JOURNAL OF MATERIALS SCIENCE 20 (1985) 1222–1236

Dry sliding wear of hard materials against a diamond composite

R. L. MEHAN, C. I. HEJNA, M. D. McCONNELL
General Electric Company, Corporate Research and Development, Schenectady, New York 12301, USA

Pin-on-disc wear tests using ceramic and metal pins running against diamond composite discs were conducted in air at room temperature. Pin wear rate and the coefficient of friction were measured. The pin wear rate did not consistently increase with decreasing hardness, and the lowest wear rate was obtained with a cemented tungsten carbide pin.

1. Introduction

Diamonds, either as individual stones or as sintered diamond compacts* [1], are used for industrial purposes primarily for material removal operations such as grinding, cutting, and sawing. In such applications it is the hardness and wear resistance of these diamond products which makes the use of such tooling feasible.

Although diamonds have excellent wear resistance, there are relatively few industrial applications where diamond products are used in sliding wear applications. Perhaps the largest use of diamonds as a wear part is in wire drawing dies [1, 2]. Diamonds are also used for phonograph styli [3], hardness indenters, and as tracer points and anvils on measuring and control devices for machinery [4]. The volume of diamond products used for such applications is slight compared to the amount used for material removal applications.

In spite of the current low use of diamond products as wear parts, there is recognition that there are applications for such products. Examples include paper and textile guides [5, 6], pump components, gauge blocks and extrusion dies [7]. The use and practicality of such wear parts has been enhanced by the development of composite coatings containing diamonds [6, 7], as well as diamond composites consisting of diamonds imbedded into a silicon + SiC matrix [8]. The diamond composite materials, consisting of diamond volume fractions of the order of 50 to 70%, allow considerable flexibility in fabricating various shapes; for example, small cylindrical Si–SiC/diamond composite rods 4.75 mm in diameter have been experimentally evaluated as textile yarn guides [9]. Similarly, 3.18 mm diameter rods consisting of diamonds imbedded into a nickel matrix have been evaluated for the same use [6].

Previous studies [8] conducted in this laboratory concerning the mechanism of the dry sliding wear of diamond composites against themselves led to the conclusion that wear proceeded in a fashion first described by Crompton *et al.* [10]. For the case of single crystal diamonds rubbing against other materials, they postulated that diamond wear was caused by small diamond fragments (of the order of 10 to 100 nm in dimension) dislodged from diamond surfaces by repeated impact and subsequent wear of the diamond was due to mechanical attrition. This explanation assumes, of course, that the conditions under which wear occurs are such that thermal effects such as diamond oxidation or graphitization do not occur.

Additional wear tests of both diamond compacts and composites against metals have been conducted in this laboratory utilizing a ring and block test technique [11]. That study, as well as similar studies [6], was largely phenomenological in nature, with little attempt being made to deduce fundamental wear mechanisms and determine whether these material combinations obeyed

---

*Diamond compacts consist of randomly oriented sintered diamonds with a diamond volume fraction ⩾ 90%. See [1].

0022–2461/85 $03.00 + .12

some of the rules of wear observed for metals and ceramics [12, 13]. That fundamental sliding wear mechanisms have not been studied for diamond compacts or composites is hardly surprising; compacts were not available prior to 1972 and composites at an even later data. Most of the studies related to diamond compacts have been devoted to machining studies, which accounts for its major usage. Lately, wear mechanisms have been studied for diamond compacts used in drill bits [14]. Neither of the wear mechanisms involved in machining or rock abrasion are directly applicable to sliding wear, although some common relations must be present.

The purpose of this paper is to extend the examination of dry sliding wear of diamond–diamond composites [8] to include a variety of hard metals and ceramics sliding against a diamond composite. The practical intent of such tests was to identify suitable material sliding combinations for possible bearing or other sliding systems. It was also desired to examine the nature of the wear process of both diamond and metal/ceramic materials by examination of the wear debris and analysis of the diamond surface to determine if chemical effects were significant in contributing to wear. As in the previous study of diamond composite wear [8], it is hoped these data will aid in any future assessment of diamond composite/metal or diamond composite/ceramic wear surfaces for use as sliding systems.

2. Experimental procedure

2.1. Wear testing

The wear tests were conducted with no lubrication on a commercially available† wear test machine operating in a pin-on-disc configuration. The pins were 1.27 cm long and 4.78 mm diameter, with a polished 4.78 mm hemispheric end. Where diamond composite-diamond composite wear data are discussed, the pin end geometry was conical rather than hemispherical [8]. The diamond composite discs in all cases consisted of a 1.0 mm thick diamond composite disc with an outside diameter of 19.8 mm and an inside diameter of 15.8 mm. The disc was epoxy bonded into a recessed metal block (to accept the disc) 38.1 mm o.d., 9.5 mm i.d., and 9.52 mm in height.

The Falex machine uses a pin rotating circumferentially on a stationary disc. In all cases the sliding speed was 125 cm sec^{-1} (1000 rev min^{-1}). The load was applied through a 2:1 loading arm and ranged from 454 g to 4.09 kg. Most of the tests were run at a load of 454 g. Coefficient of friction measurements were obtained from a load cell attached to the shaft holding the stationary disc. In conducting a wear test, a clean pin was run against the diamond composite for a certain time, the test stopped, and the disc and pin cleaned ultrasonically in acetone and the latter weighed to determine the volume change. In cases where the weight loss was quite small and of the order of the weighing error (~ 0.1 mg), the pin wear flat was photographed and the wear volume calculated. No attempt was made to measure the wear of the diamond composite disc other than examining individually worn diamonds.

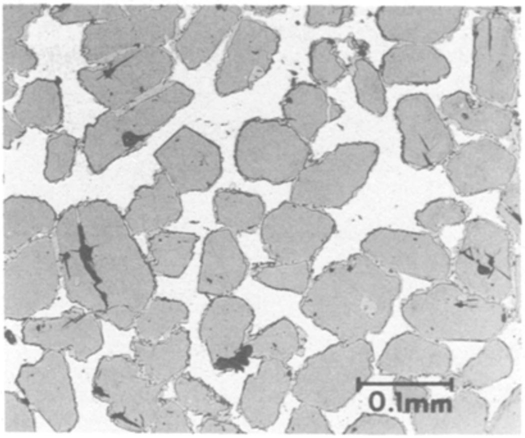

Figure 1 Photomicrograph of a diamond composite.

In some experiments involving the study of surface reactions and wear debris, the pin-on-disc configuration was not used and individual natural diamonds approximately 1.0 mm in dimension were wear tested. These tests will be described at the appropriate point in a following section.

2.2. Materials

The microstructure of the diamond composite is shown in Fig. 1, and the fabrication technique has been previously described [15]. The diamonds used were Man-Made‡, and were 150 to 190 μm in dimension. In preparing the diamond composite discs, after fabrication the wear surface was ground flat with a diamond wheel and then

---

†Falex No. 6 Wear Tester, Faville-LeValley Corporation, Aurora, Illinois, USA.

‡Registered trademark of the General Electric Company.

TABLE I Wear of various pin materials against diamond composite discs

Material	Hardness ($kg\,mm^{-2}$)	Equilibrium wear rate ($10^{-15}\,cm^3\,g^{-1}\,cm^{-1}$)	Friction coefficient
Diamond composite	8000	5.55[*]	0.1–0.2
Si_3N_4	3100	3.74	0.14
SiC	2670	152.0	0.20
Al_2O_3	2000	42.2	0.20
WC + 6% Co	1710	2.04[†]	0.005–0.15
Si	800	2 140.0[‡]	0.05
440C	690	48.0[§]	0.12
Ti–6Al–4V	300	12 000.00	0.6
1020 Steel	173	3 220.0	0.3
Brass	132	98 300.00	0.3
2024 Al	125	9 000.0	0.12

[*] From ref [8], standard deviation = $1.38 \times 10^{-15}\,cm^3\,g^{-1}\,cm^{-1}$.
[†] Standard deviation (21 tests) = $1.12 \times 10^{-15}\,cm^3\,g^{-1}\,cm^{-1}$.
[‡] Variable, ranging from 1.0×10^{-10} to 2.14×10^{-12}.
[§] For the case where only a small amount of Fe_2O_3 was present. See text.

polished with 30 μm diamond paste. This polishing step rounded off the diamond edges and also removed some of the Si + SiC matrix so the rounded diamonds protruded from the composite surface. In subsequent rubbing, therefore, the rotating pin came into contact with only the diamonds.

It may be noted that the wear behaviour of a metal or ceramic pin against the diamond composite surface is critically dependent on the composite surface preparation. In the as-ground condition, for example, the composite acts as a cutter rather than a wear surface. This occurs because the softer matrix is rapidly worn away exposing the sharp diamond edges, which then cut the rotating pin. Similar behaviour can occur if the polishing step is performed incorrectly, leaving sharp diamond edges, or diamonds at irregular heights. As will be discussed later, the optimum diamond composite wear surface is a polished surface which has been rubbed with a hard pin to remove surface irregularities.

The pin materials examined included diamond composite pins (previously reported by Mehan [8]), hot pressed Si_3N_4 and SiC, 99% dense Al_2O_3, WC + 6% Co (cemented tungsten carbide, Carboloy 883[§]), Si, 440C steel (a martensitic stainless steel), and four softer materials. Other materials tested but not discussed because their behaviour was similar to those above included a tool steel and sintered SiC.

3. Experimental results

3.1. Wear testing

A summary of wear tests conducted is shown in Table I with the materials ranked in order of decreasing hardness. It may be noted that at some hardness level, the diamond composite acts as a cutter rather than a wear surface. Wear debris for these softer materials was generally in the form of discrete chips. Polishing and cutting are related ways of material removal, and at a critical value of various material properties (in which hardness contributes but is not necessarily the sole property), wear is replaced by cutting. That hardness is not the sole material property affecting this cross-over point is clear from the data in Table I. Wear resistance and hardness do not correlate well.

The wear rate of a 440C pin both against itself and a diamond composite are shown in Fig. 2. The metal/metal wear rate of $9.8 \times 10^{-13}\,cm^3\,g^{-1}\,cm^{-1}$ is similar to the value of $8 \times 10^{-13}\,cm^3\,g^{-1}\,cm^{-1}$ reported by Archard and Hirst for metal/metal wear for steels with a similar hardness, $690\,kg\,mm^{-2}$ [12]. It may be seen the wear rate decreases a factor of 20 when run against the diamond composite. The nature of the two tests was quite different; in the metal/metal case the test was rough and noisy and chattering occurred. In contrast, the metal/diamond composite test ran smoothly with no chatter, and this difference is reflected in the two friction coefficients (0.76

[§] Registered trademark of the General Electric Company.

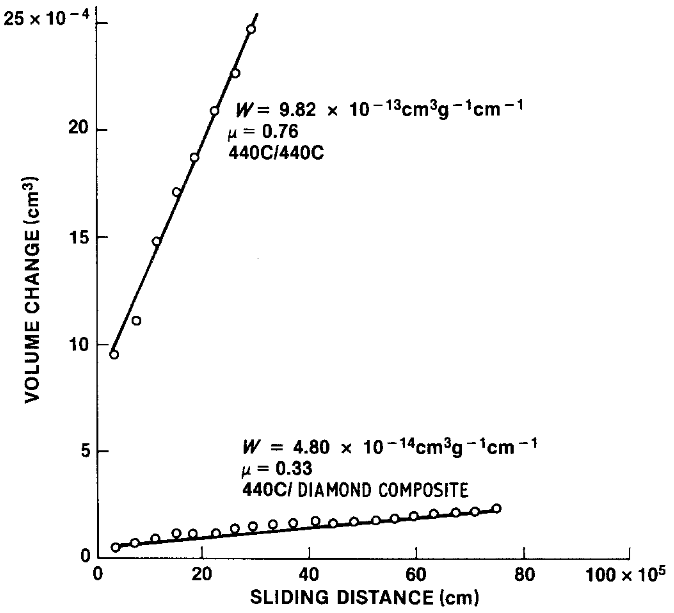

Figure 2 Wear rate and friction coefficient of a 440C steel pin rubbed against itself and against a diamond composite.

compared with 0.33, respectively). It may be noted that the steel pin was rubbed against the diamond composite for short intervals prior to cleaning and weighing. This procedure minimized the formation of iron oxide which can significantly affect the wear rate.

This effect is illustrated in two ways in Fig. 3. It was observed that after about 3500 m sliding distance, the presence of wear debris both on the composite and pin surface could be clearly seen. X-ray diffraction analysis identified this debris as Fe_2O_3 (major phase), Cr or $Cr_{23}C_6$ and Fe_3O_4 (trace amounts). Previous work [11] has shown that the presence of Fe_2O_3, a hard ($\sim 1100\,\mathrm{kg\,mm^{-2}}$) oxide, can completely dominate the wear process via third body abrasion in diamond compact/metal wear. Similar, if not as severe, effects were noted in the 440C pin-on-diamond composite disc tests. The lower curve in Fig. 3 shows the pin wear after successive runs with 3730 m between cleaning and weighing (low wear rates), and with 7470 m between runs (higher

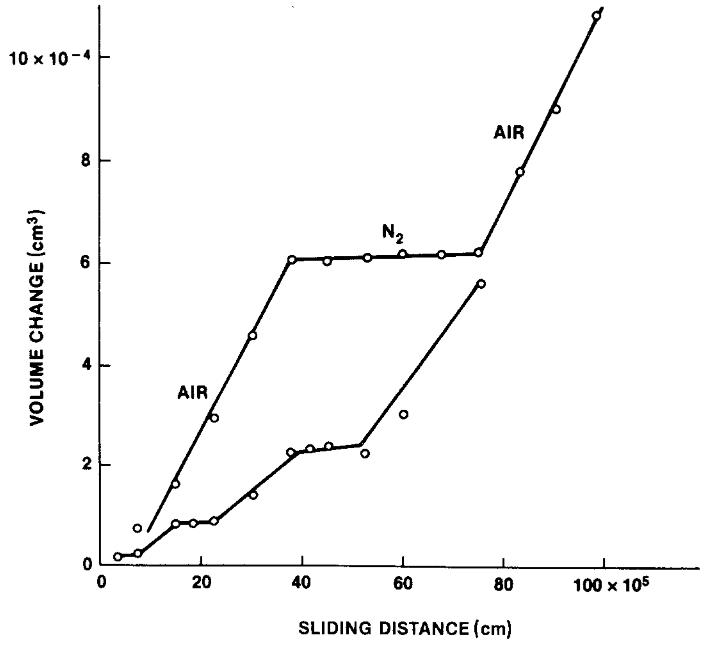

Figure 3 Effect of Fe_2O_3 on the wear of a 440C steel pin rubbing against a diamond composite. Lower curve: run at successive intervals of 3730 m between cleaning (low wear rate) and 7470 m intervals (high wear rate). Upper curve: run successively in air and N_2.

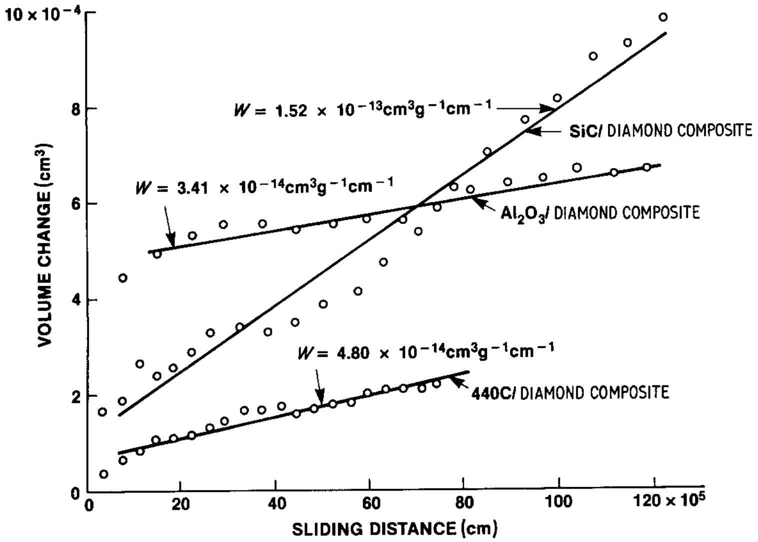

Figure 4 Wear rate of SiC, Al_2O_3, and 440C steel rubbing against freshly prepared diamond composites.

wear rates). As may be seen, when Fe_2O_3 was allowed to accumulate, significantly higher pin wear occurred. The upper curve illustrates the wear behaviour of a 440C pin run against a diamond composite successively in air and in flowing N_2 (7470 m between cleaning and weighing). As may be seen, the wear rate where Fe_2O_3 formation was inhibited (N_2 atmosphere) was much lower than when it was present. The wear rate in an N_2 atmosphere was somewhat lower than the runs in air at 3730 m intervals, because small amounts of Fe_2O_3 were formed continuously and hence affected the wear rates of all tests in an air atmosphere.

This strong effect of wear debris was only noted when the debris formed by reaction with the environment was harder than the pin itself. For the other wear couples examined (diamond, ceramics, and metals), the wear debris consisted primarily of the parent material and greater or lesser amounts of debris present during rubbing did not seem to have such a strong effect on wear rate, although some influence was noted.

Fig. 4 shows the wear behaviour of SiC and Al_2O_3 against freshly prepared diamond composites (the 440C/composite data are re-plotted from Fig. 2). Fig. 4 shows a point of interest that was observed several times during these studies. Although all the pins tested showed some degree of wear-in, where the initial volume loss was higher than it was subsequently, some materials (noteably Al_2O_3 and cemented carbide) showed a large initial volume loss followed by a low wear rate. As will be discussed below, this occurred only on a "fresh" diamond composite surface; that is, prepared as described in Section 2.2. and not previously worn. After some degree of rubbing, this large initial wear rate was not observed.

The wear rates of the materials studied can exhibit different wear behaviour for similar pins of the same material against the same diamond disc in a "fresh" polished state. This is illustrated in Fig. 5, when two Al_2O_3 pins were run against the same disc (polished between runs), and the wear rates differed by a factor of three. Such variability is considered typical¶ and is due to material variations and slightly differing diamond composite surface topography.

Reproducibility can be improved if new pins are run against diamond composites that have been previously worn. This is illustrated in Fig. 6, where two new cemented carbide pins were run against a previously worn disc. The large initial material loss observed when carbide is run against a fresh composite surface is absent, and the usual laws of wear are observed; that is, wear proportional to sliding distance, applied load, and independent of area. These relations applied for carbide, less so for SiC as far as applied load was concerned, and in the other materials studied (except the diamond composite itself) the effect of load was not examined, but in all cases with the exception of a wear-in period wear was

---

¶An exception is silicon, where the wear rates can vary by several orders of magnitude. The reason for this behaviour is not known.

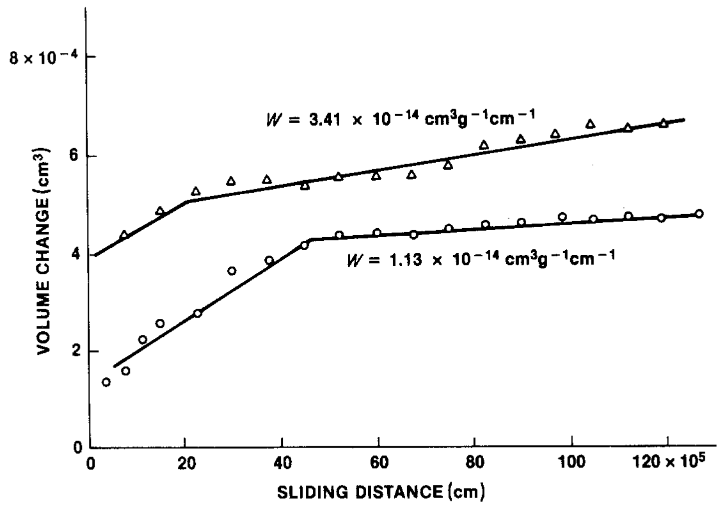

Figure 5 Wear rate of two different Al_2O_3 pins rubbing against freshly prepared diamond composites.

proportional to sliding distance and independent of area of contact.

Because of the very low wear rate of cemented carbide on the diamond composite, this wear system was studied in some detail. The wear mechanisms will be discussed in the following section; of particular interest here is the initial and subsequent wear behaviour. The general behaviour is illustrated in Fig. 7. In both cases shown, a new pin was initially used, but the upper curve shows the wear behaviour with a freshly prepared diamond composite surface; the lower curve with a previously worn composite. It is not necessary to develop the worn surface with carbide; the same behaviour was observed if an Al_2O_3 pin was used. Although the equilibrium wear rates are about equal, the initial wear rate is much greater for the "fresh" diamond surface. This is by no means an isolated phenomenon. The average initial material removed in the first 7500 or 15000 m of sliding was 5.36×10^{-6} cm^3 (standard deviation $= 6.91 \times 10^{-6}$ cm^3) based on 17 tests of WC + 6% Co on previously worn diamond composite surfaces and 308.0×10^{-6} cm^3 (standard deviation $= 314 \times 10^{-6}$ cm^3) on fresh surfaces based on seven tests. The exceedingly large variation of the latter number suggests how sensitive the initial wear rate is to the composite finishing procedure. Pin condition (worn or not worn) was not found to be a factor in the initial wear rate.

To study this behaviour in more detail, a series of experiments was conducted at shorter time periods. Starting with a freshly prepared diamond composite disc and a new pin, wear tests were conducted at short time intervals (two runs each at 5, 10, 30, 60 and 100 min) and then subsequently at longer time intervals until an equilibrium wear rate was established. Both pin and disc were cleaned after each sliding excursion. Using the same diamond composite, now with a worn surface, the procedure was repeated with a new carbide pin. Finally, a "standard" wear test,

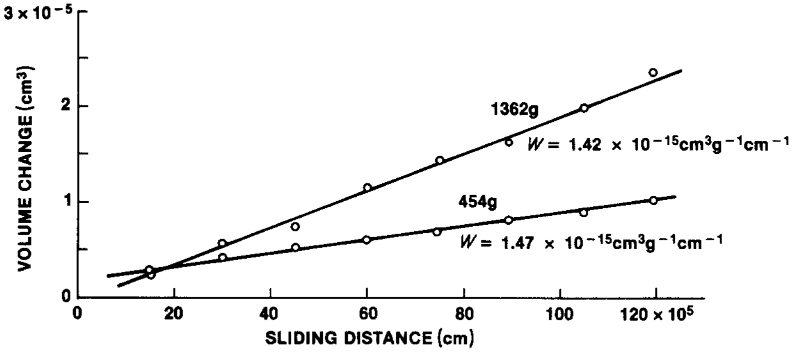

Figure 6 Wear rate of cemented tungsten carbide at different loads rubbing against a previously worn diamond composite.

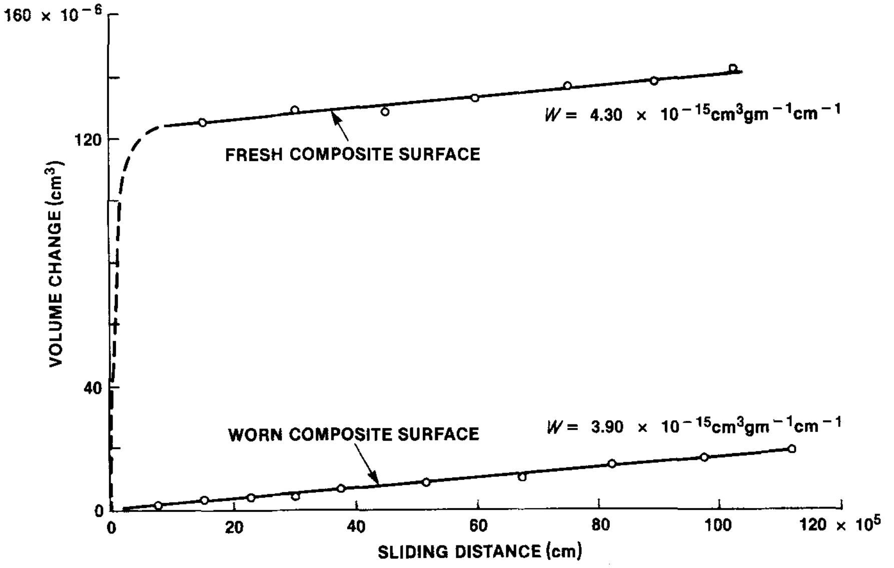

Figure 7 Wear rate of two cemented carbide pins rubbed against a freshly prepared and previously worn diamond composite.

consisting of successive runs of 200 min (15 000 m sliding distance) each was conducted on the same worn disc with a new pin.

These data are shown in Fig. 8. The upper curve is the data for the first pin, the middle for the second, and the lower curve for the last pin. Because wear debris was constantly being removed from the system, the wear behaviour is somewhat different from that depicted in Fig. 7. Nevertheless, it may be seen that as diamond wear progresses, wear of the carbide pin decreases. The effect of wear debris in the system is implict in the fact that an equilibrium wear rate was established after 15000 m sliding distance for the case depicted in the upper curve of Fig. 7 and only after greater than 40 000 m for the upper curve in Fig. 8.

A typical wear track on a diamond composite is shown in the low magnification photomicrograph in Fig. 9a, and an individual diamond at a higher magnification in Fig. 9b. The direction of wear is evident by the scratches on the diamond surfaces in Fig. 9b. No difference in optical surface appearance was noted for worn diamond areas for any of the wear combinations examined. Fig. 9 is representative of what has been characterized as a worn diamond composite. Subsequent wear somewhat increases the area of diamond worn, but this increased diamond wear area did not seem to affect the wear behaviour. As indicated

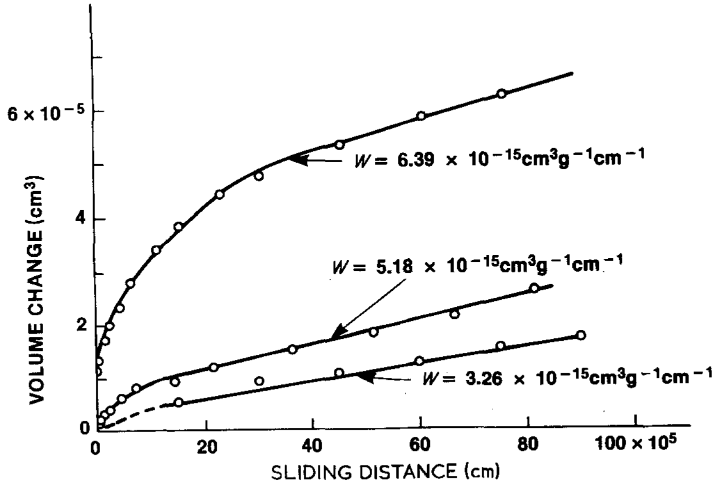

Figure 8 Wear rate of three cemented tungsten carbide pins rubbed against a diamond composite at differing time intervals. Upper curve: new pin and freshly prepared surface; middle-curve: new pin and worn composite surface from above; lower curve: new pin and worn composite surface from previous two tests.

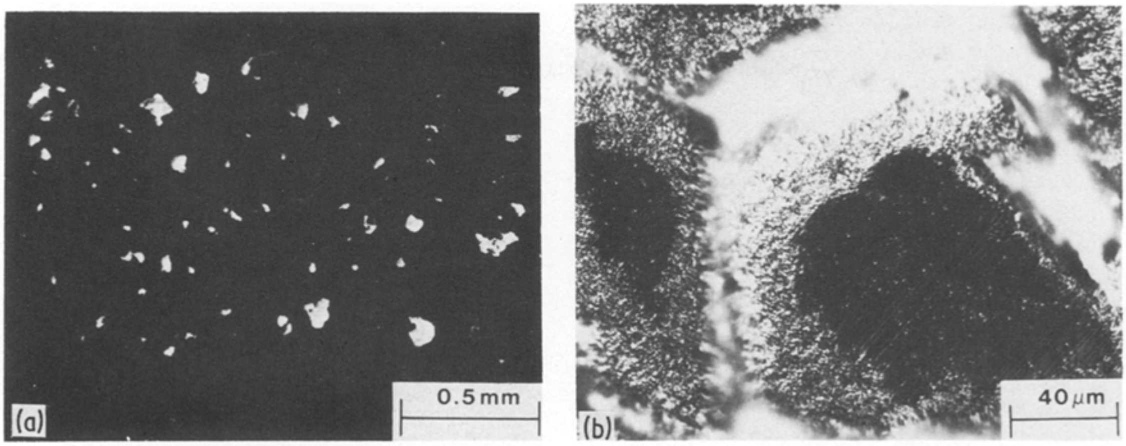

Figure 9 Diamond composite wear track at two magnifications.

earlier, and is evident from Fig. 9, only the diamonds in the composite, and not the matrix itself, contribute to the wear process.

The development of the wear flats on the diamonds in the composite is necessary to eliminate initial erratic wear behaviour for ceramic pins. The effect of "fresh" compared with worn or "conditioned" surfaces has been discussed in some detail for WC + 6% Co, where the behaviour is particularly striking because of the high initial wear rate followed by a very low wear rate. SiC pins were found to be variable in this respect, in one case (shown in Fig. 4) the initial volume lost on a fresh surface was not very great, but in another presumably similar test the initial volume lost was seven times that shown in Fig. 4. Al_2O_3 always showed a high initial wear rate when rubbed against a fresh diamond composite surface, while the wear of Si_3N_4 (three pins were tested) was not affected by the condition of the diamond surface. This behaviour may be due to the high hardness of Si_3N_4 and, as discussed below, its comparatively high fracture toughness. Similarly, metals were not particularly sensitive to the diamond condition. It seems that many ceramics, which are brittle and must wear by a process of micro-chipping, are quite sensitive to small variations in the topography of the polished diamond surface. Metals can deform plastically and hence accommodate irregularities in the diamond surface. In either case, however, the optimum wear surface (from the standpoint of uniform and reproducible wear behaviour) is a worn diamond surface which has irregular heights and surface imperfections removed. This situation will hold until sufficient diamond material is removed and the matrix level reached. At this point, the wear debris will remove matrix material and expose sharp unpolished diamond edges, and cutting will replace wear.

3.2. Wear mechanisms

As indicated in Section 1, one of the objectives of this work was to attempt to clarify the wear process when diamonds are rubbed against metals and ceramics. The wear of the metal or ceramic pins seems clear enough; material is removed by the harder diamond. It is not clear why hardness correlates so poorly with the wear behaviour, and no definite answer was obtained during this investigation. It is possible that the rate of wear is dependent, not on the hardness, but on the fracture toughness. The fracture toughness (K_{IC}) of hot-pressed Si_3N_4 and SiC is ~ 5.0 MN $m^{-3/2}$ and ~ 3.0 MN $m^{-3/2}$, respectively [16]; 4.4 MN $m^{-3/2}$ for Al_2O_3 [17]; ~ 9.2 MN $m^{-3/2}$ for WC + 6% Co [18]; and is estimated to be of the order of 20 MN $m^{-3/2}$ for 440C steel. Except for the steel, which can flow plastically, these values of K_{IC} rank the materials (except the diamond composite) in the proper order regarding equilibrium wear rate. If wear does occur by a micro-chipping process, this possible correlation between K_{IC} and wear rate seems reasonable. However, in the absence of a systematic study of wear and fracture toughness involving measuring both values on the same lot of material, this correlation must remain conjectural.

The second question relates to the wear of the diamond; specifically, is it induced mechanically by dislodged diamond particles as described by Crompton *et al.* [10], or are chemical reactions aiding in or responsible for the diamond wear. As indicated below, at least some partial answers were obtained to this question.

Wear analysis of several of the material combinations used was performed by examining the diamond composite and pin after test, as well as analysing wear debris collected during some tests during the cleaning process prior to weighing (or photographing) the pin to determine its volume change. Debris from the composite surface was carefully scraped or brushed into a glass petri dish which was then sealed for later analysis.

Metallographic examination of various pins in cross section after test failed to reveal any microstructural change near the wear surface, at least at the level of magnification (x 1000) employed. Earlier work [11] dealing with the examination of metal surfaces after being worn by a diamond compact, using both optical and scanning electron microscopy, yielded little information pertaining to wear mechanisms, and consequently not a great deal of examination of the pin after the test was performed.

The examination of worn individual diamonds in a diamond composite after test was considered critical for an assessment of the diamond wear process. However, a difficulty soon became apparent. An examination of Fig. 9 reveals worn areas on individual diamonds are quite small and, furthermore, not easily found and identified for a series of tests. Consequently, a different procedure was used to examine worn diamond surfaces.

On the not unreasonable assumption that natural and synthetic diamonds wear in a similar manner, industrial grade natural diamonds approximately 1 mm in dimension were obtained and used to examine worn diamond surfaces. The technique used is illustrated in Fig. 10. Four 1 mm diamonds were pressed into an annealed copper plate and held in place by folding copper around them and then soldering the copper. By rubbing the disc with a diamond compact rotating at 500 rpm and a load of 1.8 kg, a wear flat was formed on each stone. They were then polished with 30 μm diamond paste (the same procedure used to prepare the diamond composite surface), and then rubbed with a disc of the material of interest (Al_2O_3, WC + 6% Co, SiC, and 440C were used) until a wear flat was formed. This sequence of events is illustrated in Figs. 11 and 12. Fig. 11a shows a diamond after rubbing with the diamond compact, Fig. 11b after polishing, and Fig. 11c after a wear test (Al_2O_3 in this case). Fig. 12 shows the development of a wear flat during several stages of wear. The origin and nature of the wiggly lines on the diamond that appeared after 7600 m of rubbing and then vanished at 16 600 m is not known. The surfaces finally examined were similar to that in Fig. 12 at 16 600 m. Any wear debris was brushed off the diamond surface, but no further cleaning was performed prior to further analyses.

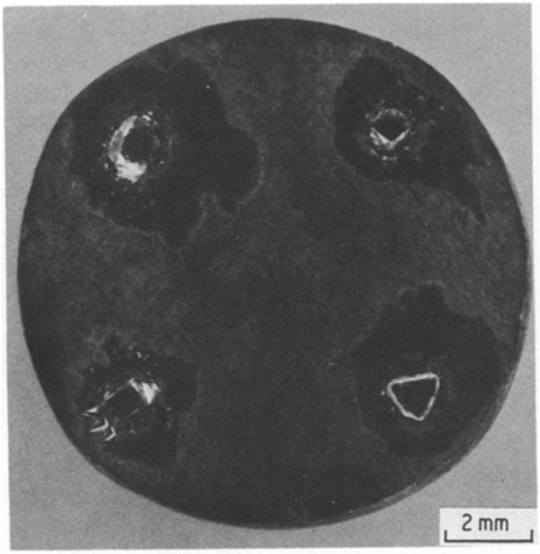

Figure 10 Large natural diamonds imbedded into a copper disc. The diamonds have been rubbed against a diamond compact.

3.2.1. Nature of the worn diamond surface

Optical examination of individual 1 mm natural diamonds after being rubbed by Al_2O_3, SiC, WC + 6% Co, and 440C showed a clear, transparent surface with no indication of material transfer other than discrete particles of wear debris. This was verified by studies of the worn diamonds in an ISI Supper III scanning electron microscope equipped with an energy dispersive X-ray detector. Surface irregularities and defects in the diamonds were noted to contain wear debris from the metal or ceramic that rubbed them. X-ray spectra from the worn diamond surface contained no elemental peaks indicative of a chemically altered layer. Since the electron excited volume from which the X-rays are generated is at least 1.0 μm in depth, the presence of a very thin

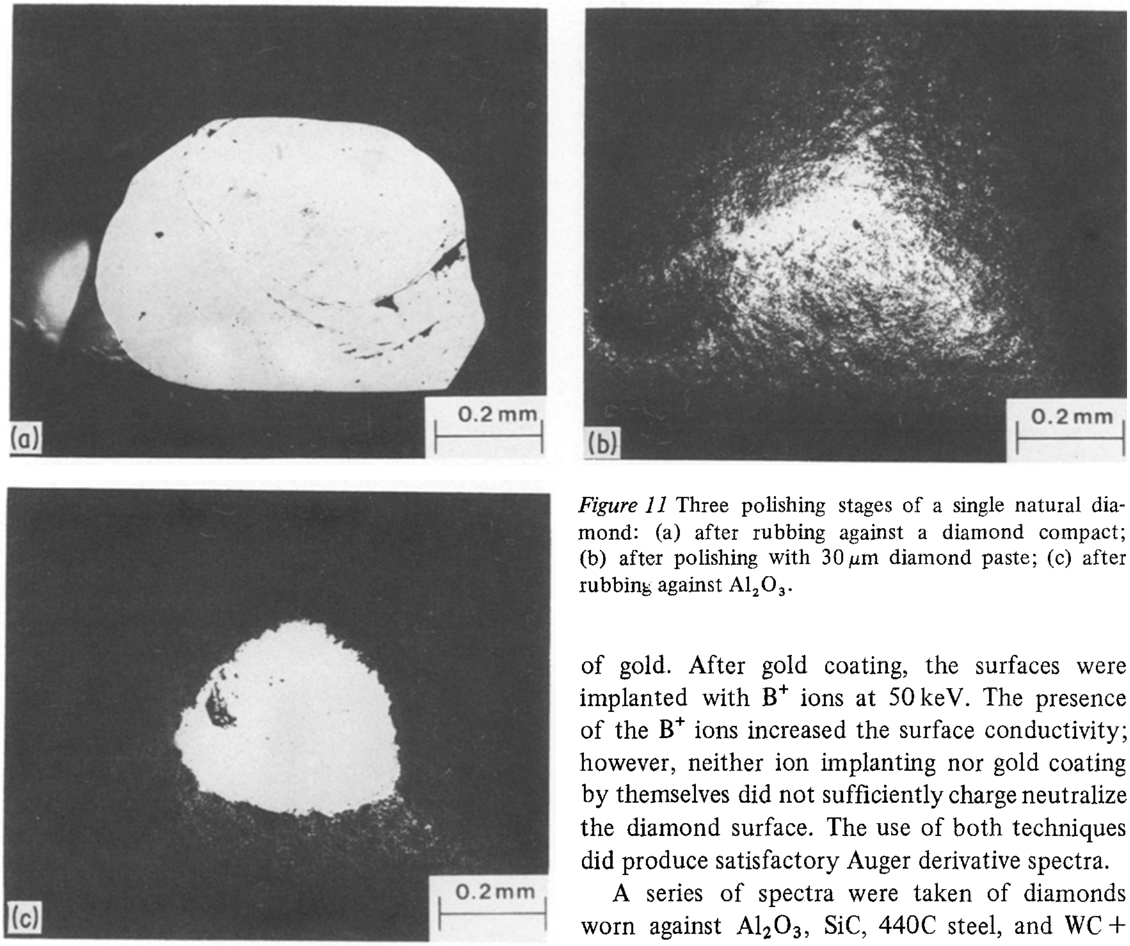

Figure 11 Three polishing stages of a single natural diamond: (a) after rubbing against a diamond compact; (b) after polishing with 30 μm diamond paste; (c) after rubbing against Al_2O_3.

altered layer would not be detected by this analytical technique.

A more surface sensitive technique, Auger electron spectroscopy (AES), was next used to analyse the diamond surfaces. AES is capable of producing elemental and chemical information in the top few atom layers of solids. Typically, a 3 to 5 keV electron beam is focused on the sample and the Auger electrons which escape into the surrounding vacuum of the sample chamber are analysed with a cylindrical mirror analyser. An *in situ* argon ion gun is used both for sputter cleaning airborne contaminants from the surface and for elemental depth profiling.

Initial analysis indicated charging of the diamond surface under the electron beam and distortion of the Auger signals, making measurement and identification of the Auger peaks difficult. Two methods were used to reduce surface charging. A grid of gold was sputtered on to the diamond surface leaving areas with a very thin coating of gold. After gold coating, the surfaces were implanted with B^+ ions at 50 keV. The presence of the B^+ ions increased the surface conductivity; however, neither ion implanting nor gold coating by themselves did not sufficiently charge neutralize the diamond surface. The use of both techniques did produce satisfactory Auger derivative spectra.

A series of spectra were taken of diamonds worn against Al_2O_3, SiC, 440C steel, and WC + 6% Co. The spectra were taken after short periods of A^+ ion cleaning to remove gold and expose a clean surface. The diamonds rubbed against Al_2O_3, SiC, and 440C did not show any chemically altered surface layers. However, the diamond rubbed against the WC + 6% Co probably contained a very thin tungsten containing layer, which was quickly removed by subsequent A^+ ion etching. This behaviour is shown in Fig. 13, and as can be seen all the tungsten had vanished after ~2.4 nm of surface material was removed. Detection limits for Auger analysis are in the range of 0.5 at % for most elements, which means the potential for detecting minor constituents is low, unless there are localized areas of higher concentration.

3.2.2. Wear debris

The analysis of wear debris is of considerable importance in understanding the wear mechanism operative in these material systems. In past work [8] on diamond composite/diamond composite wear, the positive identification of diamond wear fragments was a key item in

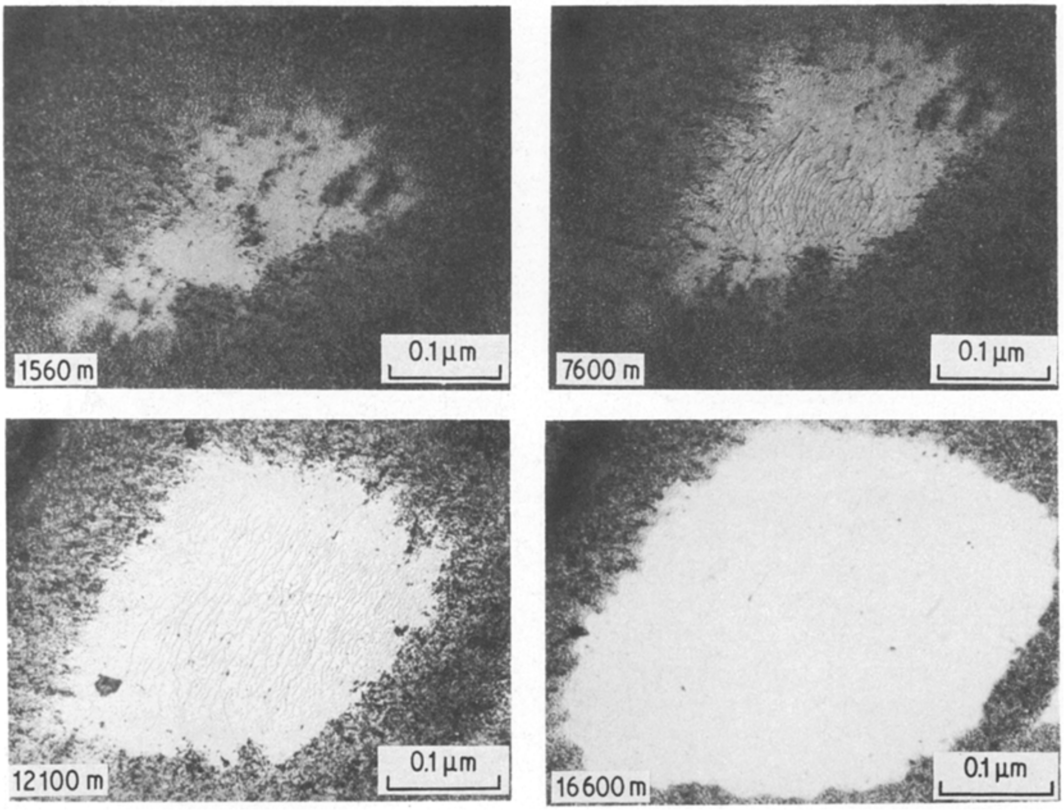

Figure 12 Development of a wear flat on a large natural diamond at various intervals while rubbing against Al_2O_3.

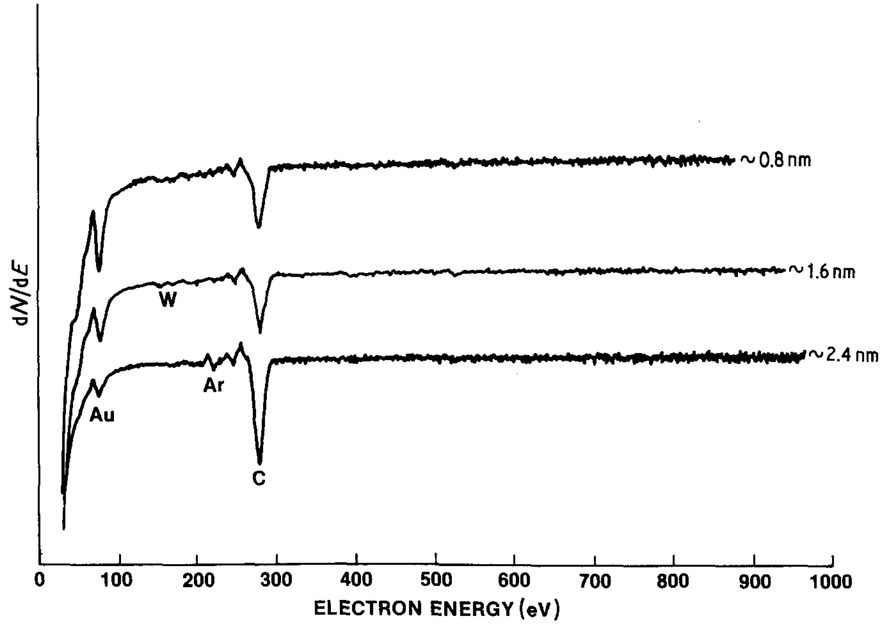

Figure 13 Auger derivative spectra of a worn diamond surface after being rubbed against cemented tungsten carbide at three levels of ion etching.

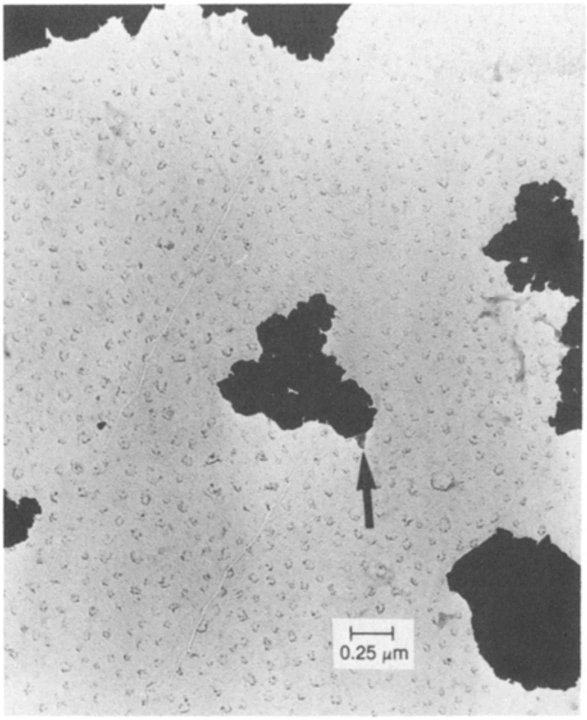

Figure 14 Transmission electron micrograph of wear debris from a cemented tungsten carbide/diamond composite wear test. A thinner crystal of WC is indicated by the arrow. The crystal is part of a thicker agglomerate of WC.

deducing how these materials wore during sliding. It is natural, therefore, that considerable effort was devoted to the analysis of wear debris.

The debris was studied by two techniques: standard X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) using electron diffraction and X-ray spectroscopy (EDS). The major amount of time was spent on the TEM work, and this work has been fully reported elsewhere [19]. The following is a summary of the results obtained.

XRD analysis was used to identify the wear debris from the pin. The amount of diamond fragments, if present, was far too small to be detected. Considering the debris generated by a 440C/diamond composite experiment, the results have been discussed earlier. Primarily Fe_2O_3 was formed, resulting in the significant changes in wear behaviour discussed with reference to Fig. 3. In all of the other cases the primary finding was that the debris consisted of the pin material itself; i.e. Al_2O_3, SiC and WC (Si_3N_4 was not analysed). Only in the case of the 440C did a chemical reaction take place that altered the nature of the wear debris.

The TEM work confirmed the above observations. Fig. 14 is a micrograph of a WC particle obtained from the wear debris of a cemented carbide/diamond composite wear test. WC particles as large as 0.5 μm were found, and were generally irregular in shape. They were sometimes observed as thin flakes, but generally they appeared to be dense agglomerates.

In addition to pin materials, diamond fragments were formed in the wear debris of some wear tests. The X-ray detector was insensitive to the $CK\alpha$ X-rays from diamond, so this phase was identified from its diffraction patterns and the absence of any detectable X-ray peak. EDS spectra were essential in identifying diamond particles; for example, cobalt and diamond both have a lattice parameter of ~0.35 nm, and the diffraction pattern for these phases would be nearly identical for many orientations.

A typical diamond fragment is shown in Fig. 15. The only single crystals of diamond which could be conclusively identified came from tests where a diamond composite was rubbed with a diamond compact. In this case a relatively large amount of diamond wear debris was generated, making its identification conclusive. Diamond particles from composite/compact tests were found in the 0.125 to 0.425 μm range, which is somewhat larger than the particle size of 0.010 to 0.10 μm suggested by Crompton *et al.* [10], but of the correct order of magnitude. Smaller diamond

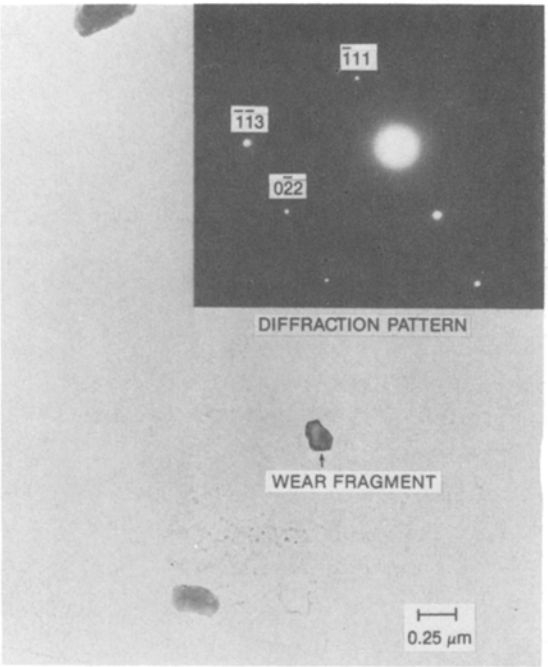

Figure 15 Transmission electron micrograph and diffraction pattern (211 direction) of a diamond single crystal in wear debris from a diamond composite/diamond compact test. The crystal shows no evidence of deformation substructure. This was typical of the diamond crystals identified in all of the wear debris extraction replicas.

particles were not observed, but were quite probably present. There was a high aggregation of particles observed in all the replicas, and some of the small particles in these aggregates may have been diamond crystals. Fig. 16 shows typical aggregation seen in the replicas; the debris is from a test of a diamond composite rubbed by a diamond compact. Collecting electron diffraction patterns for the very small crystals in an aggregate is readily possible in the transmission electron microscope since the diffracting crystal can be identified by dark field imaging. It was difficult to conclude that a particular crystal was diamond, since because of beam spreading a spectrum collected could include other elemental peaks from particles touching the one of interest. The difficulty increased as the particle size decreased. Particles were identified having the correct electron diffraction pattern for diamond in most samples of wear debris, but in all other than in diamond/diamond wear cases the EDS spectra showed the presence of other elements.

In the case of assigning electron diffraction patterns to either cobalt or diamond in debris from tests involving cemented carbide and diamond composites, it was possible to make a tentative distinction based on the relative ductility of cobalt compared to diamond. Cobalt probably

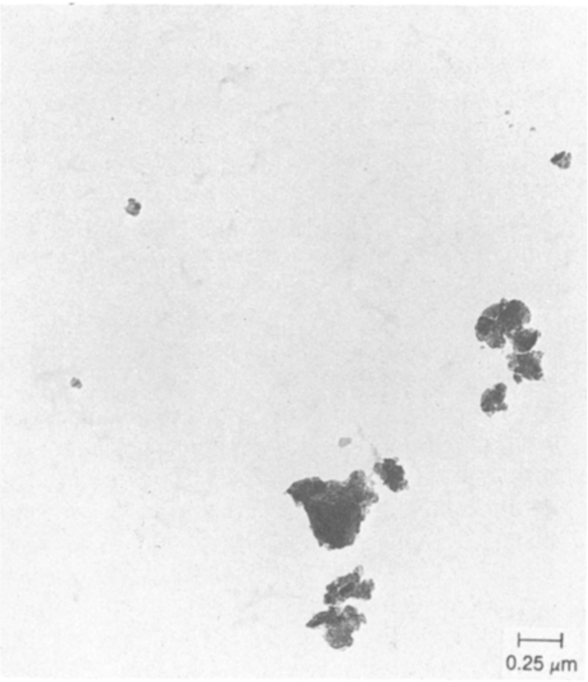

Figure 16 Transmission electron micrograph of debris from a wear test of a diamond composite/diamond compact test. The crystal aggregation shown is representative of that observed throughout all wear debris examined.

deformed somewhat in the wear process. Diamond particles would be expected to have less deformation substructure observed in the bright-field images than would the more ductile f c c cobalt. Single crystals identified unambiguously to be diamond (see Fig. 15) showed no deformation substructure. In the cases where the identity of the single crystal was in question, the crystal also contained no visible dislocations or faults. Therefore these crystals were more likely to be diamond than cobalt.

4. Discussion

It is unfortunate that it was not found possible to unambiguously identify diamond fragments in the wear debris from metal/diamond composite or ceramic/diamond composite wear tests. Such identification would tend to substantiate the Crompton *et al.* explanation of diamond wear; that is, wear caused by diamond fragments themselves leading to subsequent diamond wear. The positive identification of diamond single crystals in the wear debris resulting from diamond composite/diamond compact wear does substantiate the conclusion reached in the previous study [8] of composite/composite wear; namely that the mechanism proposed by Crompton *et al.* is probably correct for this wear system.

Although direct evidence of diamond wear particles in the wear debris of non-diamond materials sliding against a diamond composite is lacking, sufficient indirect evidence (i.e. lattice spacing and crystal morphology) is present to strongly suggest their presence. However, even if the presence of diamond wear particles is accepted, the possibility of diamond wear caused by chemical interaction with a non-diamond pin cannot be excluded. The AES and SEM analytical techniques cannot distinguish between carbon (diamond) and carbon (graphite). Nevertheless, our feeling is that if chemical reaction contributes to the wear of diamond, it is of secondary importance compared to mechanical attrition of the diamond surface by diamond wear fragments. The evidence and arguments advanced by Crompton *et al.* are persuasive regarding attrition as a wear mechanism, and the probable presence of diamond crystals in wear debris tends to support this viewpoint. Also, if chemical interaction between the pin and diamond composite were significant, one would expect a greater degree of diamond wear when rubbed by 440C steel than, say, Al_2O_3 (diamond tooling is not used to machine ferrous material because of diamond/steel reactions). This was not observed.

Although chemical effects under the sliding conditions used are not thought to significantly alter the wear of the diamond, it seems clear that chemistry plays some role in the wear process of some material combinations. This is suggested because of the behaviour of cemented tungsten carbide rubbing diamond. Of all the materials examined, WC + 6% Co had the lowest equilibrium wear rate and friction coefficient, including diamond itself. AES analysis indicated a possible trace of tungsten or WC transfer to the diamond surface, and this could lead to reduced friction and wear.

5. Conclusions

Based on the results of this investigation, the following conclusions may be drawn regarding the sliding behaviour of metals and ceramics against a diamond composite in air:

1. Wear of the pins is due to removal of the pin materials by the harder diamond and, except for steel, consists of the pin material itself. Steel wear debris oxidized to primarily Fe_2O_3 which subsequently increased pin wear.
2. Wear of diamond by hard metals and ceramics is probably due to mechanical attrition of the diamond surface by small diamond fragments dislodged from the diamond surface during rubbing.
3. No chemically altered diamond surfaces were detected except perhaps for the case of cemented tungsten carbide rubbing against diamond. This material also has the lowest equilibrium wear rate of any material examined.
4. Initial wear of the hard ceramics can be quite high until diamond surface irregularities are removed by wearing of the diamond composite. An equilibrium wear rate is then established which was lowest for cemented tungsten carbide, followed by Si_3N_4, Al_2O_3, 440C steel, and SiC. Wear did not correlate with pin hardness, but fracture toughness did (with the exception of steel).
5. Materials with a hardness less than 440C steel did not wear but material was removed by a cutting mechanism. The exception was silicon, which was harder than 440C but had a high wear rate.

Acknowledgements

We would like to acknowledge the contributions of G. C. Buczkowski, who fabricated the diamond composites, and to R. C. DeVries, who initially developed the mounting method for large diamonds. We are indebted to D. G. Flom and C. R. Morelock for many useful discussions on the wear of diamond composites and to R. B. Bolon, W. G. Morris and A. M. Ritter for advice on analytical procedures.

References

1. R. H. WENTORF, R. C. DeVRIES and F. P. BUNDY, *Science* **208** (1980) 873.
2. P. A. BEX, *Ind. Diamond Rev.* **43** (1983) 75.
3. E. J. MARCUS and M. V. MARCUS, *J. Audio. Eng. Soc.* **18** (1970) 51.
4. N. R. SMITH, "User's Guide to Industrial Diamonds" (Hutchinson Benham, London, 1974) pp. 69–71.
5. D. D. ROSHON, *IBM J. Res. Dev.* **40** (1979) 251.
6. W. F. SHARP, *Wear* **32** (1975) 315.
7. H. WAPLER, T. A. SPOONER and A. M. BALFOUR, *Ind. Diamond Rev.* **40** (1979) 251.
8. R. L. MEHAN, *Wear* **78** (1982) 365.
9. G. C. BUCZKOWSKI and R. L. MEHAN, *J. Mater. Sci. Lett.* **1** (1982) 170.
10. D. CROMPTON, W. HIRST and M. G. W. HOWSE, *Proc. Roy. Soc.* **A333** (1972) 435.
11. R. L. MEHAN and S. C. HAYDEN, *Wear* **74** (1981) 195.
12. J. F. ARCHARD and W. HIRST, *Proc. Roy. Soc.* **A236** (1956) 397.
13. K. MIZOSHI and D. H. BUCKLEY, *ASLE Trans.* **22** (1979) 245.
14. L. E. HIBBS and G. C. SOGOIAN, "Wear Mechanisms for Polycrystalline Diamond Compacts as Utilized for Drilling in Geothermal Environments – Final Report", Sandia National Laboratories Report SAND 82-7213, May (1983).
15. P. D. ST PIERRE, C. R. MORELOCK and J. D. BIRLE, US Patent 4 200 455, September (1980).
16. D. C. LARSON, "Property Screening and Evaluation of Ceramic Turbine Engine Materials", Technical Report AFML-TR-79-4188, October (1979).
17. G. D. SWANSON, *J. Amer. Ceram. Soc.* **55** (1972) 48.
18. J. L. CHERMANT and F. OSTERSTOCK, *J. Mater. Sci.* **11** (1976) 1939.
19. C. I. HENJA, "Transmission Electron Microscopy Study of Wear Debris from Various Diamond Composite/Ceramic and Diamond Composite/Metal Wear Couples", General Electric Report 84CRD103 (1984).

Received 12 June
and accepted 6 July 1984