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Chemical vapour deposition of diamond using low pressure flat combustion flame

MIROLJUB VILOTIJEVIĆ*, NEBOJŠA GRAHOVAC, LJILJANA MILOVANOVIĆ and SLOBODAN MARINKOVIĆ

*Vinča Institute of Nuclear Sciences, P. O. Box 522, 11001 Belgrade, Serbia and Montenegro
(e-mail:mige@vin.bg.ac.yu)*

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Abstract: Diamond coatings were deposited onto Mo and WC–Co substrates using a low pressure premixed acetylene–oxygen flat flame by means of a special apparatus operating at 50 mbar. Uniform diamond coatings containing significant amounts of non-diamond carbon were deposited over areas of $\approx 7 \text{ cm}^2$ onto Mo substrates, the coating thickness after 1 h deposition amounted to $\approx 1 \mu\text{m}$. Upon machining an Al–12 % Si alloy under identical conditions, the diamond coated WC–Co cutting tool inserts showed 30 % less wear than the as-received inserts.

Keywords: low pressure flat flame, Diamond CVD.

INTRODUCTION

Chemical vapour deposition (CVD) of diamond has attracted a lot of interest of researchers worldwide because it allows low pressure diamond preparation in the form of a coating.^{1,2} Of a number of CVD methods developed, several have been scaled up and are currently in use for diamond preparation. Combustion of acetylene in a mixture with oxygen is the simplest and most elegant CVD method of diamond synthesis. However, its disadvantage preventing scale-up is that it can be used to cover only small (some millimeters in diameter) areas non-uniformly if a standard burner producing a cone-shaped flame³ is employed. Another disadvantage are the extremely high heat fluxes (a few kW/cm^2) to the substrate. Efforts directed at overcoming these difficulties have resulted in a so-called flat flame which operates in a substrate-stabilized regime (the flame is detached from the burner).^{4–6} The use of an atmospheric pressure flat flame⁴ allows an increase in the diameter of the deposition area, but the high energy flux remains, while a low pressure flat flame^{5,6} circumvents both these problems.

An original flat flame deposition apparatus is reported in this paper. It was originally designed on the basis of the work of Kim and Cappelli,⁵ but it had to be substantially modified. The first results obtained with the apparatus are also presented.

* Author for correspondence.

EXPERIMENTAL

Molybdenum plate 35×35 mm were used as substrates in the first part of the investigation, aimed at establishing suitable conditions for diamond deposition. In the second part, where it was intended to deposit diamond on WC-Co cutting tool inserts (12.5 × 12.5 × 3 mm), the substrate holder had to be

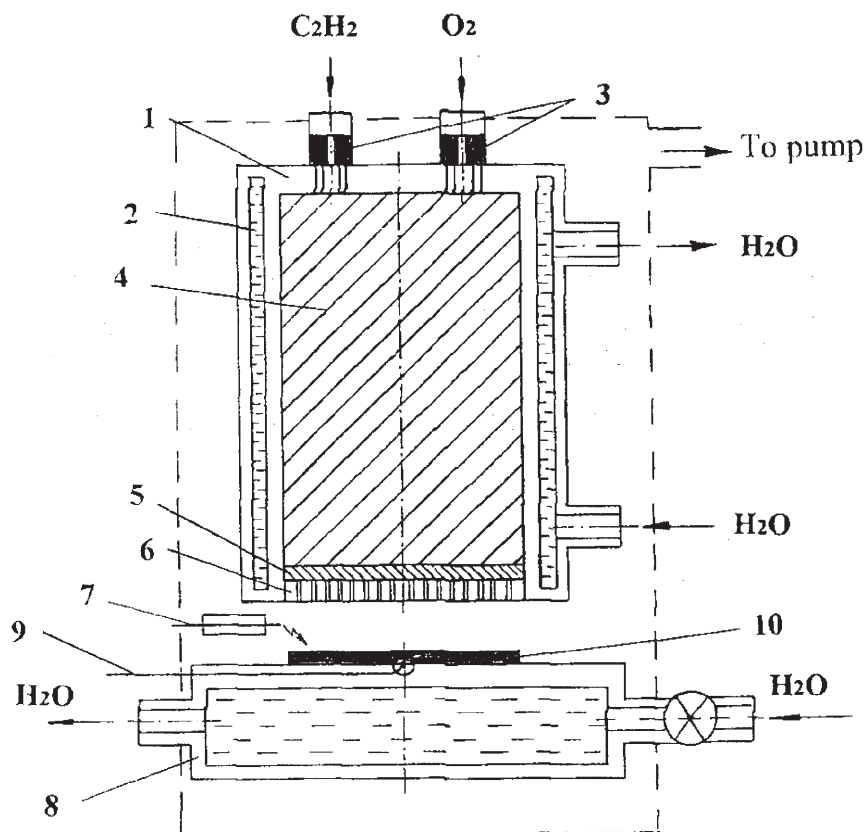


Fig. 1. Schematic view of the flat flame diamond deposition apparatus: (1) – Burner; (2) – Water cooling; (3) – Calibrated nozzles; (4) – Mixing chamber; (5) – Al_2O_3 felt; (6) – Perforated plate; (7) – Spark plug; (8) – Substrate cooler with controlled water flow; (9) – Thermocouple; (10) – Mo substrate.

modified. The whole surface of the insert was coated with diamond in a single deposition experiment. A schematic view of the deposition apparatus is presented in Fig. 1. Its original construction, similar to that described in,³ had to be significantly modified, primarily because of the explosions occurring during ignition of the $\text{C}_2\text{H}_2/\text{O}_2$ mixture, which created a momentary increase of the pressure in the deposition chamber, causing reversal of the flame and ignition of the inlet gas tube.

In the apparatus in Fig. 1, an original solution of the problem has been applied. Calibrated nozzles (3) 0.3 – 0.5 mm dia prevent flame reversal towards the gas inlet. The mixing chamber (4) was filled with steel balls ≈ 2 mm dia and at its bottom an Al_2O_3 felt barrier was placed. Such a solution ensures that the linear velocity of the explosive mixture through the burner is sufficiently low to prevent flame reversal towards the burner. In order to further improve security, a safety valve with an adjustable opening threshold (not shown) was built into the burner. If flame reversal nevertheless occurs, the safety valve closes the gas inlet *via* a microswitch and turns out the apparatus. Ignition of the gas mix-

ture was made using a high-voltage spark (7). The ignition was performed at a low pressure (≈ 30 mbar) to avoid an excessive pressure increase caused by the shock wave in the chamber. Due to the shock wave, the manometer measuring the chamber pressure had to be supplied with a restraining element. The water-cooled substrate holder enabled partial control of the water flow, thus allowing substrate temperature correction within ≈ 50 °C. Temperature control was relatively easy in the case of a Mo substrate, because of the good thermal conductivity of Mo, its high surface area and small thickness (1 mm). For the WC-Co inserts, however, the maintenance and control of the temperature presented a problem because of the considerably lower thermal conductivity, larger (3 mm) thickness and the virtual impossibility of placing a thermocouple close enough to the depositing surface. Therefore, a special WC-Co substrate holder, consisting of a massive steel block with a built-in thermocouple, was designed. The necessary temperature was adjusted by increasing or decreasing the total gas flowrate, keeping the ratio of the acetylene to oxygen flowrates ($R = C_2H_2/O_2$) constant.

In order to ensure a sufficient nucleation density, the substrate surface was subjected to a suitable treatment prior to deposition. In the case of a Mo substrate, the pre-treatment was restricted to a roughening of the surface by means of a fine grindstone. The WC-Co pre-treatment consisted of a roughening of the surface by treatment with an oxidizing flame, removal of Co from the surface by acids (essential in the case of WC-Co inserts) and ultrasound seeding by nano particles of diamond. The pre-treatment procedure was based on the results of an earlier study.⁷

With the Mo substrate, the deposition parameters were varied within the following limits: temperature, $T = 830$ – 950 °C, acetylene-to-oxygen ratio, $R = 0.95$ – 1.07 , the burner-to-substrate distance, $d = 5$ – 7 mm. The total pressure was 50 mbar in all the experiments and the total flowrate amounted to 7.5–8.3 slm (450–500 slh).

Structural characterization of the deposits, previously described in some detail,⁸ was made using scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction (XRD). In order to estimate improvements in the cutting characteristics, the diamond coated cutting tool inserts were used to cut an abrasive Al-12 % Si alloy and the results of wear were compared to those with as-received inserts. A standard procedure used in machining practice was employed in which the flank wear (in μm) of the cutting insert was followed as a function of time.¹¹

RESULTS AND DISCUSSION

The deposit uniformly covering an area of about 7 cm^2 (3 cm dia) was dark-grey in colour. Its thickness was about $1 \mu\text{m}$. Since in the initial experiments, a more uniform coating was obtained for $d = 7$ mm, this distance was used in the subsequent work.

Typical SEM, Raman and XRD results are shown in Fig. 2 a–c, respectively. The SEM photograph (Fig. 2 a) shows that all the coatings had a ball-like structure, indicating a considerable content of non-diamond carbon, and the Raman spectrum (Fig. 2 b) shows only sp^2 -carbon bands centered around 1350 and 1600 cm^{-1} , the diamond line (at 1333 cm^{-1}) being masked by the 1350 cm^{-1} band. However, the XRD (Fig. 2 c) shows clearly a diamond (111) line, in addition to lines originating from the Mo substrate. Thus, XRD was the only method with which diamond was detected. The absence of the diamond line in the Raman spectra is not surprising, however, because the Raman spectra are much more sensitive (2 orders of magnitude) to non-diamond carbon.¹³ The excitation line 514.5 nm of an Ar laser was used, as is customary.

It was found that 830 °C is the most suitable substrate temperature, resulting in the most pronounced X-ray diamond peak, higher temperatures leading to considerably weaker peaks.

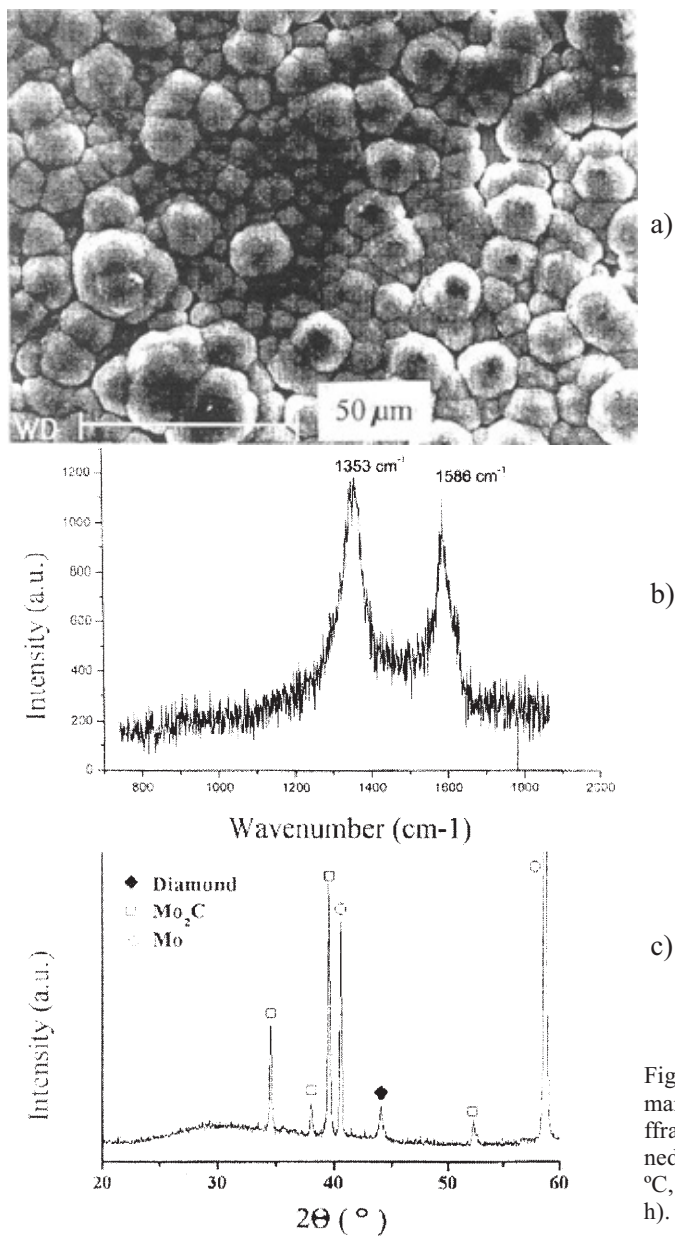


Fig. 2. SEM photograph (a), Raman spectrum (b) and XRD diffractogram of the deposit obtained on a Mo substrate ($T = 830$ °C, $P = 50$ mbar, $R = 0.85$, $t = 1$ h).

The ratio R did not show pronounced effect on the X-ray diamond peak within the above mentioned limits, but it was found that $R = 0.85$ resulted in a considerably higher peak.

With the WC-Co cutting tool insert as the substrate, similar results were obtained under similar deposition conditions. The best result (highest XRD diamond peak) was obtained with $R = 0.97$, the other parameters being $T = 830$ °C, $P = 50$ mbar.

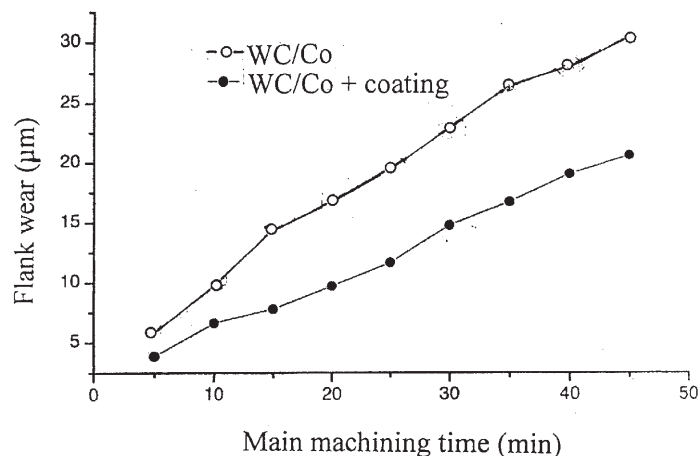


Fig. 3. Flank wear of a diamond coated and an as-received WC-Co cutting tool insert under identical machining conditions (Dry turning; Cutting speed: 400 m/min; Feed rate: 0.1 mm/o; Depth of cut: 0.5 mm).

The range of R values for which a diamond deposit was obtained is shifted to gas mixture richer in oxygen with respect to deposition using conventional welding torches at atmospheric pressure. This result is in agreement with those of other authors,¹² who also stated that the R values range in which diamond is deposited is considerably narrower in the flat flame method.

The inferior characteristics of the diamond coatings reported here with respect to the coatings obtained earlier with a conical flame^{7,9} suggest that further work is necessary in order to establish the optimum conditions of diamond deposition using a flat flame.

The machining experiments (Fig. 3) show a distinctly (30 %) lower wear of the diamond-coated insert. A comparison with earlier results pertaining to diamond coating obtained with a conical flame,¹⁰ shows that the earlier prepared inserts were distinctly superior (wear of the diamond-coated inserts 3–5 times less after 180 min machining). This difference can be accounted for by the lower thickness and lower quality of the diamond coating deposited using the flat flame.

CONCLUSION

Diamond coatings were deposited on Mo and WC-Co substrates using a low pressure flat flame. The coated area (about 7 cm²) is much larger than in the case of a standard burner producing a conical flame. The technique is scaleable. Its disadvantages are low deposition rate and the need for a vacuum chamber, thus questioning the cost-effectiveness of the procedure. Further work should concentrate on the improvement of the coating quality and deposition rate.

ИЗВОД

ХЕМИЈСКО ДЕПОНОВАЊЕ ДИЈАМАНТА ИЗ ПАРНЕ ФАЗЕ УЗ ПОМОЋ
РАВНОГ ПЛАМЕНА НА НИСКОМ ПРИТИСКУМИРОЉУБ ВИЛОТИЈЕВИЋ, НЕБОЈША ГРАХОВАЦ, ЉИЉАНА МИЛОВАНОВИЋ и СЛОБОДАН
МАРИНКОВИЋ*Институт за нуклеарне науке "Винча", б. бр. 522, 11001 Београд*

Уз помоћ ацетиленско-кисеоничног пламена на ниском притиску депоноване су дијамантске превлаке на подлогама од Мо и WC-Co, користећи специјалну апаратуру која омогућује рад на 50 mbar. На Мо подлогама су депоноване униформне превлаке на површини од $\approx 7 \text{ cm}^2$. После једночасовног депонивања дебелина превлаке износи $\approx 1 \text{ }\mu\text{m}$. При резању легуре Al-12 % Si под једнаким условима, хабање изменљивих плочицама резног алата од WC-Co са дијамантском превлаком је за 30 % мање од хабања стандардних плочица.

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REFERENCES

1. S. Marinković, in *Chemistry and Physics of Carbon*, Vol. 29, Lj. Radović, Ed., Marcel Dekker, New York, 2004, pp. 71–207
2. S. Marinković, *Dijamant sintetizovan na niskom pritisku*, Partenon, Beograd, 2001, pp. 1–166
3. Y. Hirose, S. Amanuma, K. Komaki, *J. Appl. Phys.* **68** (1990) 6401
4. M. Murayama, K. Uchida, *Combust. Flame* **91** (1992) 239
5. J. S. Kim, M. A. Cappelli, *J. Mater. Res.* **10** (1995) 149
6. N. G. Glumac, D. G. Goodwin, *Thin Solid Films* **212** (1992) 122
7. S. Marinković, S. Stanković, Z. Rakočević, *Thin Solid Films* **354** (1999) 118
8. S. Marinković, S. Zec, *J. Serb. Chem. Soc.* **58** (1993) 679
9. S. Stanković, Z. Rakočević, S. Marinković, *Diamond Rel. Mater.* **8** (1999) 207
10. N. Grahovac, S. Stanković, S. Marinković, *J. Mining Metall.* **34** (1998) 79
11. P. Stanković, *Mechanical Treatment*, Gradjevinska knjiga, Belgrade, 1978, p. 24 (in Serbian)
12. C. A. Wolden, R. F. Davis, Z. Sitar, J. T. Prater, *Diamond Rel. Mater.* **6** (1997) 1862
13. D. W. Kweon, J. Y. Lee, *J. Appl. Phys.* **69** (1991) 8329.