increases with increase in braking speed which leads to the oxidation of carbon matrix and carbon fibres near to the surface. Thus wear rate increases with increase in pressure.

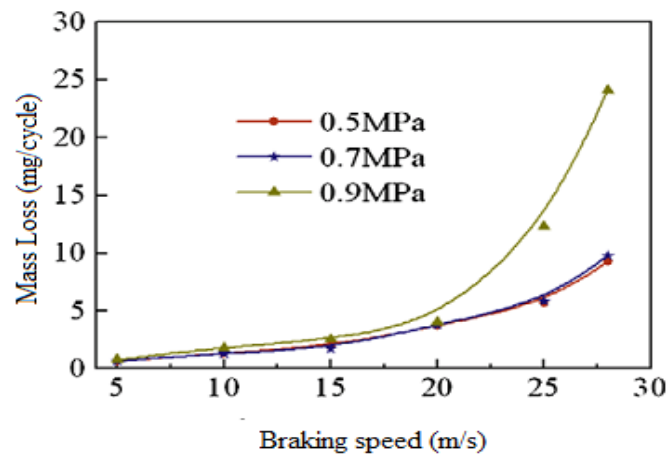


Fig. 2.25. The effect of braking pressure and braking speed on the wear rate of C/SiC brake materials [13].

Fig. 2.25 shows the effect of braking pressure and braking speed on the wear rate of C/SiC brake materials. It can be seen that at high braking speed, wear rate increases rapidly. At low braking speed, the effect of increase in pressure on wear rate is not significant. At high braking speed, increase in pressure leads to increase in wear rate.

2.2.4.6. Tribological performance under dry and wet conditions

The tribological behaviour of C/C – SiC composites under dry and wet conditions is different. Most of the studies on tribological behaviour of C/C – SiC composites is focused on dry conditions [15, 126, 128]. The studies on wet conditions are less. But tribological behaviour under wet conditions is key indicator under braking conditions [92, 126, 131]. The characteristics of C/C – SiC braking composites changes with environmental conditions. The coefficient of friction doesn't change much with the condition (either dry or wet), but change in wear rate with the conditions is significant. The variation of coefficient of friction under dry and wet conditions is shown in Fig. 2.26.

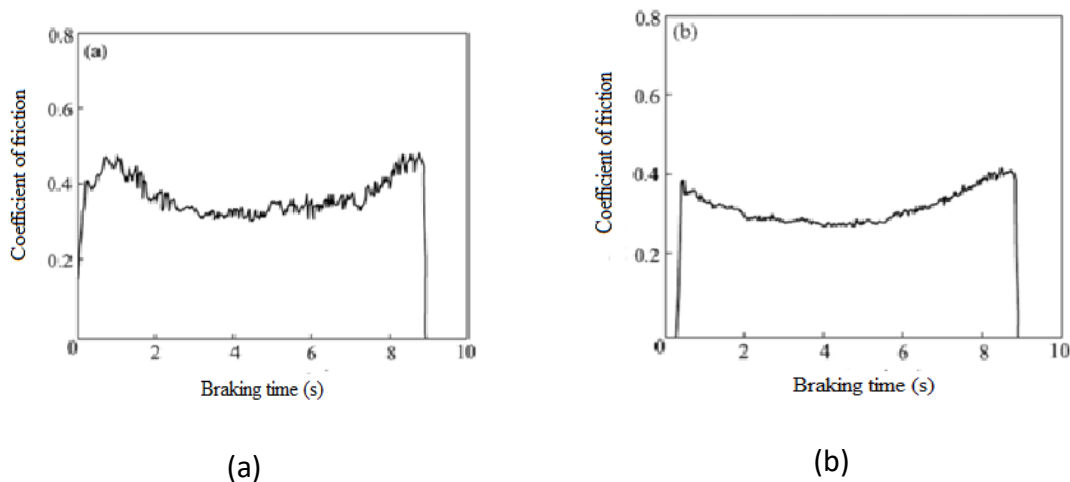


Fig. 2.26. First braking curves of C/C-SiC on different condition: (a) Dry condition; (b) Wet condition [131].

Plastic deformation and abrasion caused by ploughing are the main mechanisms of wear of C/C – SiC composites under dry conditions. This results in high coefficient of friction and wear rate in dry conditions as compared to wet conditions. There is stick sliding and plastic deformation under wet conditions. That's why coefficient of friction and wear loss are less in wet condition as compared to dry condition.

C/C – SiC composites sliding under dry condition contains hard phase SiC, resin carbon and second hard phase Si (silicon) particles. Hard phase Si particles cannot be cut by the shearing and compressive force and can easily be broken due to its lower plasticity. The coefficient of friction increases due to these hard particles at the early stage.

Under wet conditions, there is presence of moisture. Due to frictional heat, the moisture at the surface evaporates and reacts with SiC matrix and forms $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ or H_2SiO_3 [132, 133]. This results in formation of friction films. These friction films combine with the subsurface of C/C – SiC composites which leads to low shearing strength and high brittleness of the composites. They tend to break partially due to the existence of shearing and compressive forces [134]. The worn debris unite and try to fill the pits in the worn surface. The reunited debris spreads continually unless formation of friction film takes place again. This results in decrease in coefficient of friction film and wear rate. The main wear mechanisms under wet conditions are oxidation and adhesion.

2.2.4.7. Effect of graphitization of C/C preform on tribological properties of C/C – SiC composites

The processing of porous C/C preform is very important step because the processing parameters effect the microstructure and properties of preform. Tribological properties depends upon the microstructure and properties of preform [92, 135].

The effect of graphitization on microstructure and mechanical properties of C/C –SiC composites is investigated by many researchers but effect of graphitization on tribological properties of C/C – SiC composites has not been investigated much [136-139].

Fig. 2.27 shows the curves of coefficient of friction of samples (a: without graphitization, b: with graphitization) as a function of braking time.

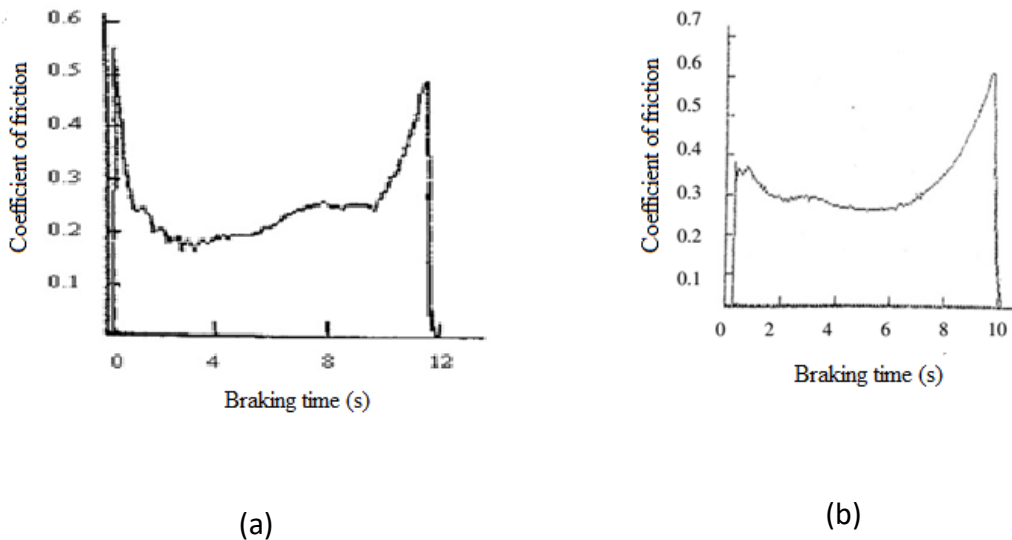


Fig. 2.27. The curve of friction coefficient of samples as a function of braking time (a, without graphitization; b, with graphitization) [114].

It is clear from Fig. 2.27 that at the start of braking, coefficient of friction is high for composites without graphitization than composites with graphitization. This leads to locking of braking system. Thus it is harmful for braking. This locking phenomenon can be greatly modified by graphitization of C/C preform. The phenomenon behind this nature of curve is explained earlier in this chapter.

Hardness of the material plays an important role in tribology [140, 141]. Graphitization increases the content of hard SiC in C/C – SiC composites. Due to graphitization some graphite crystallite forms [135] which results in softening of turbostratic structure carbon. During braking, hard SiC inserts into soft turbostratic structure carbon easily and deeply [136]. This results in increase in coefficient of friction. However graphite have a good solid lubricant property because it has weakly bonded layer structure [136, 139]. This lubricating property helps to avoid the initial high peak in coefficient of friction and moderate the fluctuation in coefficient of friction at the latter stage. In spite of this lubricating effect, the coefficient of friction of graphitized C/C – SiC composites is higher at latter stage. This cannot be explained by only lubricating property. At latter stage the effect of material hardness is more than lubricating action. Fig. 2.28 shows the coefficient of friction as a function of number of braking tests.

The wear rate of graphitized C/C – SiC composites is higher than non- graphitized C/C – SiC composites. This is due to shearing of large amount of soft graphite particles by ploughing effect under high braking load. Though wear rate of graphitized C/C – SiC composites is higher but is under acceptable limits.

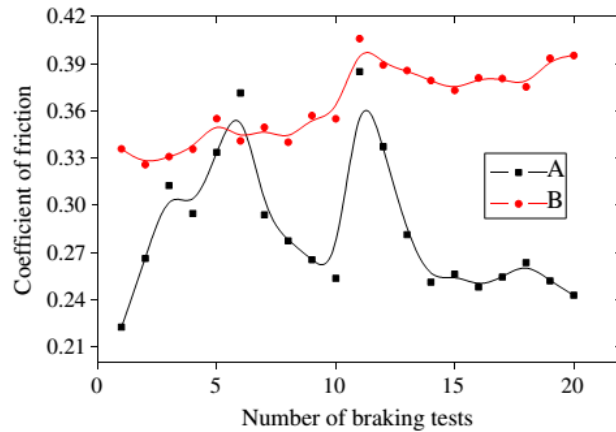
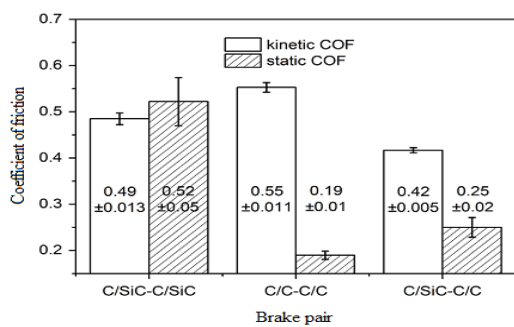


Fig. 2.28. Friction coefficient as a function of number of braking tests (A, without graphitization; B, with graphitization) [114]

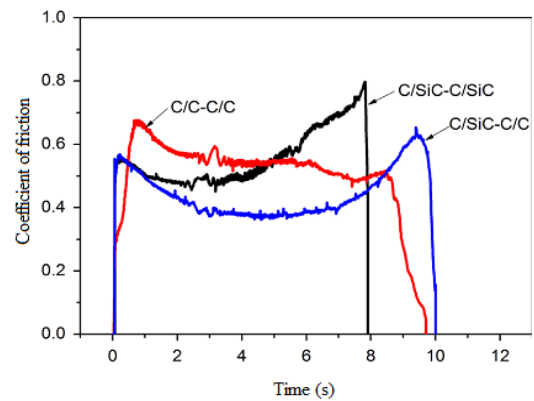
2.2.4.8. Effect of C/C composite and C/C – SiC composite as counterface material

C/C composites possess high strength, high thermal conductivity, high heat capacity, low thermal expansion coefficient, good wear property, low density and self-lubricating capability [20, 95]. However C/C composite brakes have poor oxidation resistance and unstable coefficient of friction [11, 142-144]. The static coefficient of friction of C/C composite is very low. To overcome these problems, C/C – SiC composites were developed. C/C – SiC composites have stable frictional properties, low wear rate and long life [92]. C/C – SiC composites have good resistance to oxidation, high static coefficient of friction and sensitivity to environment is low. This makes C/C – SiC composites a potential material for aircraft braking system [145, 146]. However the density of C/C – SiC composites is higher than C/C composites which makes C/C – SiC composites heavier than C/C composites and limits their applications in some weight sensitive aircrafts.

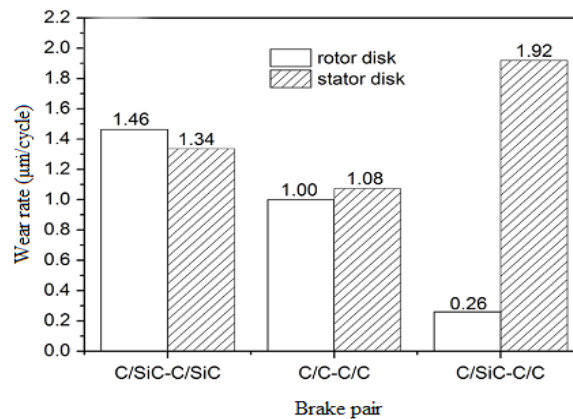
Some matrix modification can be done to overcome the disadvantages of C/C and C/C – SiC composites [147-150] but this requires a lot of time and plenty of experiments. Thus to meet the requirements of high performance and light weight for weight sensitive aircrafts, C/C – SiC and C/C brake pair can be used instead of using same material on both disks [151][74]. Fig. 2.29 shows the friction and wear properties of different brake pair system in dry condition.



(a)



(b)



(c)

Fig. 2.29. Friction and wear properties in dry conditions: (a) Kinetic and static friction coefficient, (b) Typical brake curves, (c) Linear wear rates [151].

Fig. 2.29 indicates the comparative behaviour of C/C and C/C – SiC brake pair, C/C disk as the stator disk and C/C – SiC disk as the rotor disk.

The dynamic coefficient of friction of C/C – SiC and C/C brake pair is little lower than C/C self mated pair but static coefficient of friction is higher. Thus taxiing distance of aircrafts before take-off can be reduced [152]. At the end of the braking, the coefficient of friction of C/C and C/C – SiC brake pair is higher than C/C self mated pair, due to which braking distance reduces. As most of wear occurs in C/C brake disk than C/C – SiC brake disk, thus C/C disk is made thicker and C/C – SiC disk is made thinner which also reduces the weight of aircraft brake assembly. Due to high heat capacity of C/C composites [95], the C/C and C/C – SiC brake pair doesn't suffer much from high surface temperature.

The nature of braking curve of C/C – SiC self mated braking pair can be explained by shearing, deformation, breaking of asperities, ploughing effect etc. as explained earlier in this article. However in case of C/C self mated and C/C – SiC brake pairs, C/C composites easily form flaky debris and flaky debris easily form friction film. Due to the formation of friction film, coefficient of friction reduces and gets stabilized. In case of C/C and C/C – SiC brake pair, ploughing effect increases the coefficient of friction and wear rate of C/C disk.

This chapter was written to provide the detailed literature review regarding C/C and C/C-SiC composites. Subsequent chapters will present the tribological behaviour of C/C and C/C-SiC composites under dry, brake oil, and freezing environments with variation of laminate orientation and surface conformity for unidirectional and reciprocating sliding conditions.