

Critical parameters in hot filament chemical vapor deposition of diamond films on tool steel substrates with CrN interlayers

M. Gowri ^{a,*}, H. Li ^a, T. Kacsich ^b, J.J. Schermer ^a, W.J.P. van Enckevort ^a, J.J. ter Meulen ^a

^a Institute for Molecules and Materials, Radboud University Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

^b Iombond Netherlands BV, Groethofstraat 22b, 5916 PB Venlo, The Netherlands

Received 28 June 2006; accepted in revised form 28 September 2006

Available online 21 November 2006

Abstract

The accomplishment of adherent and continuous diamond coatings on tool steel substrates with CrN interlayers is determined by many key parameters such as appropriate surface finish, interlayer thickness, substrate temperature and system pressure. A detailed study is carried out to probe the effect of these parameters on diamond nucleation and growth. Substrates with different surface finishes are prepared by electrical discharge machining (EDM) and CrN interlayers of various thicknesses are deposited onto these substrates by arc plating. Samples with a CrN interlayer of 2.5 μm are found to provide a continuous diamond film at a low pressure value of about 5 mbar. Nonetheless, the process window for obtaining such diamond layers is small, which results in limited reproducibility.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Steel; Diamond film; Substrate surface finish; CrN interlayer; Interlayer thickness; HFCVD

1. Introduction

Research on the growth of diamond films on steel surfaces has been going on intensively because of their potential applications in high performance machining industry. Various types of interlayers have been investigated addressing the problems that are generally involved in obtaining diamond coating on steel substrates [1–5]. In our previous work, it was found that under certain process conditions the use of chromium nitride (CrN), obtained by Physical vapor deposition (PVD) technique, as an interlayer can be successful to obtain adherent diamond coatings on steel [6,7]. However, interlayer properties and other parameters such as substrate surface finish and deposition conditions are found to be prominently influential in accomplishing the desired outcome. The key problems are non-uniform nucleation and delamination of the diamond layer which often result in lack of reproducibility. Particularly, the

nucleation process is proved to be very crucial in determining the film properties like morphology, homogeneity and adhesion [8]. Even a small change in one of the above mentioned parameters causes a considerable difference in nucleation and growth of the diamond coating. In this study, a number of critical parameters are explored and their influence on the deposited diamond coatings is reported.

2. Experimental

For this study, tool steel samples (DIN: 1.3247), 18 mm in diameter and 4 mm in thickness were used as substrates. These samples were cut from a 18 mm diameter tool steel rod by electrical discharge machining (EDM). Substrates with different surface finishes were obtained with this technique as was further elaborated in Section 3.1. On these substrates, CrN layers of three different thicknesses (2.5, 5 and 8 μm) were deposited by the PVD technique of arc ion plating at 350 °C. The commonly used pretreatment of ultrasonic abrasion with diamond particles (size 1–2 μm) in 2-propanol suspension was applied to promote the diamond nucleation density. During hot filament chemical

* Corresponding author.

E-mail address: m.gowri-manickam@science.ru.nl (M. Gowri).

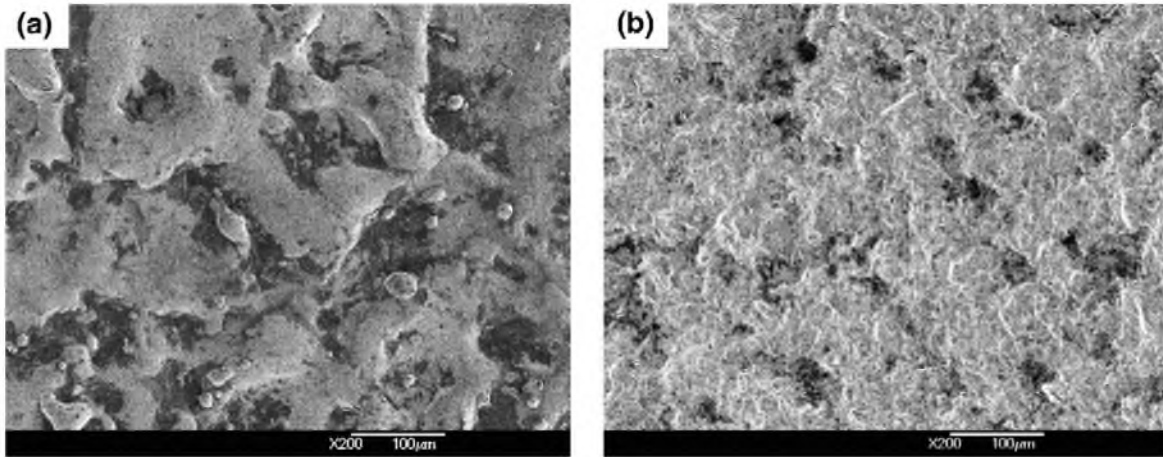


Fig. 1. SEM images showing the topography of the samples prepared by (a) probe EDM and (b) wire EDM.

vapor deposition (HFCVD) of the diamond films, pressures (P) ranging from 5 to 50 mbar and different substrate temperatures (T_s) from 550 °C to 650 °C were employed. For all the diamond deposition runs a growth time of 4 h and a fixed $\text{CH}_4:\text{H}_2$ volume ratio of 0.5% were used. The gas mixture was activated by a Ta

filament and the filament temperature was maintained at 2100 °C which was measured using an infrared thermometer. The substrate was placed on the Mo substrate holder at a distance of 8–10 mm from the filament. After the EDM cutting process, the surface roughness (R_a) was measured with a

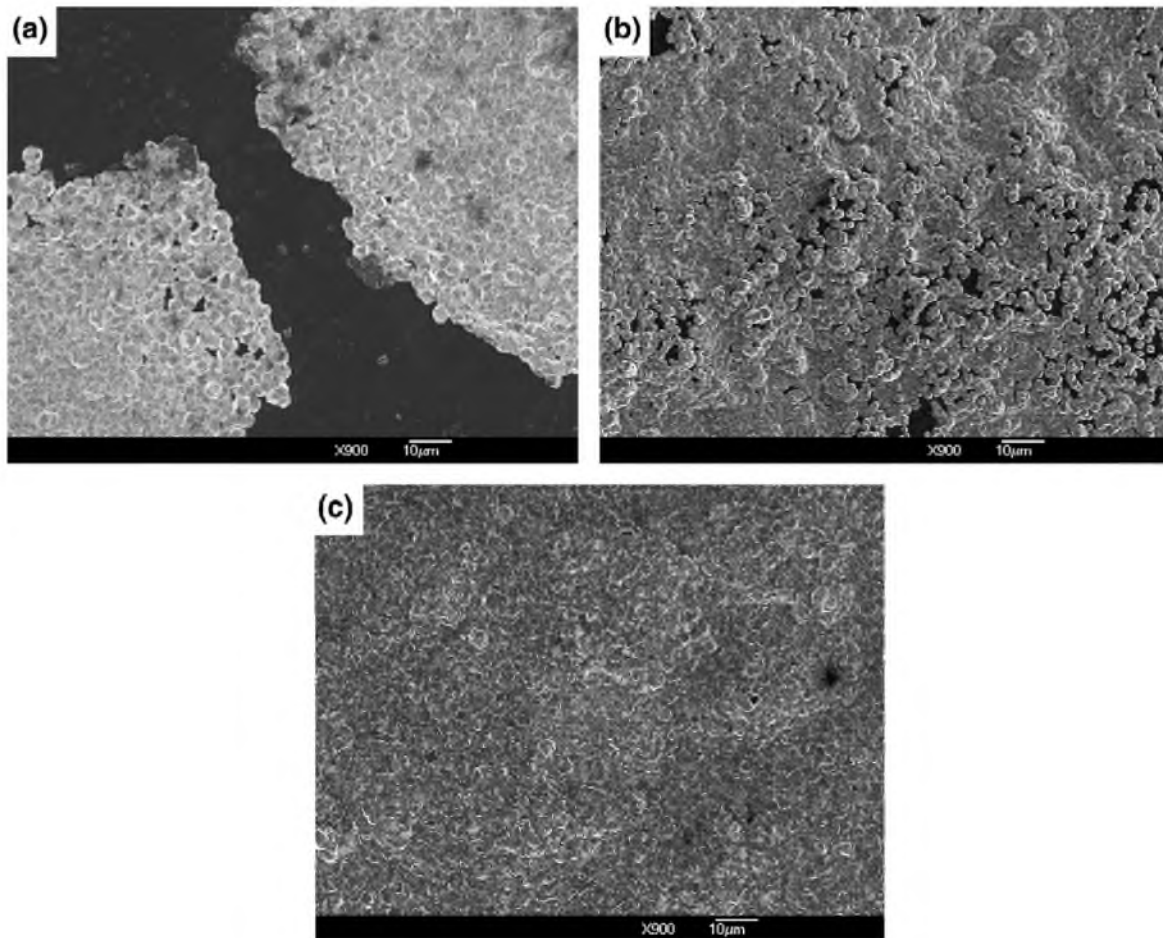


Fig. 2. SEM images of diamond films coated on tool steel samples with a 2.5 μm thick CrN interlayer. (a) Probe EDM ($R_a=2\ \mu\text{m}$), (b) wire EDM ($R_a=1\ \mu\text{m}$) and (c) surface spark erosion ($R_a=1\ \mu\text{m}$).

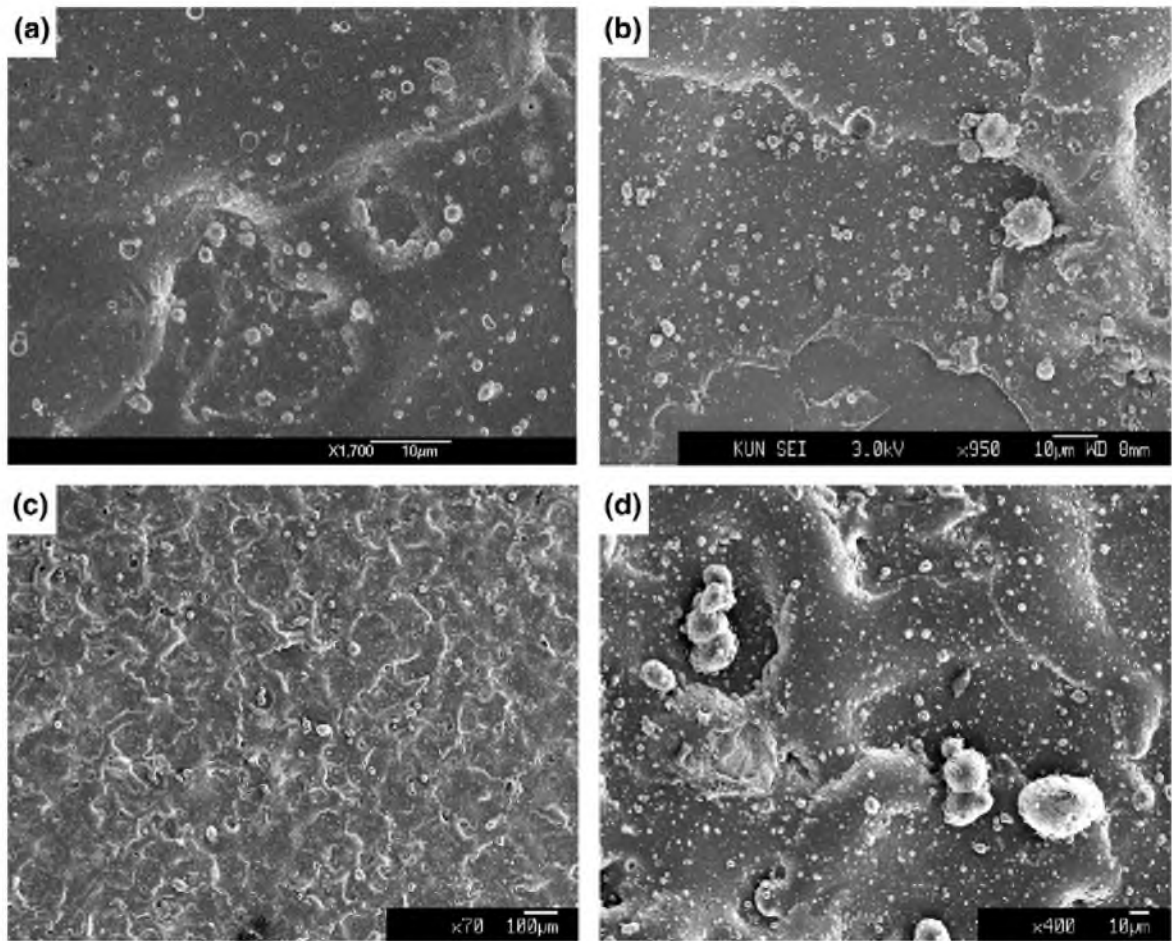


Fig. 3. SEM Images of CrN interlayers with a thickness of (a) 2.5 μm , (b) 5 μm , (c) and (d) 8 μm on tool steel substrates at different magnifications.

perthometer (Perthen Perthometer M4P). Scanning Electron Microscopy (JEOL JSM 6330 F) was used to observe the morphology of the CrN and diamond layers. Raman spectroscopy (Renishaw system 1000) was employed to evaluate the quality and stress state of the diamond films using the excitation wavelength of 514 nm.

3. Results and discussions

3.1. Substrate preparation by EDM

Electrical discharge machining, also known as spark machining, is a process used for hard metals which are very

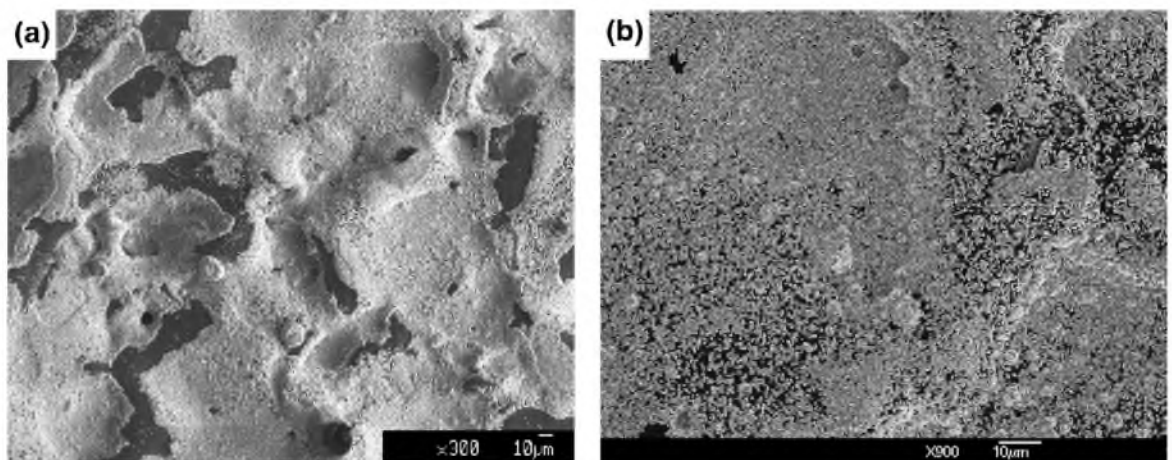


Fig. 4. SEM images of diamond films on tool steel using CrN interlayers with a thickness of (a) 5 μm and (b) 8 μm .

difficult to machine with traditional techniques. EDM is a thermal process [9], where a rapid series of electrical discharges is produced between the work piece electrode and a counter electrode, resulting in local melting and vaporisation of the work piece. Based on the type of electrode used, EDM is classified into two types. In the conventional method, commonly referred to as probe EDM, a copper probe is employed as counter electrode, while a brass wire is used in the

second method which is known as wire EDM. In the probe EDM process, hydrocarbon oil is used as a dielectric liquid and deionized water is used in wire EDM. The dielectric fluid works as a coolant medium and reduces the extremely high temperatures generated in the process. Moreover, it helps to flush away the eroded particles between the work piece and the electrode. Depending on the metal removal rate, a large range of surface finish can be obtained by these techniques. For the

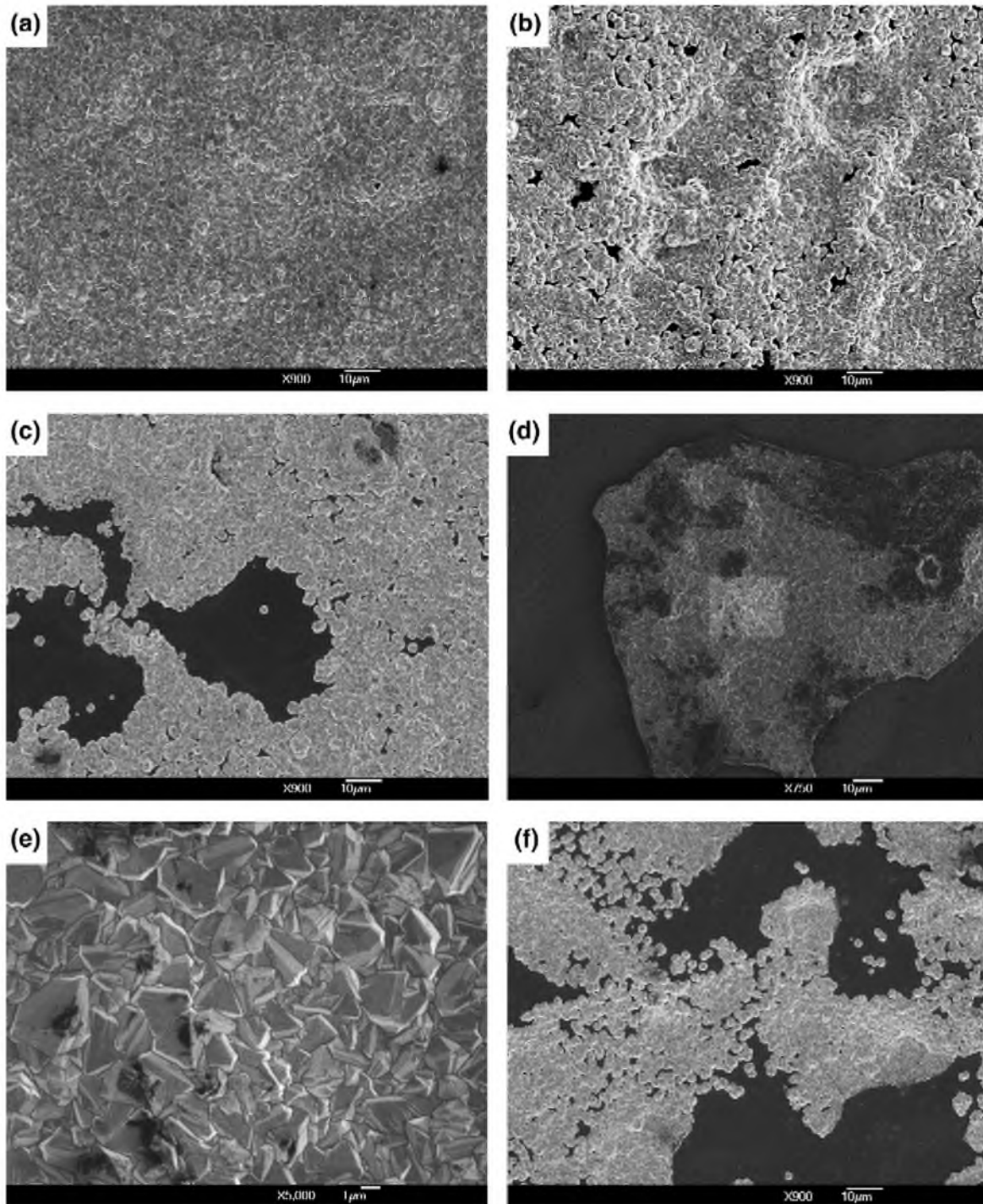


Fig. 5. Diamond coated tool steel samples with CrN interlayers. The diamond films are grown during 4 h at $T_s = 600^\circ\text{C}$, $\text{CH}_4:\text{H}_2 = 0.5\%$ under various pressures of (a) 5 mbar, (b) 6 mbar, (c) 7 mbar, (d, e) 10 mbar at different magnifications and (f) 50 mbar.

present study, tool steel samples with three types of surface finish were prepared. Samples with a surface roughness (R_a) of 2 μm were cut from the tool steel rod using probe EDM, while samples with a R_a of 1 μm were made using wire EDM. Although the basic mechanism is the same for both cutting methods, a substantial difference is found in the topography of the prepared samples. The SEM images of the substrates surfaces prepared by probe EDM and wire EDM are shown in Fig. 1. A unique crater-textured surface is observed on the samples cut by probe EDM while no such distinctive features are seen on samples prepared by wire EDM. When attempting to prepare samples of lower roughness values ($\sim 1 \mu\text{m}$) by probe EDM, it turned out to be far more time consuming than we anticipated. Hence, the material was initially cut by employing wire EDM and then to obtain the unique texture produced by the probe EDM, this latter technique was used on the surface providing a roughness of 1 μm . This third type of surface preparation is cited as surface spark erosion hereafter in this paper.

In a first series of experiments, tool steel samples prepared with probe EDM, wire EDM and surface spark erosion were coated with a 2.5 μm thick CrN interlayer and subjected to diamond growth. Fig. 2 shows the SEM images of the samples after 4 h of diamond deposition under the following conditions: $T_s=600 \text{ }^\circ\text{C}$, $\text{CH}_4:\text{H}_2=0.5\%$ and $P=5 \text{ mbar}$. The film on samples prepared by probe EDM suffers from severe delamination. Probably, the higher surface roughness causes this adhesion failure. The surface spark eroded samples and the samples prepared by wire EDM both show better results. The nucleation density and growth rate seem to be almost similar for all the samples. Nevertheless, the diamond surface coverage of the surface spark eroded samples is clearly the best due to a better mechanical interlocking. The effect of the surface preparation by EDM was from the surface texture rather than the roughness value. In addition to this investigation on the effect of surface finish by EDM, many experiments were done with tool steel samples of various surface roughness values

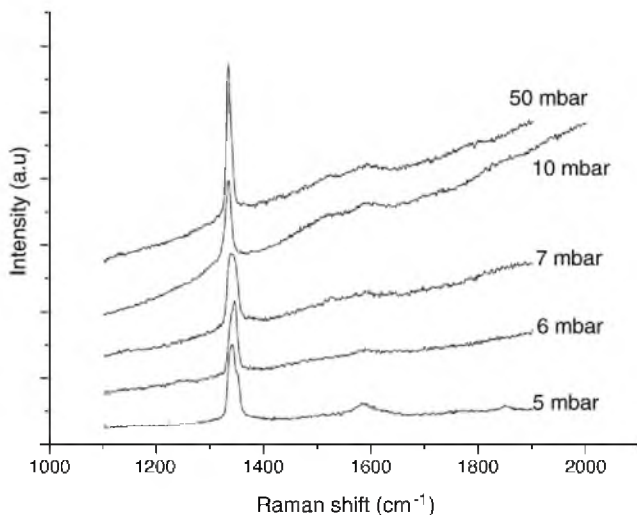


Fig. 6. Raman spectra of diamond films deposited at various pressures on tool steel substrates with 2.5 μm thick CrN interlayers.

Table 1

Raman peaks and stress state of diamond films deposited under various pressures

Deposition pressure (mbar)	Diamond Raman peak (cm^{-1})	Stress (GPa)
5	1340	-9
6	1345	-14
7	1337	-5
10	1335	-3
50	1333	-1

prepared by grinding. The diamond films on these samples obtained by grinding had very poor adhesion irrespective of the roughness values (results not shown here). There was a lack of mechanical interlocking in the substrates prepared by grinding when compared to the EDM'd substrates. There are many reports explaining the effective role of mechanical interlocking in ensuring the adhesion in thin film systems [10,11]. The crater like features on the surface obtained in EDM'd samples seem to promote a better mechanical interlocking, which in turn improves the adhesion of the diamond film obtained on these samples. It can be concluded that the surface texture plays the most important role and not the roughness, because the wire EDM'd substrates of the same roughness value ($R_a=1 \mu\text{m}$) and the substrates prepared by grinding did not yield similar results. Therefore, surface spark erosion is selected to prepare the tool steel samples that are further used in this study to examine the influence of interlayer thickness and diamond deposition parameters.

3.2. Interlayer thickness

The effect of interlayer thickness on the growth of diamond film is studied next. CrN layers of three different thicknesses: 2.5 μm , 5 μm and 8 μm were coated on tool steel samples prepared by surface spark erosion. As shown in Fig. 3 these layers show a rough, corrugated surface and exhibit several so called droplets, which are typical defects produced in the PVD arc deposition process [12]. From Fig. 3, it can be inferred that the corrugated features as well as the droplets, whose size and density increase more than linearly with the thickness of the CrN layer, make the surface significantly rougher with increasing interlayer thickness.

Figs. 2c and 4 show the surface of the diamond coated tool steel samples with different CrN interlayer thicknesses after 4 h of diamond deposition at $T_s=600 \text{ }^\circ\text{C}$, $\text{CH}_4:\text{H}_2=0.5\%$ and $P=5 \text{ mbar}$. The diamond film obtained with a CrN interlayer of 2.5 μm is highly continuous and little or no delamination is observed. Fig. 4a shows the remains of a closely packed continuous diamond film deposited on a sample with a 5 μm thick CrN interlayer with large parts delaminated. The absence of diamond nuclei on the parts of the sample where the coating has disappeared indicates that the delamination must have occurred during cooling down due to thermal stresses. Samples with CrN layers of 8 μm thickness show a very poor and non-uniform nucleation density and non-uniform nucleation. For both 5 and 8 μm CrN layers, the presence of droplets is suspected to have quite an effect on the diamond layer adhesion, since the

droplets are known to be poorly bonded to the film and can easily come out [13]. In addition, the increase in roughness due to these droplets, as mentioned earlier, can also be a reason for adhesion failure of the diamond film. From the above results, it is clear that a CrN interlayer with a thickness of 2.5 μm is providing the best result for diamond deposition. Therefore, for further investigations, surface spark eroded samples coated with CrN interlayers of 2.5 μm thickness are used.

3.3. Deposition pressure

Using a temperature of 600 $^{\circ}\text{C}$ and a $\text{CH}_4:\text{H}_2$ ratio of 0.5%, a series of diamond deposition experiments was performed for a wide range of pressure values (5, 6, 7, 10 and 50 mbar). Fig. 5 displays the SEM pictures of the surface of the samples after diamond deposition. In contrast to the diamond coating obtained at 5 mbar (see Fig. 5a) the diamond film deposited

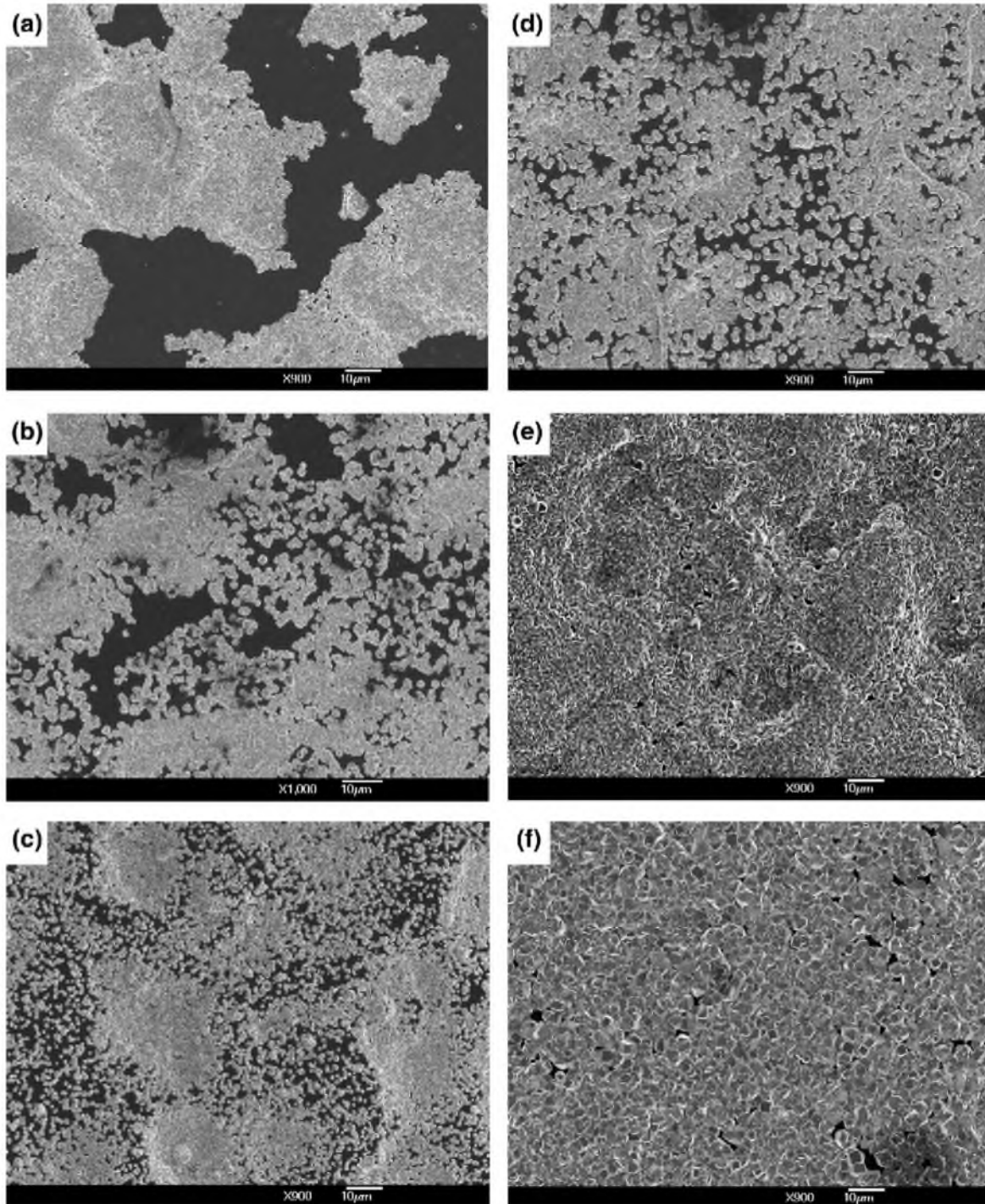


Fig. 7. Diamond films deposited on tool steel samples using 2.5 μm thick CrN interlayers. The films were grown at a reactor pressure of 50 mbar (a) 650 $^{\circ}\text{C}$, (b) 600 $^{\circ}\text{C}$, and (c) 550 $^{\circ}\text{C}$ and under a pressure of 5 mbar at a temperature of (d) 650 $^{\circ}\text{C}$, (e) 625 $^{\circ}\text{C}$ and (f) 600 $^{\circ}\text{C}$.

Table 2
Coverage percentage for a range of temperatures at high and low pressures

Pressure (mbar)	Temperature (°C)	Surface coverage (%)	Cause
50	650	25%	Delamination
	600	35%	Non-uniform deposits, poor nucleation and delamination
	550	30%	Non-uniform deposits and locally poor nucleation
5	650	45%	Poor nucleation and delamination
	625	80%	Delamination in a few areas
	600	65%	Grains not fully grown together

under 6 mbar (Fig. 5b) is not completely continuous. A further increase of the pressure to 7 mbar results in partial delamination of the diamond coating. Since this film is not completely closed, the degree of delamination is much less compared to samples coated at a pressure of 10 mbar, which are almost completely delaminated. These results can be explained by the fact that an increased pressure initially leads to a larger amount of active species resulting in a higher diamond nucleation density and subsequently a higher growth rate. In accordance to this mechanism, the high magnification picture of the sample coated at 10 mbar (Fig. 5e) shows a continuous diamond film with well-facetted grains. This, unfortunately, increases the amount of stress in the film and causes severe delamination. However, at a higher pressure of about 50 mbar, nucleation itself is very poor while on the other hand in those few areas where the crystallites coalesced and formed nearly continuous islands, delamination has occurred. The poor nucleation density can be imputed to the fact that, although the amount of active species is larger at elevated pressures, the mean free path of the radicals becomes increasingly smaller so that the effective density of active species available for diamond nucleation and growth is reduced to a large extent at the sample surface. This is in agreement with Kang et al. [14], who suggested that at low pressure there is enhanced nucleation which can be attributed to an increased mean free path. According to these authors, the increase of mean free path with decreasing pressure leads to an increase of

active species impinging on the substrate and hence results in a favorable environment for the diamond nucleation and growth.

Fig. 6 shows the Raman spectra of the diamond coatings which were grown at different pressures. The intensity of each spectrum has been multiplied to present them with similar signal to noise ratio when mounted together. It is clear that the background luminescence increases significantly with increasing pressure. The origin of the luminescence background is usually related to the presence of non-diamond phases [15]. In the samples coated under high pressure values, the films have more uncovered areas either due to delamination of diamond film or due to insufficient or poor diamond nucleation. Hence the luminescent background is increasing with pressure. For unstrained diamond layers the diamond peak position ν_0 in the spectrum is at 1332 cm^{-1} . For the samples in the present work, however, this position is shifted to higher wavenumbers as a result of compressive strain. The biaxial stress τ in the layers can be calculated from the shift in the peak position using [16]

$$\tau = -1.08 \text{ GPa/cm}^{-1} (\nu_s - \nu_0)$$

Where ν_s is the observed position of the singlet. Table 1 lists the diamond Raman peak and the stress state for the diamond films deposited at different pressures. From the table it is clear that the diamond films obtained at higher pressures are less strained. This is related to the fact that these films are non-continuous either by insufficient nucleation or by severe delamination, so that the stress is released to some extent.

3.4. Substrate temperature

In order to determine the influence of the deposition temperature on the properties of the diamond coatings a series of deposition runs was carried out at different temperatures under both 5 and 50 mbar pressure. The results of these experiments are shown in Fig. 7 and summarized in Table 2. The films deposited at 650 °C under 50 mbar (Fig. 7a) show severe delamination. But the remaining parts of the coating indicate that the nucleation density is sufficient to obtain a

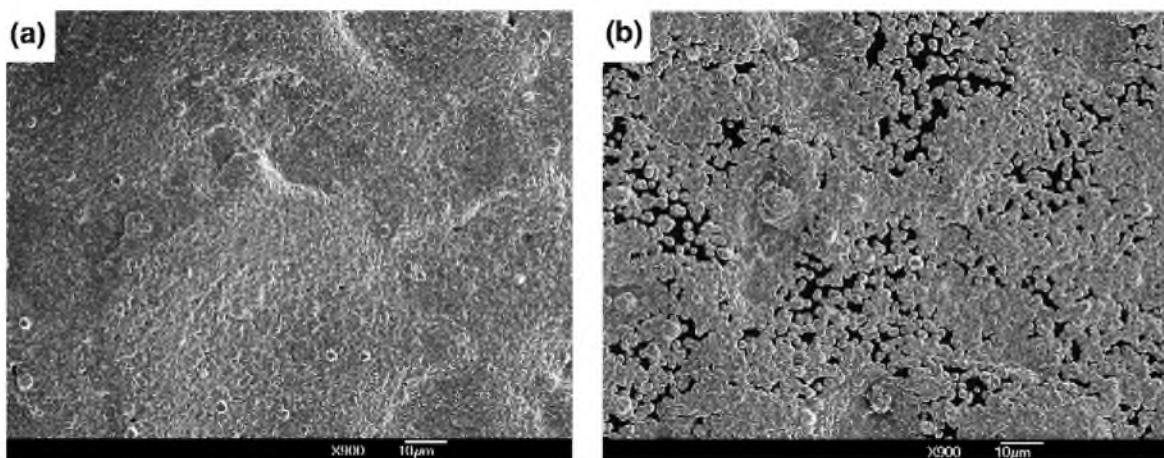


Fig. 8. Lack of reproducibility under similar conditions.

continuous diamond film. This is in contrast to the samples grown at 600 and 550 °C for which the nucleation density is highly inhomogeneous and locally not sufficient to obtain a continuous diamond coating (see Fig. 7b and c). Also the sample grown at a pressure of 5 mbar and a temperature of 650 °C shows a poor homogeneity resulting in a low nucleation density in some areas and delamination of the coating in other areas. Using a pressure of 5 mbar the best coatings in terms of surface coverage were obtained at 600 and 625 °C (see Fig. 7e and f). The results indicate that at 600 °C the grains are just not grown together to form a continuous layer, while at 625 °C small parts are already delaminated. This indicates that there is only a small process window to obtain a continuous diamond coating over the entire surface of the tool steel sample using a CrN interlayer. This is confirmed from the results of the experiments done under similar diamond deposition parameters. It is found to be difficult to reproduce the results obtained at 5 mbar and 600 °C. In total about 100 samples were evaluated and the percentage of reproducibility was roughly 70%. Fig. 8 is given as an example showing SEM images of two diamond coated tool steel substrates with a 2.5 µm CrN interlayer. Although both are surface spark eroded samples and the diamond deposition parameters, $P=5$ mbar; $T_s=600$ °C; $CH_4:H_2=0.5\%$, are the same for both samples, on one sample (Fig. 8a) a continuous diamond film is obtained without any delamination whereas another sample (Fig. 8b) shows inhomogeneous nucleation and insufficient growth rate. The substrate to filament distance can also account for this limited reproducibility. The filament loses its initial shape and position in the carburization process performed prior to diamond deposition. It is not possible to change the position of the filament after carburization because it becomes very brittle. Even though due care is given to position the filament to be exactly the same every time prior to carburization, it is practically impossible to maintain the same filament to substrate distance and the same filament configuration for all the deposition runs in our HFCVD reactor.

4. Conclusions

The present study shows that the process window to produce continuous diamond layers on tool steel with a CrN interlayer is extremely small. The main causes for the limited reproducibility are found to be non-uniform nucleation and delamination. These depend critically on a number of factors. Firstly, the method of tool steel sample preparation is found to be very important. The unique surface texture obtained in the surface spark erosion with probe EDM process plays a significant role in ensuring the adhesion by providing the necessary mechanical interlocking. Secondly, the quality of the interlayers plays a crucial role. CrN interlayers obtained by arc plating are quite rough and have a lot of droplets formed during the deposition. The size and density of these droplets increase more than linearly with the thickness of the CrN layer. Because these droplets are poorly bonded to the substrate, the thickness of the interlayer has a considerable impact on the adhesion of the

diamond layer. Thirdly, the reactor pressure and substrate temperature during diamond growth are found to be of large importance to obtain a continuous diamond coating. The best diamond coatings are obtained for tool steel samples prepared by surface spark erosion with a 2.5 µm thick CrN interlayer under 5 mbar pressure at 600 °C substrate temperature. However, the reproducibility of these growth runs is found to be difficult. In addition to the narrow process window, factors such as filament to substrate distance and the filament configuration, which cannot be controlled precisely, may have a considerable impact on the diamond deposition. The process window is expected to be larger for a more fine grained CrN structure such as CrN obtained by magnetron sputtering along with other parameters. So presently in our lab, bias enhanced nucleation (BEN) and magnetron sputtered coating are under investigation and the results obtained will be reported in a forthcoming paper.

Acknowledgements

The authors are grateful to Leander Gerritsen for his technical support and wish to express their sincere thanks to Edwin Sweers and Harrie van Brakel for the preparation of samples by electrical discharge machining. This work was supported by the Dutch Ministry of Economic Affairs as part of the innovation-driven research programme (IOP).

References

- [1] A. Fayer, O. Glozman, A. Hoffman, *Appl. Phys. Lett.* 67 (16) (1995) 2299.
- [2] S. Kumar, M. Malhotra, *Diamond Relat. Mater.* 7 (7) (1998) 1043.
- [3] J. Narayan, V.P. Godbole, G. Matera, R.K. Singh, *J. Appl. Phys.* 71 (2) (1992) 966.
- [4] H. Chen, M.L. Nielsen, C.J. Gold, R.O. Dillon, J. DiGregorio, T. Furtak, *Thin Solid Films* 212 (1–2) (1992) 169.
- [5] R. Polini, F.P. Mantini, M. Braic, M. Amar, W. Ahmed, H. Taylor, *Thin Solid Films* 494 (1–2) (2006) 116.
- [6] J.G. Buijnsters, P. Shankar, W.J.P. van Enckevort, J.J. Schermer, J.J. ter Meulen, *Diamond Relat. Mater.* 13 (4–8) (2004) 848.
- [7] J.G. Buijnsters, P. Shankar, W. Fleischer, W.J.P. van Enckevort, J.J. Schermer, J.J. ter Meulen, *Diamond Relat. Mater.* 11 (3–6) (2002) 536.
- [8] P.E. Pehrsson, F.G. Celii, J.E. Butler, in: R.F. Davis (Ed.), *Diamond Films and Coatings, Development, Properties, and Applications*, Noyes Publications, Park Ridge, New Jersey, 1993, p. 68.
- [9] C.A. Huang, G.C. Tu, H.T. Yao, H.H. Kuo, *Metall. Mater. Trans., A Phys. Metall. Mater. Sci.* 35A (2004) 1351.
- [10] A. Lahmar, J.P. Bardon, N. Hmina, *J. Phys., Condens. Matter* 13 (18) (2001) 3931.
- [11] K.-W. Chae, Y.-J. Baik, D.-Y. Kim, *Diamond Relat. Mater.* 8 (6) (1999) 1018.
- [12] S. Baragetti, M. Gelfi, G.M. La Vecchia, N. Lecis, *Fatigue Fract. Eng. Mater. Struct.* 28 (7) (2005) 615.
- [13] S.H. Ahn, Y.S. Choi, J.G. Kim, J.G. Han, *Surf. Coat. Technol.* 150 (2–3) (2002) 319.
- [14] J. Kang, C. Xiao, Y. Xiong, Y. Wang, Q. Meng, Z. Lin, K. Feng, *Diamond Relat. Mater.* 9 (9–10) (2000) 1691.
- [15] M. Grus, A. Jankowska-Frydel, J. Bohdanowicz, K. Zawada, *Cryst. Res. Technol.* 36 (8–10) (2001) 961.
- [16] J.W. Ager III, M.D. Drory, *Phys. Rev. B* 48 (4) (1993) 2601.