Available online at www.sciencedirect.com
SCIENCE DIRECT®
Diamond and Related Materials 13 (2004) 610–615
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

Enhancing nucleation density and adhesion of polycrystalline diamond films deposited by HFCVD using surface treaments on Co cemented tungsten carbide

H. Sein[a], W. Ahmed[a,*], M. Jackson[b], R. Polini[c], I. Hassan[a], M. Amar[a], C. Rego[a]

[a]*Department of Chemistry and Materials, Manchester Metropolitan University, Chester Street, Manchester, M1 5 GD, UK*
[b]*Department of Mechanical Engineering, Tennessee Technological University, P.O. Box 5014, Cookeville, TN 38505, USA*
[c]*Dipartimento di Scienze e Tecnologie Chimiche, Universita' di Roma 'Tor Vergata', Via Della Ricerca Scientifica, 00133 Roma, Italy*

Abstract

The deposition of diamond films by chemical vapour deposition onto tungsten carbide is an attractive proposition since it can lead to improvements in the life and performance of cutting tools. However, deposition of diamond onto cemented tungsten carbide (WC-Co) dental burs and inserts are problematic due to the cobalt binder in the WC that provides additional toughness to the tool but it causes poor adhesion and low nucleation density. A number of surface treatments can be used to overcome these problems including chemical etching, ion implanting, interlayer coating and bias treatment. Negative biasing of the substrate is attractive because it can be controlled precisely; it is carried out in-situ, gives good homogeneity and results in improved adhesion. On flat substrates, such as copper and silicon, biasing has been shown to give better adhesion, improved crystallinity and smooth surface. In this study, we have used a modified hot filament chemical vapour deposition (HFCVD) system to coat complex shaped tools such as dental burs with polycrystalline diamond films, which have good adhesion and crystallinity. By applying a negative bias to the substrate, we show that the nucleation density, adhesion and surface properties can be improved. The effects of various process parameters such as bias time, emission current, bias voltage and the filament arrangement on the film properties are reported. For machining applications CVD diamond coatings must be hard, wear resistance and having a good quality film.

Keywords: Cutting tools; Nucleation; WC-Co; Chemical vapour deposition (CVD)

1. Introduction

Diamond films are of significant interest for cutting tools applications, such as rotary drills and inserts due to their excellent physical and chemical properties. The deposition of adherent high quality diamond onto substrates such as cemented carbides, stainless steel and various metal alloys containing transition elements present a considerable challenge due to poor adhesion and low nucleation density [1–7]. Chemical vapour deposition (CVD) of diamond coatings has the potential to prolong the lifetime of WC-Co cutting tools when applied to the machining of highly abrasive non-ferrous metallic alloys, composite and ceramic materials. However, the presence of cobalt (Co) binder, typically at levels of 6–10%, in the cemented carbide substrates has a detrimental influence on the deposition process. Binder materials such as Co can suppress diamond growth favouring the formation of non-diamond carbon phases, i.e. graphitic deposits with poor adhesion [8]. The high Co content in the substrate has been reported to be the main cause of poor adhesion [9]. To promote adhesion chemical treatment using Murakami agent and acid etching has been used to successfully remove the Co binder from the substrate surface [10].

Nucleation of diamond is an important step in the growth of diamond thin films, because it strongly influences the diamond growth process, film quality and morphology [11]. Generally, seeding or abrading with diamond powder or immersing in diamond paste containing small crystallites processed in an ultrasonic bath enhances nucleation. The most promising in-situ method for diamond nucleation enhancement is negative substrate biasing during the initial stage of deposition [12]. Some has been done on negative bias enhanced nucle-

*Corresponding author. Tel.: +44-161-247-1423; fax: +44-161-247-6357.
E-mail address: w.ahmed@mmu.ac.uk (W. Ahmed).

0925-9635/04/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2003.11.023

ation (BEN) for flat WC-Co inserts using microwave plasma CVD (MWCVD). In this article, we report the results obtained on negative BEN of diamond films deposited onto complex three-dimensional shaped rotary cutting tools, e.g. cemented WC-Co dental bur using a modified vertical hot filament CVD system.

2. Experimental

The system was built with a water-cooled stainless steel chamber as described previously [13]. The gas sources used were 1% methane with excess hydrogen; the hydrogen flow rate was 200 sccm while methane flow rate was 2 sccm. The deposition time and pressure in the vacuum chamber were 10.0 h and 26.6 mbar (20 Torr), respectively. The filament temperature was measured using an optical pyrometer and values between 1700 and 2100 °C were obtained. Substrate temperature was measured to be between 800 and 1000 °C using a K-type thermocouple in direct thermal contact with the dental bur. The system allowed independent dc bias to be applied between the substrate and the filament. Tantalum wire, 0.5 mm in diameter, 12 cm in length (uncoiled) was used as the hot filament. The filament is mounted vertically with the dental bur held in between the filament coils as opposed to the horizontal position in the conventional HFCVD systems. The new vertical filament arrangement used in modified HFCVD systems improves the thermal distribution [13].

Rotary cutting tool made of WC-Co dental bur 1 mm in diameter and 10 mm in length of cutting edge, which contained 6% cobalt as binder was used as the substrate. Prior to deposition, the substrate was chemically pretreated with Murakami agent followed by acid etching [14]. The dental bur was vertically mounted on the diamond coated molybdenum substrate holder and positioned centrally and coaxially within 5-mm distance of the coiled filament [15]. Before deposition with CVD diamond, the filament was pre-carburised for 30 min in 3% methane with excess hydrogen to enhance the formation of TaC layer on the filament surface in order to reduce the tantalum evaporation during diamond deposition [16].

A negative bias voltage up to −300 V was applied to the substrate relative to the filament. This produced emission currents up to 200 mA. The nucleation times used were between 10 and 30 min. In the activated deposition chamber, CH_4 and H_2 were decomposed into various chemical radicals species CH_3, C_2H_2, CH_2, CH, C and atomic hydrogen H by the hot tantalum filament. The methyl radicals and atomic hydrogen play are known to be important roles in diamond growth. In the biasing process, electrons were emitted from diamond coated molybdenum substrate holder and moved to the filament after they gained energy from the electrical field. When the negative bias was applied to the anode

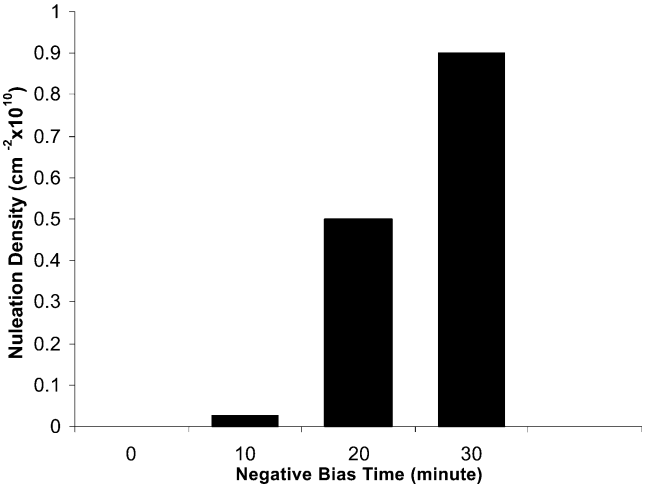

Fig. 1. The different bias times related to the density of nucleation at −300 V.

the voltage was gradually increased until a stable emission current was established and a luminous gas discharge was formed near the substrate [17].

3. Results and discussions

The crystallinity and nucleation characteristics of the as-grown diamond films were characterized using scanning electron microscopy (SEM) (Jeol JSM-5600LU). The applied bias voltage was maximum of −300 V and methane concentration was kept at 3%. The nucleation density of diamond was calculated from the SEM micrographs. Figs. 1 and 2 show the effects of bias time on the nucleation density at bias voltage of −300 V. It is clearly evident that as the bias time is increased the nucleation density also increases. The highest nucleation density was calculated to be 0.9×10^{10} cm^{-2} for a bias time of 30 min. At a bias time of 10-min the nucleation density obtained was 2.7×10^{8} cm^{-2}.

Fig. 3 shows the variation of the emission current as a function of the negative bias applied to the substrate holder where the bias emission current increased rapidly after −180 V [18]. Wang et al. also reported that an increase in the emission current produced higher nucleation densities [19]. Since, the bias voltage and emission current are related, the enhancement of the nucleation density cannot be attributed to solely ion bombardment or electron emission of the diamond coated molybdenum substrate holder, but may be a combination of these mechanisms [20]. Our result was purely based on negatively bias enhanced nucleation related to the grounded filament. However, Polo et al. reported that very low electric biasing current values (microampere) were detected for applied substrate biases voltages either positive or negative. Furthermore, when increasing negative biases of up to −200 V resulted in value of nucleation density is similar to that obtained with posi-

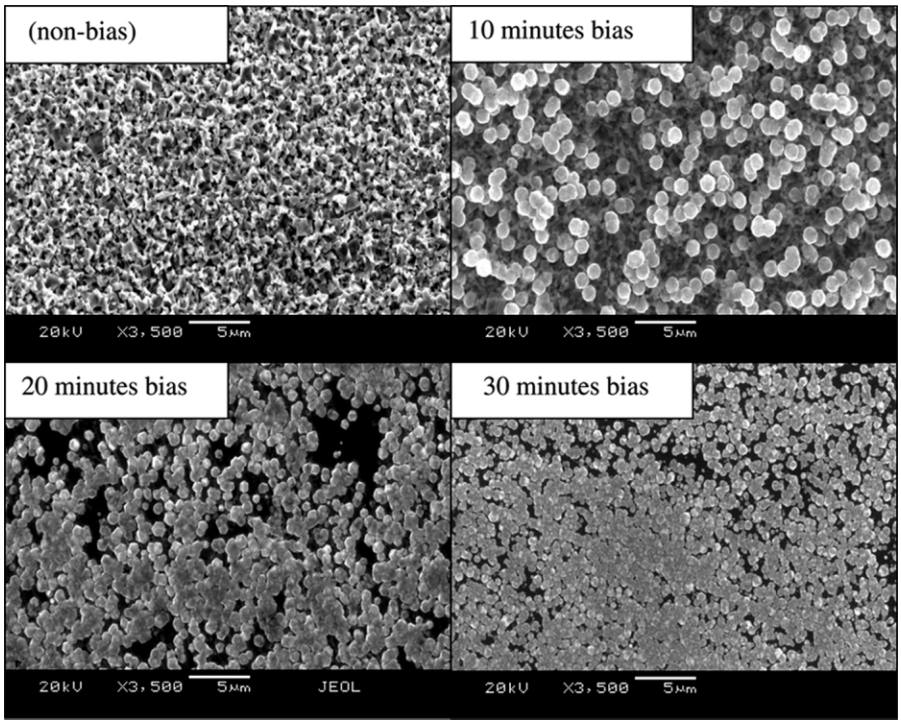

Fig. 2. SEM of nucleation densities at different bias time at −300 V.

tively bias enhanced nucleation related to the filament. In contrast, an application of negative bias applied to the substrate at −250 V resulted in (10^{10} cm^{-2}) maximum values of nucleation density. The enhancement in the nucleation density could be attributed to the electron current from the filament by increasing the decomposition of H_2 and CH_4 [20]. The increase in the nucleation density is as expected since negatively biasing the substrate increases the rate of ion bombardment into the surface creating greater numbers and density of nucleation sites. Therefore, the greater the density of nucleation sites the higher the expected nucleation den-

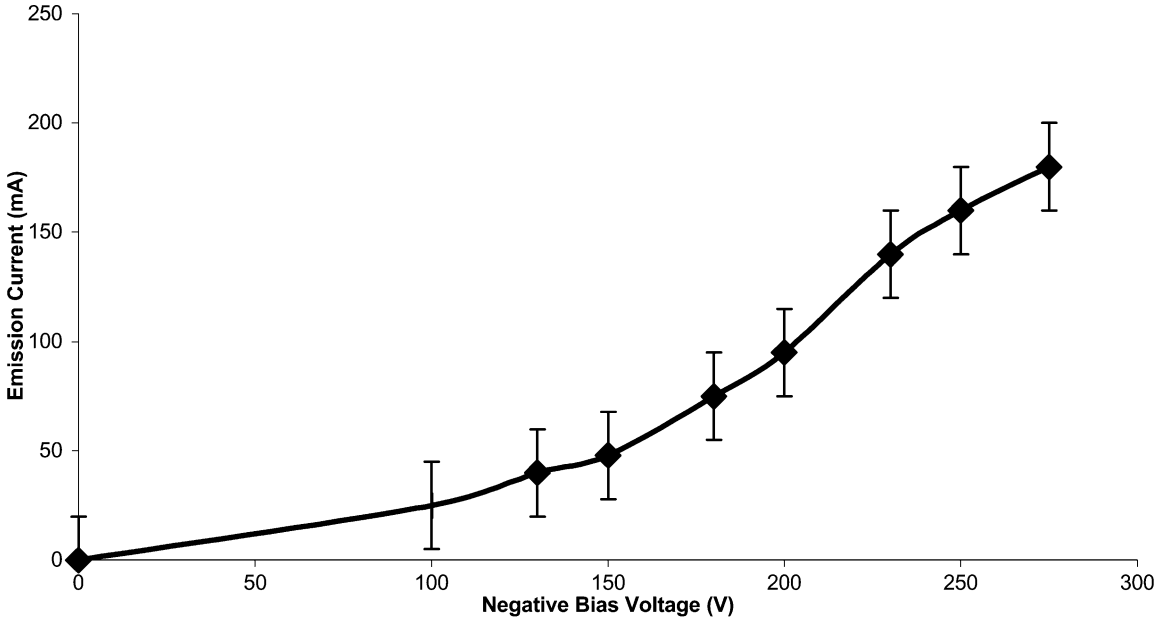

Fig. 3. The variation of emission current against function of negative bias voltage.

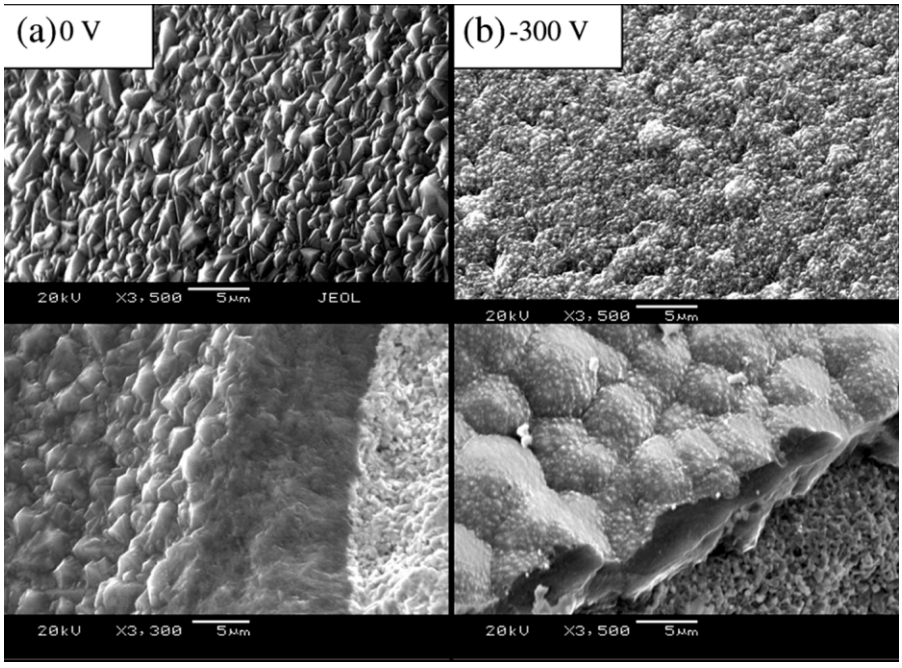

Fig. 4. (a) Diamond crystallite size and cross section of film at non-bias, (b) Diamond crystallite size and cross section of film at −300 V (negative bias).

sity. Kamiya et al. reported that reproducibility of the experiment was poor and that no definite trend in the nucleation density could be found with respect to different bias conditions [21].

Fig. 4 shows SEM's of diamond crystallites and cross section of diamond films at non-bias (a) 0 V and (b) at −300 V negative substrate bias for 30 min and followed by 10 h growth. In general, as the negative bias voltage was increased the average crystallite size decreased with the surfaces of the film become smoother. Without biasing the average crystallite size was ∼2–2.5 μm. However, at −300 V negative bias the crystallite size decreased to ∼0.1 μm representing a decrease in crystallite size by a factor of ∼20. It is evident from the SEM that the biased film was much smoother than the non-biased diamond coating. This result could be significant in applications requiring ultra smooth hard coatings such as optical lenses and biomedical implants. The BEN pre-treatment has proven to be very efficient not only in enhancing the nucleation density but also in growing adherent oriented diamond films [21]. The advantage of the BEN process is that it minimizes physical damage to the substrates in contrast to other nucleation enhancing pre-treatments such as abrading or scratching. In addition BEN gives better control in creating nucleation sites for subsequent diamond growth. It could provide uniformity of diamond film on cutting edge, which ideal for cutting and machining of dental burs used in laboratory and clinical surgery.

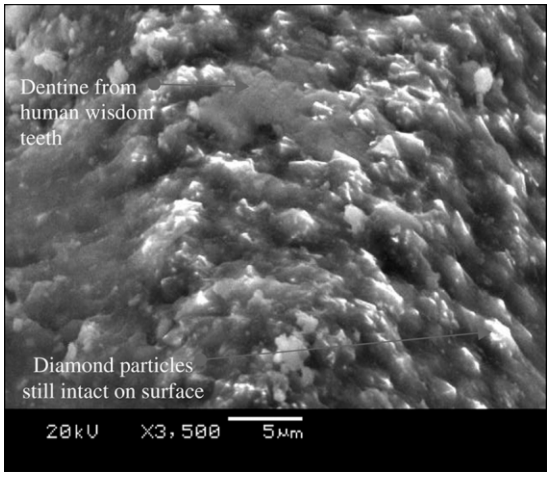

Fig. 5. Diamond film on cutting edge of WC-Co dental bur after testing on human teeth.

Application of negative bias enhanced nucleation is one of the surface treatments of dental burs, which are used in the dental laboratory and clinical surgery for removing unwanted material from teeth. The diamond coated WC-Co dental burs were tested with human teeth in order to observe their adhesive strength of diamond particles on the surface. The coated burs have been tested on extracted human wisdom teeth, which have a difference in hardness between enamel and dentine. The teeth were cut in a bench device using an ultra high-speed hand piece (air rotor). A frequency meter moni-

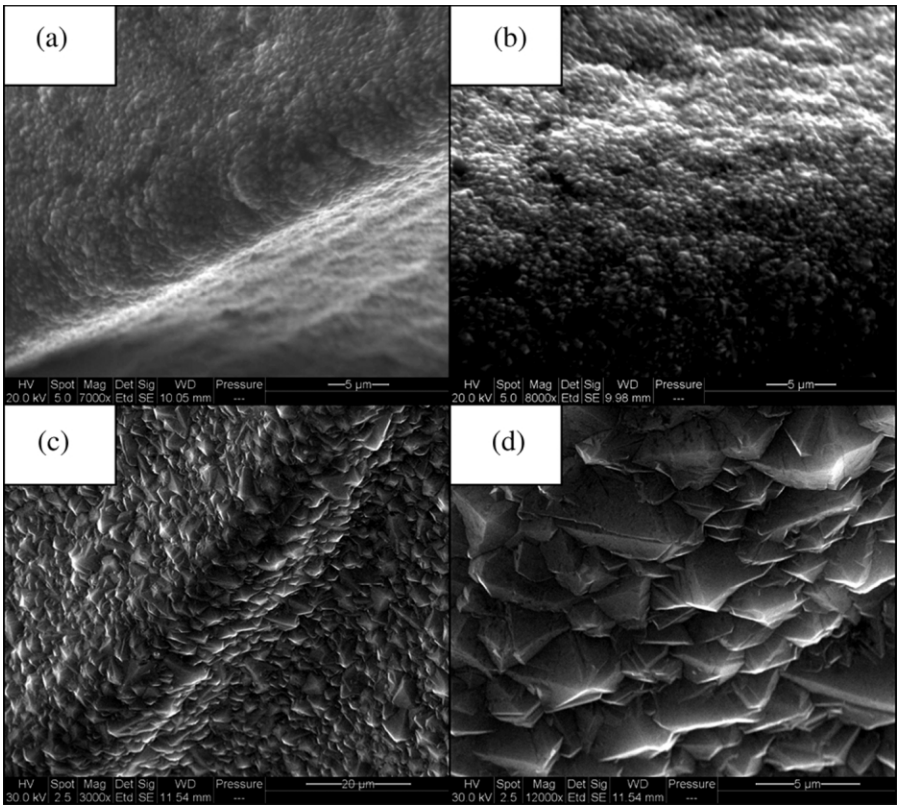

Fig. 6. (a) and (b) Negative bias assisted diamond film on cutting edge of dental bur, (c) and (d) Non-bias assisted diamond film on cutting edge of dental bur.

tored the speed of the hand piece, which was between 20 and 250 K rev./min. Water-cooling device was used to prevent the tool over heating. The SEM micrograph of tested dental bur has shown that diamond film was still intact after the application of highly abrasive cutting at a speed of 250 000 rev./min for 2 min (Fig. 5). These results are extremely encouraging and clearly demonstrate the extreme toughness and durability of the diamond films using our modified HFCVD system.

Fig. 6 shows SEMs of diamond on the cutting tool edges with negative biasing (a and b) and without any bias treatment (c and d). It is evident that the cutting edges are uniformly coated with CVD diamond in both cases. However, when biasing is employed there is a considerable reduction of average crystal size, therefore negative biased enhanced nucleation (BEN) creates more nucleation sites for uniform diamond growth resulting in smaller average crystallite sizes.

The interfacial crack extension behavior was simulated by finite element method (FEM). The amount of energy released when the crack extends by a unit area (energy release rate), was calculated by FEM [22,23]. The average load required to scratch off these diamond particles from the substrate surface was obtained to be 46 mN. The energy release rates for mirror-polished silicon substrate as compared to non-bias WC-Co substrate were measured 5 and 14 Jm^{-2}, respectively [24]. It is expected that better results can be obtained using the bias process as shown by our highly abrasive clinical test on extremely tough tooth material. Kamiya et al. proved that the maximum value of adhesive toughness, approximately 30 Jm^{-2} is the highest one obtained in their experience in the adhesion of diamond films on bias enhanced flat WC-Co substrate [21].

Trava et al. have analysed the cost implications of scaling up the hot filament CVD process for depositing diamond onto dental burs for industrial scale production. If a single reactor is employed the average cost of the coating is of the order of approximately £5. However, if a 50-reactor system is used in parallel then there is a 50% reduction in the overall cost of the coated bur to approximately £2.50. Further scaling up the process to utilise a 100-reactor system reduces the cost to an economically feasible £0.60. With this system the impact of film-thickness is minimal whereas for a single reactor system there is a significant increase in the cost when thicker coatings are deposited [25].

4. Conclusions

The use of negative substrate biasing and chemical etching enhanced the nucleation density of diamond.

Short bias times of the order of 10, 20 and 30 min were sufficient for the subsequent growth of quality diamond films. Smoother diamond films were obtained after biasing at higher voltages (−300 V). This study can be contributed that re-nucleation of diamond was required by repeated application of negative biasing during the standard deposition process as future work. This may be due to secondary nucleation mechanisms of diamond on the deposited surfaces, which produced thicker films with an increased nucleation density.

Acknowledgments

H. Sein is grateful to the Faculty of Science and Engineering at MMU for the studentship. Prof. A. Mainwood is acknowledged for providing a travel grant to the Diamond-2003 conference. Ms A.N. Jones is acknowledged for useful assistance. Mr N. Jenkinson (MMU) is acknowledged for SEMs analysis.

References

[1] T. Leyendecker, O. Lemmer, A. Jurgens, S. Esser, J. Ebberink, Surf. Coat. Technol. 48 (1991) 253.
[2] M. Murakawa, S. Takeuchi, Surf. Coat. Technol. 49 (1991) 359.
[3] T. Yaskiki, T. Nakamura, N. Fujimori, T. Nakai, Surf. Coat. Technol. 52 (1992) 81.
[4] J. Reineck, S. Soderbery, P. Eckholm, K. Westergren, Surf. Coat. Technol. 57 (1993) 47.
[5] H.Z. Wang, R.H. Song, S.-P. Tang, Diamond Relat. Mater. 2 (1993) 304.
[6] A. Inspector, C.E. Bauer, E.J. Oles, Surf. Coat. Technol. 68/69 (1994) 359.
[7] K. Kanda, S. Takehana, S. Yoshida, R. Watanabe, S. Takano, H. Ando, et al., Surf. Coat. Technol. 73 (1995) 115.
[8] S. Amirhaghi, H.S. Reehal, R.J.K. Wood, D.W. Wheeler, Surf. Coat. Technol. 135 (2001) 126.
[9] A. Inspector, E.J. Oles, C.E. Bauer, Int. J. Refract.; Metal Hard Mater. 15 (1997) 49.
[10] H. Itoh, T. Osaki, H. Iwahara, H. Sakamoto, J. Mater. Sci. 26 (1991) 370.
[11] G.F. Zhang, V. Buck, Surf. Coat. Technol. 132 (2000) 256.
[12] I. Gouzman, A. Hoffmann, Diamond Relat. Mater. 7 (1998) 209.
[13] H. Sein, W. Ahmed, C. Rego, Diamond Relat. Mater. 11 (2002) 731–735.
[14] R. Haubner, S. Kubelka, B. Lux, M. Griesser, M. Grasserbauer, J. Phys. C5 (5) (1995) 753, 4th Coll.
[15] P. May, C. Rego, R. Thomas, M.N. Ashfold, K.N. Rosser, Diamond Relat. Mater. 3 (1994) 810.
[16] W. Wang, K. Liao, J. Wang, L. Fang, P. Ding, J. Esteve, et al., Diamond Relat. Mater. 8 (1999) 123.
[17] B.B. Wang, W. Wang, K. Liao, Diamond Relat. Mater. 10 (2001) 1622.
[18] Y.K. Kim, Y.S. Han, J.Y. Lee, Diamond Relat. Mater. 7 (1998) 96.
[19] W.L. Wang, K.J. Liao, G.C. Gao, Surf. Coat. Technol. 126 (2000) 195.
[20] M.C. Polo, W. Wang, G. Sanshez, J. Andujar, J. Esteve, Diamond Relat. Mater. 6 (1997) 579.
[21] S. Kamiya, N. Yoshida, Y. Tamura, M. Saka, H. Abe, Surf. Coat. Technol. 142–144 (2001) 738.
[22] S. Kamiya, A. Inoue, M. Saka, H. Abe, J. Am. Ceram. Soc., submitted.
[23] G.C. Sih, H. Liebowitz, in: H. Liebowitz (Ed.), Fracture, 2, Academic Press, New York, 1968, p. 67.
[24] S. Kamiya, H. Takahashi, R. Polini, E. Traversa, Diamond Relat. Mater. 9 (2000) 191.
[25] V.J. Trava-Airoldi, E.J. Corat, E. Del Bosco, N.F. Leite, Surf. Coat. Technol. 76-77 (1995) 797.