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Hybrid plasma CVD of diamond-like carbon (DLC) at low temperatures

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Diamond-like carbon coatings have been deposited onto various substrates at 100–150 °C using a hybrid plasma assisted chemical vapour deposition technique activated by radio frequency at 13.56 MHz. The coatings have been characterized using a number of techniques including scanning electron microscopy, Raman spectroscopy, thermoanalysis and pin-on-disc wear testing. Results show the films to be diamond like, with the addition of nitrogen (prior to deposition) promoting the formation of crystallites. In addition the condition and type of substrate have been found to have a strong influence on the structural characteristics of the deposited diamond-like films. SEM analysis of diamond-like carbon coatings deposited onto metal matrix composite materials such as Si–Al MMC is reported. The hybrid CVD technology enabled films to be deposited evenly onto the porous MMC structure. Commercially manufactured drills, coated with DLC and titanium nitride (TiN), have been compared to examine their cutting wear resistance characteristics.

1. Introduction

Plasma assisted chemical vapour deposition (PACVD) has become an important technology for the deposition of a variety of coatings for a number of applications, in the fields of electronics, tooling, surgical implants and optics [1, 2]. The major advantages of PACVD over other thin film deposition techniques include low deposition temperature, high deposition rate, good control over stoichiometry, cleanliness and low particulate levels. Although scientific interest in carbon coatings, particularly diamond, has been considerable over the past twenty years [2–7], it is only recently that the commercial promise of thin films of diamond and related materials such as diamond-like carbon (DLC) has become an industrial reality [8]. DLC is an intermediate amorphous carbon coating having some diamond-like characteristics [3] and has been used in applications including cutting tools, dies, surgical implants, combustion engine components [9], fibre optic cables, catalysis, heat sinks and micro-electronics [10]. Diamond is a material with a unique combination of physical, chemical, electrical and optical properties which make it potentially attractive for a large number of important industrial applications [11]. For example, its extreme hardness and wear resistance makes it ideal for coating tools, drills, moving parts in mechanical machinery such as car engines, etc. In electronics its transparency, insulating properties, radiation hardness and excellent thermal conductivity make it a good candidate for future applications [12] in circuit packaging, high power, electro-optic and semiconductor devices. The optical properties of diamond are important in lenses, laser windows and optical devices, etc. [8].

Thin film carbon coatings can be divided into three main categories; polycrystalline diamond, diamond-like carbon (DLC) and graphite [3]. The challenge in technological development for industrial application onto large substrates at low temperature are significant for polycrystalline diamond and become considerably less demanding for graphite. A number of techniques [13, 14] have been used to deposit carbon coatings including hot filament chemical vapour deposition (CVD), ion plating, plasma assisted CVD, ion beam deposition, mass selected ion beam deposition, combustion synthesis, etc. However, it has been shown [5] that plasma assisted chemical vapour deposition is one of the most promising techniques for low temperature deposition of DLC and polycrystalline diamond for large-scale industrial use. For low temperature deposition the precursor gases need to be activated using microwave, laser, radio frequency (RF) or d.c. plasma to achieve respectable growth rates. Without this enhanced precursor activation, extreme substrate temperatures are required and this severely limits the number of potential applications. In order to improve the adhesion, crystallinity and density of the films, the deposition system used in this work was modified. A venturi magnetic confinement ring and a filament were incorporated to increase the plasma intensity. The high intensity bombardment of the growing film could affect the properties of the deposited film in a beneficial way. For many CVD coatings, the substrate surface structure can have a pronounced influence on the coating characteristics. In this publication DLC coatings, produced using a hybrid low temperature RF plasma assisted CVD system (BEP Grinding Ltd.) [15–17], were investigated using different substrates.

2. Experimental details

The hybrid plasma assisted CVD system i.e. a system which incorporates aspects of physical and chemical vapour deposition [10], used to deposit the coatings consisted of a gas handling and preheated assembly reactor vessel, with a RF plasma generator and vacuum pumping system and is shown in Fig. 1. The plasma reactor comprised a double skinned water cooled non-magnetic circular stainless steel vessel (C). The loaded system had an ultimate vacuum of 1.333×10^{-2} Pa using a rotary pump roots blower combination. The substrate holder (E) was located above the multi-pumping ports and was attached to the powered electrode (D). The ports were fitted with ceramic restrictors for plasma confinement. Precursor gases were introduced into a preheating chamber prior to entry into the plasma region. An RF power supply and matching network was used to generate the plasma between the two electrodes. To produce a high negative bias potential at the substrate holder at low input power, a stainless steel cage and venturi magnetic confinement ring (B) was fitted to the interior of the vessel. The cage and capital venturi ring were electrically isolated and at floating potential to the plasma. The RF power supply and matching network impedance was set for automatic match in hydrogen between 2.7×10^{-1} and 67 Pa. The substrates were pre-cleaned prior to entry into the vacuum system where they were subjected to additional plasma cleaning in hydrogen and argon plasmas prior to deposition. Both plasma cleaning and deposition were carried out at 8 Pa with 300 and 600 V d.c. negative bias voltages at the substrate, respectively. The gas following technique was used with a single gas delivery line. Hydrogen, argon and/or nitrogen followed by butane were introduced into the reactor, thus facilitating a smooth process and eliminating gas change-over problems. Reflected power was always kept to below 10 W. To enhance ionization of the plasma, an electron filament was (D) incorporated into the reaction zone. The deposition conditions were optimized using Taguchi methods.

The coatings produced were characterized using a variety of analytical techniques. These techniques included Raman spectroscopy (RS) of coatings on glass substrates, scanning electron microscopy (SEM) of coatings on Al/Si MMC and thermoanalysis (TA) of coatings on aluminium and steel. Wear resistance characteristics when cutting metal were assessed using 1/4 inch (6.35 mm) drills coated with DLC and TiN, powered by a Bridgeport CNC machine. The drills were originally manufactured from high speed steel.

For the determination and identification of various forms of carbon present in the films deposited [18] the thermoanalysis technique was employed. It utilizes temperature controlled heating of the sample in an oxygen atmosphere resulting in the formation of oxides of carbon. The amount of carbon oxides are continuously monitored as a function of temperature. Accurate data on the high temperature stability of DLC coating/substrate is essential in predicting industrial performance. A LECO Corporation RC-412 instrument was used for this investigation.

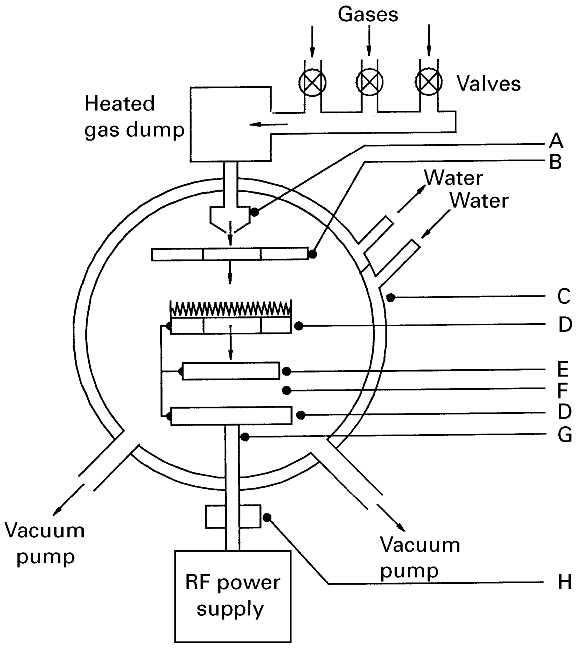

Figure 1 Schematic of the hybrid plasma assisted CVD system.

Pin-on-disc wear testing of a DLC coating on a zirconia substrate was also carried out. The DLC was not doped with a secondary material such as silicon and it gave adequate coating adhesion without the use of secondary materials [6] and an interface coating was not considered necessary. A BICERI universal wear machine, in the pin-on-disc configuration, was used to undertake the investigation [19]. The test procedures conformed to those now accepted internationally [20, 21]. The zirconia substrate was polished to an Ra value of 35 nm prior to deposition. The as-deposited DLC coating assembly was aged in air under natural conditions for one year before testing. The following wear conditions where used: geometry, pin-on-disc with vertical pin of 10 mm diameter AISI 52100 ball; 20 N load; 0.033 m s^{-1} speed; 14408 s duration and 21 °C test temperature.

3. Results and discussion

Raman spectra were recorded between 200 and 1800 cm^{-1} in order to obtain information regarding the degree of crystallinity of the coatings. Figs 2 and 3 show Raman spectra recorded for two samples of DLC on glass substrates grown under similar deposition conditions using butane as the source gas. In the second sample, nitrogen was introduced into the system prior to deposition, the gas sequence being argon and butane for sample 1 and argon, nitrogen and butane for sample 2. In both cases the spectra are very

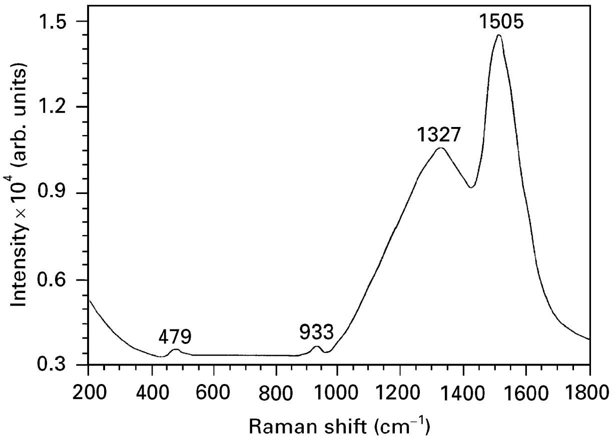

Figure 2 Raman spectrum of DLC without nitrogen in the process.

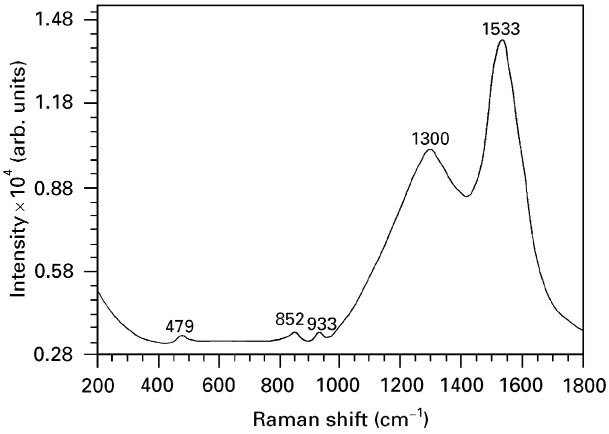

Figure 3 Raman spectrum of DLC with nitrogen introduction prior to deposition.

similar with two major peaks between 1000 and 1800 cm^{-1} and minor peaks at the lower end of the spectra. The spectrum for sample 1 (without nitrogen) shows the major peaks appearing at 1365 and 1575 cm^{-1}. However the addition of nitrogen results in better resolution and a shift from 1365 to 1350 cm^{-1} and from 1575 to 1585 cm^{-1}. The two major peaks are referred to as G and D bands [1, 22]. In crystalline graphite only the G band appears at 1575 cm^{-1} with a narrow bandwidth. For pure diamond a sharp single band is expected at 1332 cm^{-1}. The D band occurs at around 1360 cm^{-1} and shows the presence of finite crystallite sizes from pyrolytic graphite, glassy carbon and carbon powders and could be a consequence of sp^3 bonded species. It is found that the D band shifts to higher wave number with increasing disorder. In these experiments, the addition of nitrogen caused the D band to shift slightly to a lower wave number, perhaps indicating a small improvement in the degree of crystallinity. The reason for nitrogen causing improved crystallinity is unclear, however, it may be related to the exclusion of oxygen from the surface prior to deposition. This observation has been reported in the literature [1] and requires further investigation. These results indicate, due to the shift of the D band, that the films consist of small crystallites of diamond characteristic of DLC material. It has been shown [1] that the D/G ratio is proportional to the reciprocal of crystallite sizes ($D/G \propto 1/C_s$). The D/G ratio indicates that the crystallite size is approximately 10 nm [1, 22].

DLC films were deposited using the hybrid plasma assisted CVD system onto aluminium and stainless steel substrates. Fig. 4 shows a thermoanalysis spectrum for films deposited onto an aluminium substrate and Fig. 5 shows a spectrum for films deposited on a stainless steel substrate. The coating deposited on a stainless steel substrate exhibits two peaks, a strong peak at 520 °C and a very weak peak at about 790 °C perhaps due to the oxidation of two types of species. However the film deposited on an aluminium substrate shows a single peak at 535 °C. These films were deposited under identical conditions in the hybrid PACVD system. The major peak for synthetic diamond appears at between 650–750 °C and for plasma deposited polycrystalline diamond film at 1072 °C [18]. For amorphous carbon the major peak is usually shown between 420–490 °C [18]. It appears from the initial analysis that for both experimental coatings, irrespective of the substrate, small crystallites of diamond in a graphite matrix are present, with those on steel containing a greater degree of diamond crystallinity. These results show that the characteristics of the substrate surface can have a significant effect on the structural properties of the carbon coatings. This is well known since CVD is a surface sensitive process and thus highly dependent on the surface structure and composition for a variety of coatings [23]. The quantification of carbon on both substrates showed the average surface concentration to be in the order of 150 $\mu g\,cm^{-2}$ and 70 $mg\,cm^{-2}$ for aluminium and stainless steel, respectively.

Fig. 6a shows a scanning electron microscope (SEM) micrograph of DLC deposited by hybrid PACVD at low temperature onto aluminium/silicon metal matrix composites (MMC). The figure reveals a typical MMC substrate structure which is porous with numerous voids and a matrix of material. For applications such as the modernized two-stroke engine, structures of this type of material make them light and durable. However, deposition of a number of coatings onto these materials is difficult using conventional vacuum deposition methods such as PVD and CVD, due to the porosity and inhomogeneous surface of the material. SEM examination reveals these voids to be variable in size but typically in 5–25 μm range. The DLC coating structure deposited onto the MMCs is very dense with a rough surface. There are several factors which contribute to the film density and adhesion to the substrate. An important consideration is that the magnetic confinement and the substrate bias which confine the electrons and ions in the region above the substrate and positive ions are accelerated towards the substrate causing dense films and much improved adhesion. The beneficial effects of ion-bombardment on the density and adhesion of coatings have been discussed in ion-assisted PVD processes [6]. In other ion-assisted processes, such as unbalanced magnetron sputtering and dynamic recoil mixing, the ions bombard the growing film giving superior adhesion [8]. An additional feature of the current

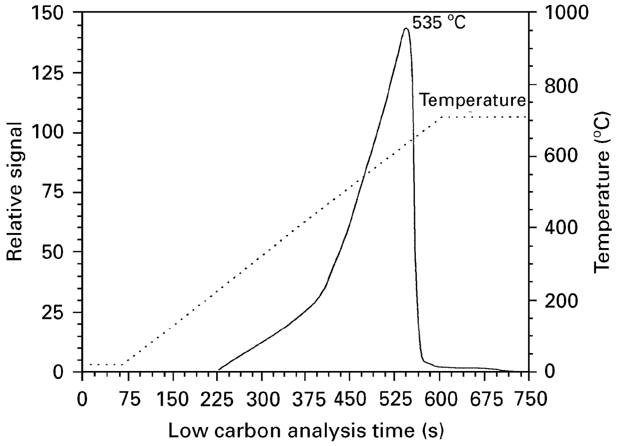

Figure 4 Thermoanalysis of DLC on aluminium.

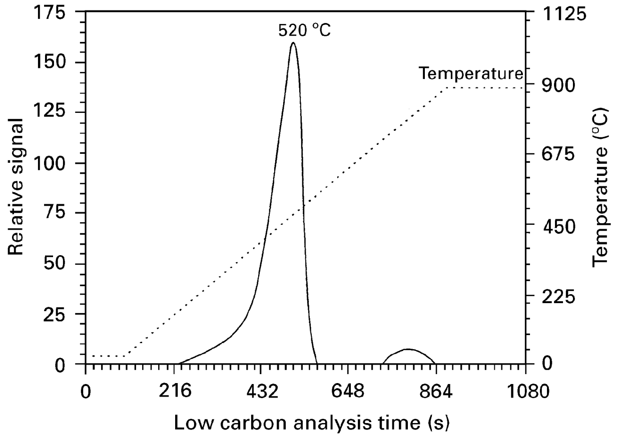

Figure 5 Thermoanalysis of DLC on stainless steel.

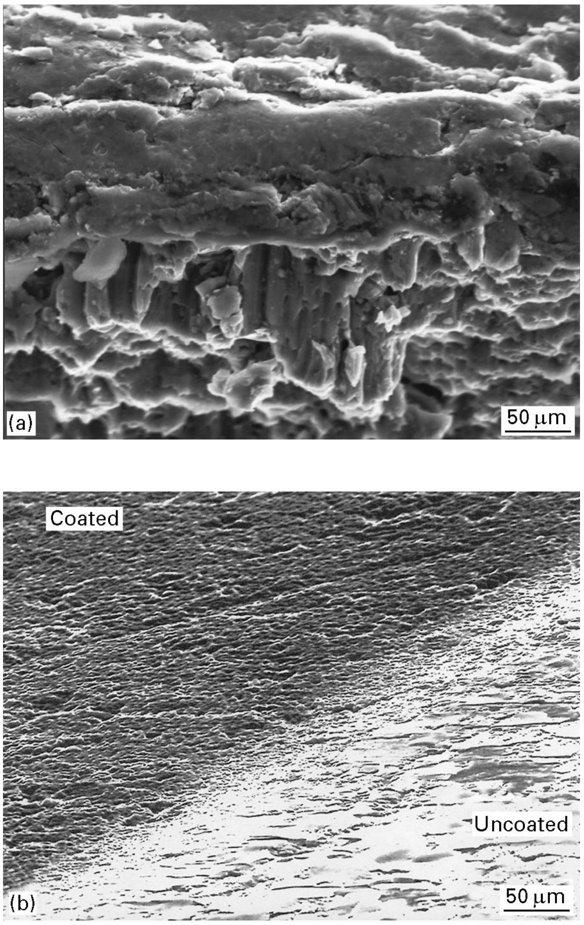

Figure 6(a) SEM of DLC coating onto MMC substrate. (b) SEM of coated and uncoated regions of MMC substrate.

process is the use of an electron filament which increases the ionization efficiency of the plasma as the electrons continuously bombard the space in the gas phase near the surface. An essential consideration for improving wear performance in coated components is the surface characteristics such as the degree of the surface roughness. Fig. 6b shows an SEM micrograph of DLC coated and uncoated region of MMC substrate. The uncoated region appears to have a flaky surface whereas the coated region has a rough appearance. Variable flakes up to about 30 μm appear in the uncoated MMC and this effect could be due to the surface preparation techniques employed. At higher magnification the surface differences are more apparent with the coated surface being much rougher than the uncoated surface. One would expect a conventional CVD process to procedure a surface roughness not too different from the substrate [22]. Therefore it is probable that in the modified CVD process other factors need to be taken into consideration to explain the unexpected observation. A possible explanation for the rougher coated surface may be attributed to high energy ion bombardment of the growing film due to the use of an electron filament, magnetic confinement and substrate bias. As mentioned earlier, all these factors will have an additive effect and will tend to increase the plasma intensity and ion bombardment. Energetic positive ions bombard the negatively biased coating/substrate and their high energy causes sputtering of the growing films thus giving rise to the rough surface observed. The effects of the plasma parameters, substrate temperature and system pressure need to be investigated further.

Table I outlines the wear resistance tests performed on 1/4 inch HSS drills using a Bridgeport CNC machine. The use of a CNC machine ensured that all tests were carried out under identical and consistent conditions. These drills were coated with DLC and were compared to drills coated with TiN. Test 2 shows that DLC was superior to TiN. In this test the drills were used on thyroplast steel.

Pin-on-disc wear testing illustrated some interesting behaviourial information including an initial low friction and wear before a steady state is achieved. These phenomena are shown in Figs 7 and 8. The displacement wear, which is typical of DLC coatings, is seldom mentioned by expert tribologists as the mechanisms at work in the contact wearing process are not fully understood [24, 25]. Wear test results are given in Table II.

Based on microstructural observations, the behaviour of the DLC coating–substrate system when tested for wear with the pin-on-disc machine can be explained in the following way. In the early test period there is little interaction between the pin and coating because interface temperatures are low and this results in low friction coefficients. Increasing temperatures at the contact point result in rapidly rising friction and

TABLE I Cutting and wear resistance trials on 1/4 inch steel drills coated with DLC and TiN

Drill number	Initial inspection comments	Number of holes	Final inspection comments
11	Carbon, dark grey on tyre steel	76 DU	AMG 1.3 2250 r.p.m. × 657 mm min^{-1}. Arcs on chisel. Cutting edges worn most at corners. Coating off lands and flutes behind lands.
Control	TiN on tyre steel	200 SC	AMG 1.3 2250 r.p.m. × 657 mm min^{-1}. Cutting edge corners slightly worn. Still cutting.
19	Carbon, dark grey on thyroplast steel	137 DU	AMG 1.5 1555 r.p.m. × 178 mm min^{-1}. Cutting edge corners worn. Heels slightly worn. Coating off lands and flutes behind lands.
Control	TiN on thyroplast steel	115 BO	AMG 1.5 1555 r.p.m. × 178 mm min^{-1}. Worn down 13 mm front point.
16	Carbon, dark grey on stainless steel	132 SC + 11 SC + 4 DU	AMG 2.2 650 r.p.m. × 85 mm min^{-1}. 715 r.p.m. × 93 mm min^{-1}. 786 r.p.m. × 102 mm min^{-1}. Swarf adhesion at cutting edges. Chisel corner worn. Cutting edge and corners worn. Coating off lands and flutes.
Control	TiN on stainless steel	132 SC + 11 SC + 4 DU	AMG 2.2 650 r.p.m. × 85 mm min^{-1}. 715 r.p.m. × 93 mm min^{-1}. 786 r.p.m. × 102 mm min^{-1}. Corners, cutting edges and chisel badly worn. Coating off lands and flutes.
15	Carbon, dark grey on cast iron	125 SC	AMG 3.1 1540 r.p.m. × 203 mm min^{-1}. Cutting edge and chisel slightly worn. Coating off lands.
Control	TiN on cast iron	125 SC	AMG 3.1 1540 r.p.m. × 203 mm min^{-1}. Cutting edge slightly worn. Chisel corner worn.

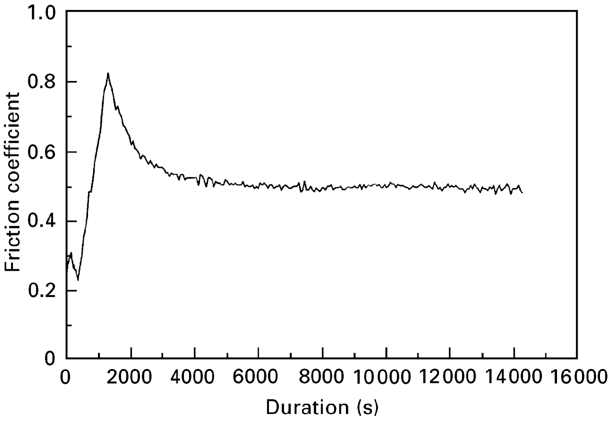

Figure 7 Friction behaviour of DLC.

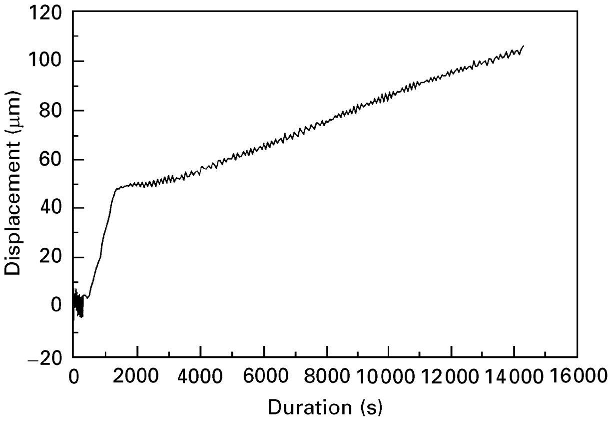

Figure 8 Wear characteristics of DLC.

consequent wear. A steady state is achieved and a relatively constant proportion of the wear track is covered with transferred material from the pin or ball. The test then turns into a steel on transferred steel test and the coefficient of friction gradually reduces as the contact surface is worn smoother and lubricated with the

TABLE II Pin-on-disc wear test results of DLC coating on zirconia substrate

Wear test results	
Overall wear	115 μm
Ball ring loss	0.0011 g
Ring mass gain	0.0008 g
Final friction coefficient	0.48
Minimum friction coefficient	0.23
Maximum friction coefficient	0.83

DLC. Oxidation processes at the contact point and in close proximity may also contribute to the physical characteristics of the friction and wear of DLC coatings on zirconia substrates [6].

4. Conclusions

DLC films have been deposited using a hybrid plasma assisted CVD with RF excitation of butane with no independent heating of the substrate. The addition of nitrogen to butane prior to the deposition of the film can aid growth of crystallites during deposition probably due to the elimination of oxygen from the surface. As with all surface sensitive deposition processes including CVD and PVD, both scanning electron micrographs and thermoanalysis showed that the substrate, such as MMCs, will have a significant influence on the film properties [26]. Increasing the plasma intensity by using a venturi magnetic confinement ring, electron filament and substrate bias have been shown to have beneficial effects on the film adhesion, density and microstructure [22]. The hybrid plasma CVD method was successful in depositing coatings onto the inhomogeneous surface of the MMC substrate [26]. DLC was also found to have superior cutting and wear resistance properties compared to TiN when deposited on HSS drills.

References

1. T. DINES and D. TITHER, *Carbon* **29** (1991) 225.
2. D. TITHER, *Technovation* **10** (1990) 39.
3. D. V. FEDOSEEV and B. V. DERJAGUIN, "Science" paper published by Nauka, Moscow, 1984.
4. P. BACHMAN, *Phys. World* **10** (1991) 16.
5. D. HOOVER, SUI-YUAN LYNN and DIWAKER GARG, *Solid State Techn.* **104** (1991) 24.
6. K. ENKE, Goram Advanced Materials Conference, London, May 1990 (Presentation) (Goram Advanced Materials, London, 1990).
7. H. E. SPEAR and J. P. DISMUHES, "Synthetic Diamond, Emerging CVD Science and Technology", The Electrochemical Society Series (John Wiley & Sons, New York, 1994).
8. K. V. RAVI, Dimond Technology (John Wiley and Son Inc., New York, 1994).
9. D. TITHER, W. AHMED, M. SARWAR and E. AHMED, *J. Mater. Sci. Lett.* **14** (1995) 1062.
10. D. TITHER, A. MATHEWS, P. JOHN, J. WILSON, *Surf. Coatings Technol.* **38** (1989) 251.
11. J. E. FIELD (Ed.), Diamond and Hard Materials (Academic, London, 1979).
12. D. R. DECKER, A. J. SCHORR, *IEEE Trans. Electron Devices*, **ED 17** (1970) 739.
13. J. RUSSEL, *Diamond Deposition*, **4** (1993) 172.
14. R. MESSIER, in Proceedings ICMC, 1987 (ICMI, San Diego, 1987).
15. Plasma 8 Workstation: Application note (BEP Grinding Ltd., Manchester, UK, 1994).
16. Low temperature RF Plasma Enhanced system 100: Application Note (BEP Grinding Ltd., Manchester, UK, 1994).
17. W. MORAWSKI and D. TITHER, in Proceedings Catal-Warsaw, 1992 (Catal-Warsaw, Poland, 1992).
18. Z. CIZEK, P. BOREK, J. FIALA and B. BOGDAIN, *Mikrochim. Acta (Wien)* **III** (1990) 163.
19. R. PENGELLY, Application notes, Universal Wear Testing Machine, (BICERI Ltd, Slough, UK, 1994).
20. M. G. GEE, Guidelines for unlubricated sliding wear tests, Part 1 General approach (National Physical Laboratory, Teddington, UK, 1993).
21. Idem, Guidelines for unlubricated sliding wear tests, part 2. Procedures for pin-on-disc testing (National Physical Laboratory, Teddington, UK, 1993).
22. D. TITHER, A. BEHBI, P. HOLIDAY, A. MATHEWS, A. G. FITZGERALD, A. E. HENDERSON, B. E. STOREY, T. J. DINES, P. JOHN and J. I. B. WILSON, *Carbon* **28** (1990) 641.
23. M. SARWAR, W. AHMED and D. TITHER, in Proceedings of the First International Conference on Quality and Reliability, Vol. 2, edited by W. S. Lau, T. C. Lee, H. C. Tsang and C. Y. Tang, 11–12 April 1995, Hong Kong, (The Hong Kong Polytechnic University, Hong Kong, 1995) pp. 233–236.
24. F. M. KUSTAS, M. S. MISRA, R. WEI and P. J. WILBUR, *Tribology Trans.* **36** (1993) 1.113.
25. D. KLAFFKE, R. WASCHE and H. CZICHOS, *Wear* **153** (1992) 149.
26. D. TITHER, W. AHMED, M. SARWAR, T. KOLSAKER and E. AHMED, *Islamabad J. Sci.* (1996) (in press).

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