JOURNAL OF MATERIALS SCIENCE 32 (1997) 681–686

Influence of environment and temperature on "dusting" wear transitions of carbon–carbon composites

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This paper describes an investigation on the combined influence of environment and temperature on the tribological behaviour of a carbon–carbon (C/C) composite material with a particular reference to the interaction between water vapour and oxygen in air and the carbon surface. Experiments were conducted in nitrogen and air with a low-speed three-pins-on-disc apparatus and a high-energy ring-on-ring apparatus. Like conventional graphitic carbon materials, C/C composites exhibited a high friction and wear phenomenon, also known as "dusting", in dry nitrogen from room temperature up to 700 °C owing to the lack of lubricant gases and vapours in the environment. In ambient air, however, C/C composites exhibited three temperature-dependent tribological regimes. Abrupt increases in the friction at 150–200 °C and 650–700 °C marked the transitions between different regimes. The transition phenomena were explained in terms of the desorption of physisorbed water vapour and chemisorbed oxygen from the rubbing surface.

1. Introduction

Because of their exceptional refractory properties and low density, carbon fibre-reinforced carbon matrix composite materials, also known as carbon–carbon composites, are now widely used as friction materials for aircraft brakes. Carbon–carbon (C/C) composite materials generally consist of polyacrylonitride-based or pitch-based carbon fibres embedded in a carbonaceous matrix made by chemical vapour infiltration (CVI) and/or impregnation of organic binders. Since the fibre constituent typically has a much higher crystalline perfection compared to the matrix constituent, these materials can essentially be considered as a heterogeneous mixture of graphite and non-graphitic carbon [1]. As a result, C/C composites have tribological properties that are parallel to that of conventional graphite and carbon materials [2].

Although there are relatively few published studies concerning the fundamental friction and wear mechanisms of carbon–carbon composites, the tribology of conventional graphite and carbon materials has been studied for over sixty years. Based on X-ray diffraction results, Bragg [3] in 1928 concluded that the slipperiness of graphite is due to the weak bonding strength between adjacent basal planes, which allows one layer to slip freely over another. The low shear strength view implies that the lubricity of graphite is an intrinsic behaviour associated with the crystal structure. However, researchers [4–6] later discovered graphitic carbon materials to exhibit a high friction and wear phenomenon in vacuum and inert environments, also known as "dusting" owing to the rapid disintegration of graphite into a cloud of dust. In the dusting wear regime, the friction of graphitic carbon materials is high ($\mu = 0.3$–1.0) and erratic, and the wear rate is typically 10^2 to 10^4 times higher than that encountered in the "normal" wear regime in ambient air [4–7]. Savage and other researchers [5, 8, 9] have shown that the presence of water or organic vapours in the environment is necessary to prevent dusting and maintain the low friction behaviour. Oxygen can also inhibit the dusting of graphite but is considered to be less effective than water and other hydrocarbon vapours [5, 10]. Other diatomic gases such as nitrogen and hydrogen, however, cannot inhibit dusting even at atmospheric pressure [4–7, 10, 11].

It is widely believed that the interaction between the unsaturated covalent bonds of carbon atoms created by wear is responsible for the high friction behaviour during dusting [12]. While this view implies that the chemisorption of water and organic vapours is required to inhibit the dusting wear of graphite and carbon materials, experimental evidence [5, 8, 13] suggests that the adsorption of these vapours is predominantly physical in nature. Lancaster and Pritchard [9] have reconciled the two views by proposing a "reservoir" model, in which water and lubricant molecules are first physisorbed onto the basal planes

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of graphite and subsequently migrate to the high-energy edge sites to neutralize dangling covalent bonds created by wear. Dusting occurs when the "reservoir" of physisorbed lubricant molecules on the surface are depleted. More recently, other researchers [14] have modified this model by suggesting that some water molecules dissociate and interact with carbon atoms to form hydrogen and hydroxyl complexes, to which other mobile physisorbed water molecules subsequently attach themselves. In spite of the differences, both theories attribute the effectiveness of gases and vapours in inhibiting the dusting wear of carbon materials to the high mobility of physisorbed lubricant molecules that are weakly attached to the available polar sites on the surface. The fact that the lubrication process involves the physical adsorption of lubricant molecules implies that temperature may influence the tribological properties of graphite and carbon materials. Indeed, Ramadanoff and Glass [6] have found water vapour ceasing to lubricate graphite at approximately 170 °C. Lancaster [15] has observed a normal-to-dusting wear transition in ambient air for graphite at 150–185 °C and has attributed it to the desorption of water vapour from the graphite surface. Similarly, a recent study [1] has shown C/C composites to undergo the same transition in ambient air at 150–200 °C.

The aforementioned studies are mostly concerned with the influence of environment on the friction and wear transitions of conventional graphite and carbon materials at relatively low temperatures. Since C/C composite friction materials are required to absorb a tremendous amount of energy in the form of heat during braking, the temperature on the rubbing surface can reach as high as 1000 °C under severe braking conditions [16]. It is conceivable that the interaction between water vapour and oxygen in air and carbon atoms on the rubbing surface can change at elevated temperatures, which in turn, will influence the tribological behaviour of C/C composite materials.

The objective of this investigation was to study the combined effect of environment and temperature on the friction and wear transitions of a C/C composite material with a particular reference to the interaction between water vapour and oxygen in air and the carbon surface. Tribological experiments were conducted in nitrogen and air using a wide range of load and speed conditions that allowed the specimen temperature to reach as high as 1000 °C in ambient air. Two types of apparatus with different load and speed capacities were employed in the present work: a low-energy three-pins-on-disc type of apparatus for studying the frictional behaviour at room temperature as the gas environment was rapidly alternated, and a high-energy ring-on-ring type of apparatus for investigating the frictional behaviour as the specimen temperature gradually increased with sliding distance owing to frictional heating. From these experimental results and the thermogravimetric analysis, the dusting wear mechanisms of C/C composites at elevated temperatures were discussed in terms of adsorption and desorption of oxygen on the rubbing surface.

2. Experimental details

The carbon–carbon composite material used in this work was made by an organic binder impregnation process. Chopped pitch carbon fibres in the form of thin felt were first impregnated with phenolic resin and consolidated under high pressure. The fibre/resin compact was then baked at around 1000 °C to convert the resin into a carbonaceous material. After the carbonization process, the compact was further densified with liquid pitch and then graphitized at a higher temperature. The final C/C composite material contained 40% fibre, 47% matrix, and 13% porosity. Fig. 1 shows the microstructure of the C/C composite sample with fibres randomly oriented in the plane of sliding contact.

Two types of experiments were conducted for this investigation. A low-speed three-pins-on-disc type of apparatus [7] was used to study the influence of water vapour and oxygen on the friction and wear transitions of C/C composites at room temperature. In this experiment, three C/C composite pins were mounted onto a circular holder such that they were equidistant from the centre with an angular spacing of 120° between each one. The counterface was machined from cast iron (JIS-FC250). The total apparent contact area between the three pins and the counterface was 75 mm^2. The pins–counterface assembly was enclosed by a 300 cm^3 steel chamber. The moisture content inside the chamber could be varied from 100 p.p.m. to 100% relative humidity (RH) by flowing a mixture of dry gas and saturated gas at 21 °C. A gas flow rate of $1 l s^{-1}$ was used to minimize the purging time required in changing the gas environment in the chamber. Experiments were conducted in dry nitrogen (100 p.p.m. H_2O), wet nitrogen (50% RH), dry air (100 p.p.m. H_2O), and wet air (50% RH) under a load of 95 N. The relative speed between the pins and the counterface was maintained constant at $5 cm s^{-1}$ to minimize frictional heating.

A high-energy ring-on-ring type of experiment was used to study the effect of surface temperature on the friction and wear transitions of C/C composites in dry nitrogen and ambient air. The flat surface of a C/C composite ring specimen with outer and inner diameters of 54 and 34 mm, respectively, was rubbed

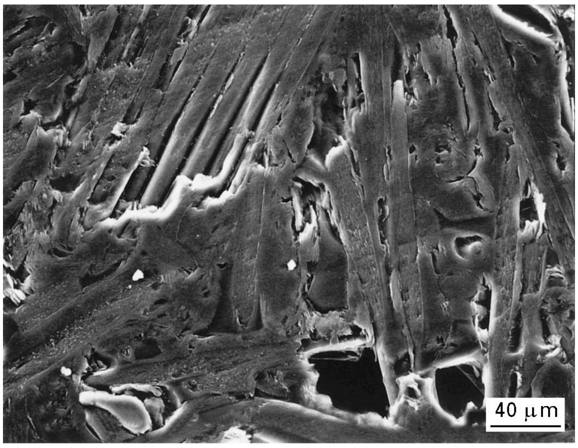

Figure 1 Scanning electron micrograph showing the structure of a carbon–carbon composite sample.

against the flat surface of another C/C ring specimen. Details concerning the test apparatus has been published elsewhere [1]. In short, it consisted of a 30 kW motor to rotate one ring specimen and a hydraulic actuator to apply the test load via the stationary specimen. The ring–ring assembly was enclosed by a 4 l environmental chamber. The rotation speed and the applied load were maintained constant throughout an experiment. Because of the relatively heavy load (400–2000 N) and high speed (2–10 m s^{-1}) conditions used, the temperature on the rubbing surface increased with distance as a result of frictional heating. The temperature of the stationary ring specimen was monitored by a thermocouple (0.5 mm diameter) situated at a depth of 1 mm below the rubbing surface. Experiments were conducted in dry nitrogen and ambient air (45–55% RH).

3. Results

3.1. Effect of environment on friction and wear transitions at room temperature

Fig. 2 shows the change in the friction of C/C composite pins rubbing against the counterface as the dry nitrogen and wet nitrogen environments are alternated using the low-speed apparatus. The C/C pins undergo dusting in dry nitrogen as indicated by the high and erratic friction behaviour. Nitrogen gas does not have a lubricative effect on C/C composites and 100 p.p.m. of water vapour in the chamber is insufficient to prevent the dusting of the C/C pins under the present load and speed conditions. Upon the introduction of wet nitrogen, the friction abruptly decreases and becomes steady, which clearly illustrates the lubricative effect of water vapour. The lubricative effect of water is reversible, that is, on decreasing the water content by the subsequent passage of dry nitrogen, the friction immediately increases to the dry state as before. The wear rate for the dusting wear regime in dry nitrogen is approximately 10^3 times that for the normal wear regime in wet nitrogen.

Fig. 3 shows the change in friction as the dry nitrogen and dry air environments are alternated. The friction decreases when dry air is admitted, which suggests that oxygen in dry air could also act like a lubricant to inhibit the dusting of C/C composites. While this work shows that 2.1×10^4 Pa of oxygen in air is enough to prevent the dusting of the C/C pins, other investigators [5, 10] have shown that higher partial pressures ($> 3.3 \times 10^4$ Pa) are required to inhibit the dusting of graphitic materials. This discrepancy can be attributed to the differences in the experimental conditions. In line with the view that the physical adsorption of gases and vapours is required in inhibiting the dusting of carbon materials, it has been shown that the amount of water vapour or oxygen required to inhibit the dusting wear of graphite increases with increasing temperature up to 170 °C [6]. The current sliding speed of 5 cm s^{-1} is approximately two orders of magnitude lower than that used in other studies [5, 10]. As a result, the frictional heating is minimized and the temperature of the pins remains low (less than 50 °C) during sliding, which accounts for the lower partial pressure of oxygen required. Alternatively, it is also possible that the minute amount of water vapour in the chamber (100 p.p.m) can interact with oxygen to inhibit the dusting of the C/C pins [11]. Oxygen is known to form various types of oxygenated complexes on the carbon surface [17], which could become polar sites for the subsequent adsorption of individual water molecules [13]. The water molecules attached to polar surface sites can then act like secondary adsorption sites for the further adsorption of water molecules via hydrogen bonds to form two-dimensional clusters on the carbon surface [13]. Fig. 4 shows the results from a previous study [7] involving graphite under the same experimental conditions. The striking similarities between the frictional behaviours of the two materials should come as no surprise because C/C composites, despite having a highly heterogeneous mechanical structure, are essentially composed of graphite and carbon materials.

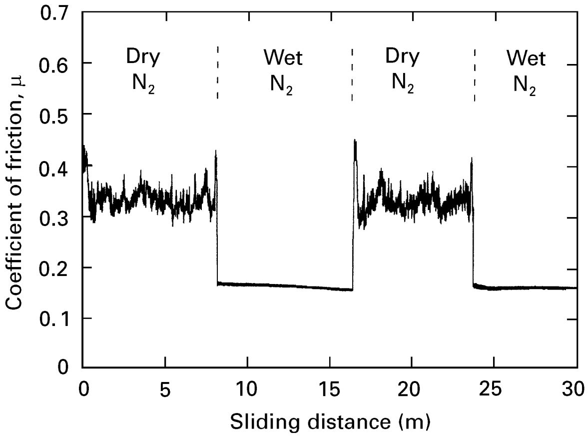

Figure 2 Friction of a carbon–carbon composite specimen as dry and wet nitrogen environments are alternated at low speed condition.

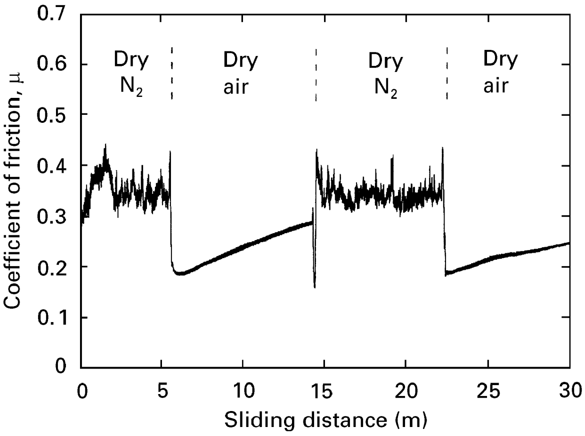

Figure 3 Friction of a carbon–carbon composite specimen as dry nitrogen and dry air environments are alternated at low speed condition.

3.2. Effect of temperature on friction and wear transitions

The typical friction and temperature profiles from the high-energy ring-on-ring testing in dry nitrogen and

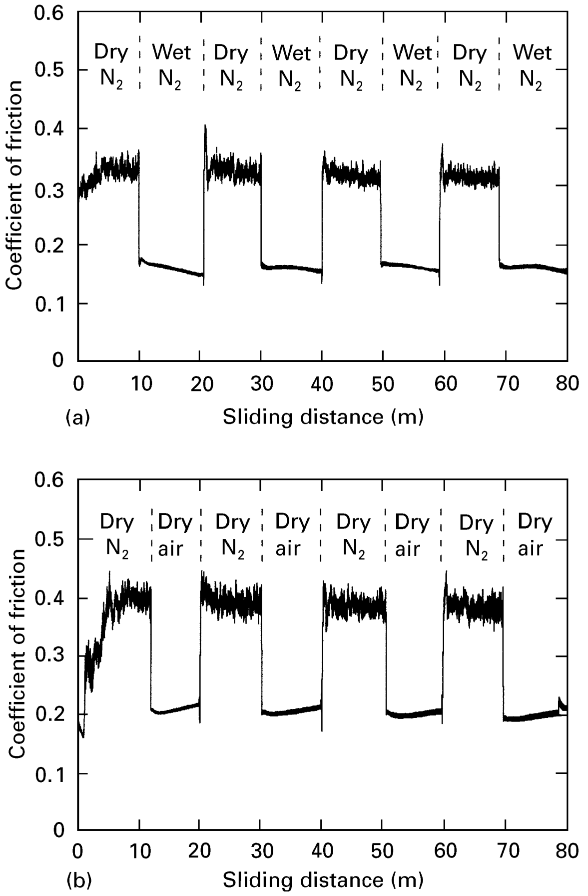

Figure 4 Effect of (a) water vapour and (b) oxygen on the friction of a graphitic carbon [7].

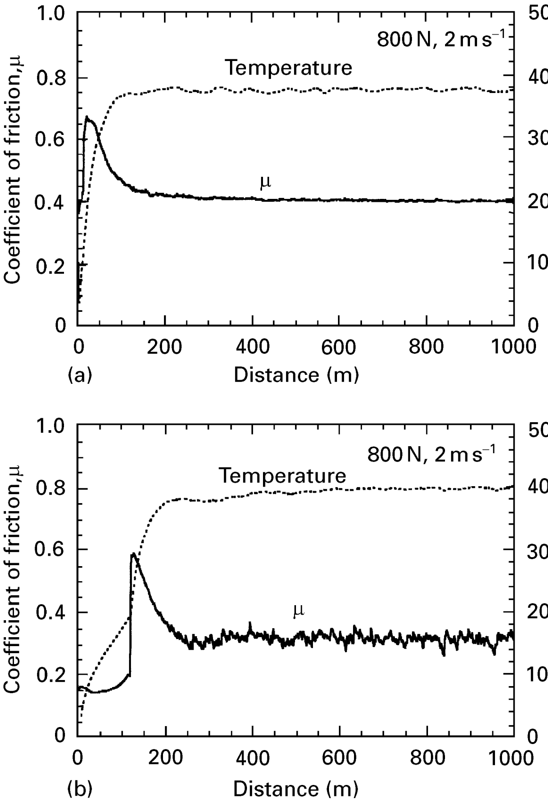

Figure 5 Variation of friction and temperature with sliding distance for a carbon–carbon composite specimen in (a) dry nitrogen and (b) ambient air at 800 N and 2 m s^{-1} conditions.

ambient air are shown in Fig. 5. The temperature of the specimen increases with sliding distance as a result of frictional heating. In dry nitrogen the friction increases rapidly and reaches a transient peak as soon as the two ring specimens are brought into contact. The transient peak in friction can be attributed to the rapid generation of loose debris by wear and the subsequent compaction of this debris into a film covering the rubbing surface [1]. The high-friction behaviour indicates that the C/C specimen also undergoes dusting wear in dry nitrogen at elevated temperatures.

In contrast to the frictional behaviour in nitrogen (Fig. 5a), the friction profile obtained in ambient air clearly shows a low-friction normal wear regime and a high-friction dusting regime divided by the transient peak. The transition from the normal wear regime to the dusting wear regime occurs at 150–200 °C, which is comparable to the transition temperature of 150–185 °C in ambient air for graphite [15]. Moreover, Lancaster [15] has attributed this normal-to-dusting transition to the desorption of physisorbed water molecules from the rubbing surface. A closer examination of Fig. 5 reveals that the coefficient of friction for the water-desorption dusting regime in ambient air is lower than that for the dusting regime in nitrogen under the same experimental conditions. This suggests that the interaction between oxygen and carbon atoms on the rubbing surface at elevated temperatures may account for the lower dusting friction in air. As explained earlier, it is generally believed that the interaction between the dangling covalent bonds of the carbon atoms is responsible for the dusting behaviour [12]. Hence, it is plausible that the chemisorption of oxygen on the rubbing surface at elevated temperatures in the form of an oxygenated complex can partially shield the interaction between the dangling covalent bonds of carbon atoms, which leads to a lower friction for the water-desorption dusting regime in air.

While the general friction profile corresponding to experiments conducted in nitrogen (Fig. 5a) remains the same as the rate of frictional heating increases at higher energy conditions, Fig. 6 shows the presence of a second transition in ambient air at approximately 650 °C. The transition from the water-desorption dusting regime to another dusting regime with higher friction generally occurs at 650–700 °C, which suggests that the transition may involve the oxidation mechanism. The thermogravimetric analysis of the C/C sample shown in Fig. 7 indicates that the critical temperature at which the onset of rapid oxidation loss takes place coincides with the transition temperature. At the critical oxidation temperature, carbon atoms on the surface are rapidly etched away by oxygen in the forms of CO_2 and CO gases. Hence, in line with the above reasoning that the chemisorption of oxygen lowers the friction, it is conceivable that the rapid desorption of chemisorbed oxygen on the rubbing surface in the forms of CO_2 and CO gases at the critical/transition temperature exposes the dangling covalent bonds of carbon atoms and leads to a higher friction.

It is interesting to note that while the transitions depend on the specimen temperature, the coefficient of

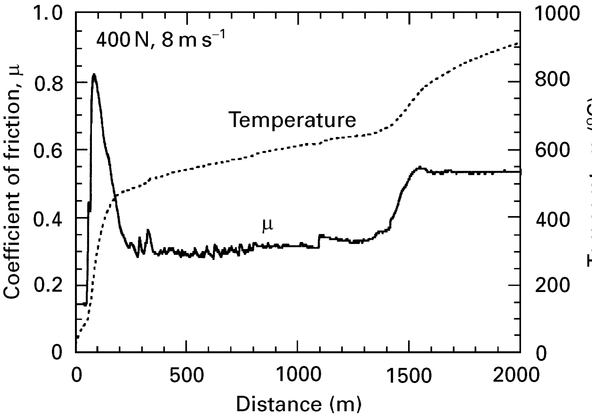

Figure 6 Variation of friction and temperature with sliding distance for a carbon–carbon composite specimen in ambient air at 400 N and 8 m s^{-1} conditions.

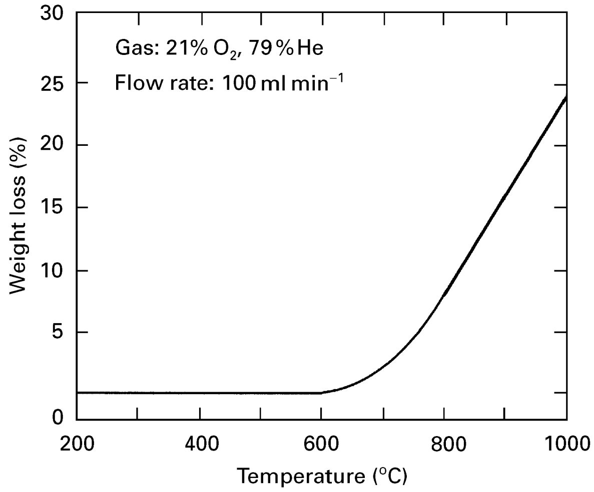

Figure 7 Thermogravimetric analysis of a carbon–carbon composite sample in a gas mixture consisting of 21% O_2 and 79% He.

friction within a given regime does not markedly vary with temperature as illustrated in Fig. 6. The coefficients of friction for the three regimes in air remain relatively constant despite a gradual increase in temperature with sliding distance.

4. Discussion

The most important result emerging from the experiments is the discovery of two dusting wear regimes for carbon–carbon composites in air at temperatures up to 1000 °C and the relevant mechanisms involved. The experiments also show the tribological properties of C/C composites and conventional graphitic carbon can be similarly influenced by water vapour and oxygen. While Lancaster [15] had found the normal wear-to-dusting wear transition for graphite at 150–185 °C in ambient air owing to the desorption of water vapour, the dusting regime in air was not closely examined. In addition to confirming Lancaster's findings with a carbon–carbon composite material, this work has also investigated the mechanisms involved in the water-desorption dusting regime and the subsequent transition. The lower friction for the water-desorption dusting regime, as compared to that for the dusting in nitrogen, and the subsequent increase in friction at the critical oxidation temperature strongly suggest that the chemisorption of oxygen at elevated temperatures has a limited lubricative effect on C/C composites by lowering the friction. It is worth noting that this inference is not in conflict with the "reservoir" model [9] because the chemisorption of oxygen at elevated temperatures does not inhibit the dusting wear of C/C composites. The subsequent desorption of chemisorbed oxygen at 650–700 °C leads to the oxygen-desorption dusting regime, in which the rubbing surface is essentially freed of physisorbed or chemisorbed lubricant molecules. Hence, this regime is comparable to the dusting regime in dry nitrogen or other inert environments. It should be noted that the oxygen-desorption dusting wear of C/C composites discussed here is different from the oxidative wear of metals at elevated temperatures, which involves the formation of oxide particles on the rubbing surface.

For two C/C composite discs in sliding contact, it is obvious that an increase in the rate of energy input and/or sliding distance would cause a corresponding increase in the specimen temperature, which determines the relevant tribological regime in ambient air. This relationship can be visualized with a simple transition diagram shown in Fig. 8. The rate of energy input is represented by the product of contact pressure (*P*) and sliding speed (*V*). Two isothermal lines mark the boundary between different regimes. The transition diagram can be used to clarify the paradox in which the landing dynamic coefficient of friction of C/C aircraft brakes is found to be consistently higher than the static coefficient of friction, 0.20–0.35 compared to 0.15 [16]. The high initial speed associated with a normal landing stop causes the brake temperature to readily exceed the transition temperature of 150–200 °C. Hence, C/C aircraft brakes essentially

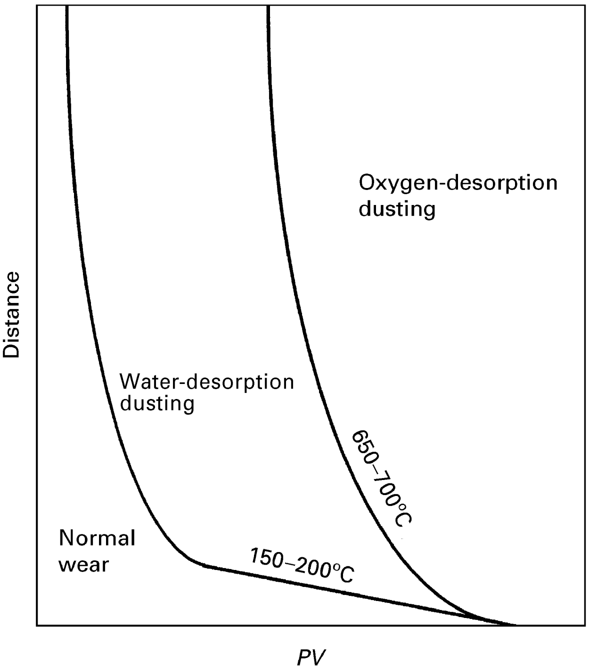

Figure 8 Transition diagram for carbon–carbon composites showing three different tribological regimes in ambient air up to 1000 °C.

operate in the high-friction water-desorption dusting regime and/or oxygen-desorption dusting regime during landing stops. Conversely, the low static friction can be attributed to the lack of frictional heating, which causes C/C brakes to operate in the low-friction normal wear regime. While conventional graphite and carbon materials rarely encounter such high energy/temperature conditions in most tribological applications, the general results discussed here should be equally applicable to these materials because the heterogeneous structure of C/C composites is unlikely to have a marked influence on the basic adsorption/desorption mechanisms, which govern the fundamental tribological behaviour of carbon materials.

5. Conclusions

A series of experiments conducted in nitrogen and air have demonstrated that the tribological properties of carbon–carbon composites, like conventional graphitic carbon materials, depend on the interaction between water vapour and oxygen in the environment and carbon atoms on the rubbing surface. Dusting wear occurs when there is a lack of lubricant gases and vapours in the environment. Alternatively, the depletion of lubricant molecules on the rubbing surface at elevated temperatures can also induce the dusting wear of C/C composites.

In dry nitrogen C/C composites undergo dusting wear because the adsorption of nitrogen does not have a lubricative effect on carbon materials. As a result, no temperature-dependent transition occurs in nitrogen up to 700 °C. In ambient air, however, the tribological behaviour of C/C composites is characterized by three temperature-dependent regimes: the normal wear regime, the water-desorption dusting regime, and the oxygen-desorption dusting regime. The transition from the normal wear regime to the water-desorption dusting regime at 150–200 °C can be attributed to the desorption of physisorbed water vapour from the carbon surface. The chemisorption of oxygen in the water-desorption dusting regime appears to have a limited lubricative effect by lowering the friction of C/C composites. The subsequent transition from the water-desorption dusting regime to the oxygen-desorption dusting regime at 650–700 °C can be attributed to the desorption of chemisorbed oxygen. The friction of C/C composites increases following each transition as the result of depletion of lubricant molecules on the rubbing surface. The lack of lubricant molecules on the rubbing surface exposes the dangling covalent bonds of carbon atoms and thus increases the friction of C/C composites. While the transition phenomena in air are temperature dependent, it appears that the friction within a given regime does not vary significantly with temperature.

Acknowledgements

The authors would like to thank Mr Y. Koya, Dr K. Onuma, and Mr S. Kasuya for their support and encouragement during the course of the work.

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Received 13 November 1995
and accepted 17 September 1996