# Investigation Of Nucleation And Growth For Diamond Coatings On Tungsten Carbide Base Cutting Tools For Machining Of Aluminium By Hfcvd Method

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***Abstract:*** In this paper, an attempt is made to deposit microcrystalline diamond films by Hot Filament Chemical Vapour Deposition (HFCVD) method on Co-cemented tungsten carbide cutting inserts. To restrict the catalytic effect of cobalt binder phase for the formation of non-diamond carbon phases such as graphite and improve the adhesion between diamond and WC, inserts were pretreated with combined HCL and $HNO_3$ solution. Seeding of the substrates was followed separately with Ti, Mo, W and diamond powders. Depositions were done at a pressure of 2.666 kPa, substrate temperature of $700^0$C, and filament temperature of $2100^0$C with constant $CH_4$ / $H_2$ flow ratio of 0.5 / 100 SCCM. Characterization and purity ($sp^3$ / $sp^2$) of the acquired coatings have been evaluated by Scanning Electron Microscope (SEM) and Raman Spectroscopy. It is observed that there was no improvement in coating morphology when the treated samples were seeded with Ti, Mo or W powders. These results suggested that a continuous diamond film with well facet morphology is deposited with acid treated sample surface seeded with diamond powder. During dry machining, compare to uncoated tool, HFCVD diamond coated tool exhibits remarkable inertness towards aluminium leading to substantial reduction of cutting force and improved work-piece surface finish.

***Index Terms* - HFCVD diamond, Morphology, Nucleation, Coating, Machining.**

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## I. INTRODUCTION

Nucleation is the first and critical step play a key role in determining the escalation morphology and coating quality in chemical vapour deposition (CVD) diamond growth. An assortment of nucleation approach mainly depend upon substrate material, substrate temperature, atomic hydrogen and carbon species concentration that produced by either hot filament or plasma discharge method. For optimizing the diamond properties such as grain size, orientation, adhesion and roughness it is essential to control nucleation for specific target applications [1]. However nucleation of diamond on residual grains entrenched into the surface after scraping with different powders act as intermediate layer [2]. The mode of nucleation toughly depends upon the substrate pretreatment technique as well as the different operating parameters used for nucleation stage. In general, substrates may be subjected to a variety of methods including: scratching or polishing with abrasive powder, ultrasonic etching, negative / positive biasing and combinations of all these techniques [3-4].This pretreatment modifies the surfaces such as sharp edges, apexes and in receipt of residual powder entrenched in to the surface [5].In a given experiment it is very difficult to separate the effect of all these aspects. However it is obvious that the entrenched abrasive particles serve up as superior locations for easy nucleation and growth. It has been observed that nucleation density on ultrasonically abraded surface depends on the progression temperature. This put forwards that surface dissemination and adsorption phenomena play a significant role in nucleation. The surface diffusion of carbon depends upon the interaction with substrate material. It is mainly divided with three types: solubility / reaction (Ag, Cu, Au, etc), diffusion of carbon only (Pd, Pt, Rh etc.) and diffusion of carbon and carbide formation (Ti, Ta, Mo, Cr, W, Co, Fe, Si, B, etc.).

Due to the high surface energy possessed by diamond, its nucleation on virgin substrates is characterized by low nucleation density and long incubation period. As a result surface pretreatment is essentially needed [3- 4].

Various researchers have broadly studied the function and role of various seeding metal powders, diamond powders and abrasive slurry during nucleation and growth stage of diamond crystals. For study of nucleation and growth transitional metal powders such as titanium, tungsten and molybdenum were taken into contemplation. In diamond nucleation the largest induction stage is related to the material that has the highest diffusion coefficient for carbon atoms. This may also regarded as the clear indication of the significance of the carbonization stage in diamond nucleation on carbide forming materials [6].

The explicit reactions lead to diamond growth is merely the catalytic activity of each metal [7- 9]. It was observed that with an increase in concentration of hydrocarbon lead to the CVD diamond formation process, such as $sp^3$bonded carbon for the development in the growth [10-11]. It is anticipated that the nearly all lively metal particles would be those with the highest chemisorption enthalpies for unsaturated hydrocarbons [12-13].

Generally diamond coating grown on cutting tool inserts not only improve their cutting performance but also make a substitute for costly poly crystalline diamond cutting tools. For conventional cutting tools of macroscopic size these coatings are required for the following reasons:

- Extreme high hardness (80-100Gpa) that helps to reduce wear [17-19]
- Low coefficient of friction against various work material that decreases the cutting and thrust force as well as reduced heat production [20]
- Low adhesion and chemical inertness to most of the work material which prevents built-up at cutting edge [21]
- Enhance the work surface finish.

## II. EXPERIMENTAL PROCEDURES AND CONDITIONS

The substrates used for CVD diamond deposition were cemented carbide turning inserts of geometry SPUN120308, ISO K 10 grade containing 6wt% cobalt. Prior to deposition the samples were cleaned with trichloroethylene and acetone followed by isopropyl alcohol to remove contaminates from the surface. Samples were etched with $HCl+HNO_3+H_2O$ (1:1:1) for 15 minutes ultrasonically at room temperature to remove cobalt and to roughen the surface. Then the inserts were seeded with diamond powder (0.2-1 µm) by ultrasonic agitation for two minutes in solvent 2-propanal, so that the seeds would enter the voids and act as nucleating site during deposition. Table 2.1 shows all the process parameters and conditions of CVD diamond on the cemented carbide inserts.

Table 2.1: Deposition parameters

| Deposition Parameters | Deposition Conditions |
|---|---|
| Substrate | WC-6wt% Co ISO K10 (Sandvik cemented carbide inserts) |
| Filament | Tungsten wire (ϕ 0.25 mm) carburized |
| Filament Temperature | 2000-2100 $^0$C |
| Substrate Temperature | 700 $^0$C |
| Filament to Substrate Distance | 5 - 6 mm |
| Chamber Pressure | 0.666 and 2.666kPa |
| Gas Consumption | $CH_4$ :0.5SCCM, $H_2$:100SCCM |
| Deposition Time | 40 and 480 min. |

These were the various steps to be carried out cautiously for seeding mechanism. In a borosil beaker metal powder(s) of 0.2 gm and 20 ml of 2-propanal were added and the suspension was prepared in an ultrasonic vessel (Frequency: 45 KHz) for two minutes to obtain the uniform mixture. With plastic forceps the pretreated insert was kept inside the solution to increase the contact between the solutions with the insert. The ultrasonic agitation was carried on up to two minutes and the inserts were took away and dried by hot air. Again the ultrasonic agitation was continued for one minute with 2-propanal to remove extra metal powder from the surface and after that the inserts were placed immediately inside the CVD chamber.

These steps corroborate that the seeds were entrenched uniformly inside the cavity of the carbide inserts. Various types of seeding material used for the experiments are shown in Table 2.2.

Table 2.2: Types of seeding material

| Sl. No. | Types of seeding materials |
|---|---|
| 1. | Titanium powder($TiH_2$) (1-2 µm) 99.99% pure, Fluka |
| 2. | Tungsten powder (0.6-1 µm) 99.99% pure, Sigma Aldrich |
| 3. | Molybdenum powder (1-2 µm) 99.99% pure, Sigma Aldrich |
| 4. | Diamond powder (0.6-2 µm) 99.99% pure, Eastern Diamond Ltd. |

Reaction pressure and temperature play a major role in nucleation and growth of each diamond crystal on carbide substrate. The flow rate of hydrogen (99.995% pure grades) and methane (99.95% pure grades) were maintained constant at 100 and 0.5 SCCM respectively by mass flow controllers (MFC) of MKS make. The pressure in the CVD chamber was controlled by MKS Baratron pressure sensor of (0.1333-13.332 kPa). The surface roughness of the carbide substrates was measured by 3P-surtonic Taylor Hobson instrument. The roughness parameters $R_a$, $R_z$ and $R_{max}$ were measured on tungsten carbide substrates at different stages with computer interface in µm. The crystal morphology and the content of cobalt / tungsten were characterized by SEM (model no: JEOL 5800 OXFORD ISIS 300) with an attachment of EDAX (Energy Dispersive Analysis of X-ray: Detector-LiSi crystal, Element analysis above atomic number 10, OXFORD-ISIS 300).The purity, orientation and individual defects states were evaluated by Micro-Raman Spectroscopy (Renishaw Laser Argon ion, Power: 8mW, Wave length: 5140Å, beam diameter 1.6µm).

The machining performances of the uncoated carbide tool and diamond coated tools were carried out at cutting speed of 365 m / min., feed 0.1 mm / rev. and depth of cut 0.5 mm in a combination turret lathe. The tool was held in a standard Sandvik tool holder mounted on a 3-D piezoelectric dynamometer (KISTLER 9257B Switzerland) for measurement of axial ($P_x$) and tangential forces ($P_z$). The signals were amplified by charge amplifiers (KISTLER 5070A, Switzerland) with the help of data acquisition card, NI-9205 and Lab View software 8.6.1(USA). Comparison has been made between axial force and tangential force of uncoated and diamond coated carbide inserts.

At a deposition temperature of 700 $^0$C experiments were conducted by heating the metal powders (Ti, Mo and W) to identify the phase change effect.

### 2.1 Heating of Ti, Mo and W powder

Titanium powder was heated in an alumina crucible at a pressure of 2.666 kPa and temperature of 700 $^0$C for 30 minutes in hydrogen rich atmosphere in our HFCVD chamber. After that this powder was taken for X-Ray analysis to identify the presence of different phases as well as existence of metal oxide, hydride or combination of both during deposition. Similar procedures were followed with Mo and W powder to identify any deviation in the formation of metal hydride. In both cases there were no changes in phases. These experiments confirmed the significance of transitional metal powder during nucleation and growth of diamond.

## III. RESULTS AND DISCUSSION

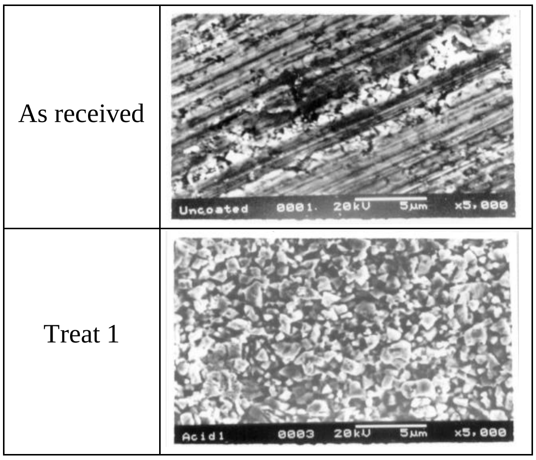



Fig.3.1: SEM micrographs of the rake surface of the carbide insert before and after Treat 1.

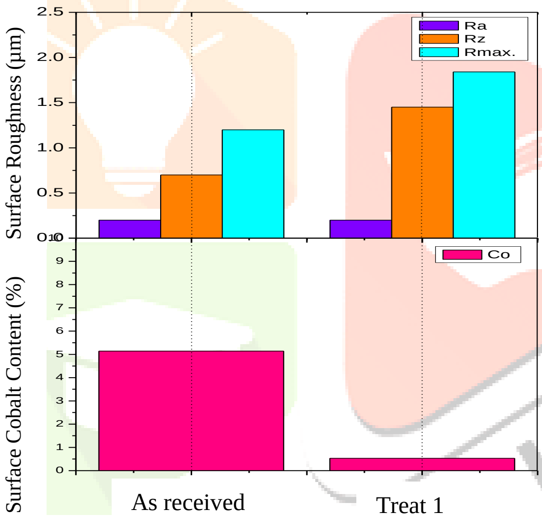



Fig.3.2: Surface roughness and cobalt content of carbide insert of the as received and after Treat 1.

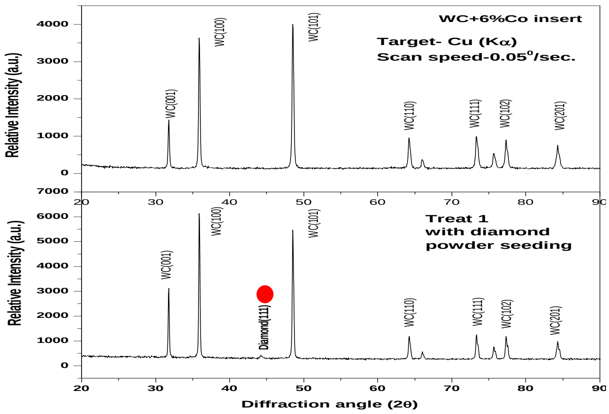



Fig.3.3:X-Ray Diffraction of as received carbide insert and diamond seeded carbide inserts pretreated with Treat 1.

Fig.3.1shows the SEM pictures of the as received substrate treated with solution of $HNO_3$+HCl+$H_2O$ (1:1:1) (Treat 1). Fig.3.2 shows the surface cobalt content that brings down Co as low as low as 0.5% and surface roughness has gone up. The pretreated inserts with (Treat 1) seeded with diamond powder entrenched inside the grooves and cavity. The analysis by EDAX in Fig.3.3 shows uniform distribution of metal powder (s) and presence of seeds. Diamond seeding shows the presence of diamond (111) plane peak; however the peak was not very strong.

The SEM micrograph of Fig.3.4 visualizes the configuration of nano-crystallites of diamond deposited at a pressure of 0.666 kPa on pretreated inserts after deposition time of 40 minutes. In the midst of these three powders, diamond powder showed the highest nucleation density as compared to molybdenum and tungsten powders. After nucleation with different powders Raman peaks in Fig.3.5 corroborate the presence of amorphous carbon with different $sp^2$ and $sp^3$ content. Equal amount of $sp^2$ / $sp^3$ content is shown with the inserts seeded with Mo and W powder. But inserts pretreated and seeded with diamond powder showed strong $sp^3$ content. In order to evade these conjectures transitional metal powder were used for studying the nucleation on pretreated inserts.

SEM pictures in Fig.3.6 depict the diamond coating after deposition time of 8 hours on different substrates. Despite the fact that cubo-octahedral crystals are formed, but some part were porous. This indicates diamond crystals are strongly attacked by surface cobalt. The pretreated inserts showed few discrete crystals were also formed without diamond seeds. At the initial stage due to the strong encroachment of transitional metal powders enter into the cavity nucleation density have been improved [5, 6, 9]. In spite of few argument found in different research papers we have conducted the experiments with three major transitional metal powders.

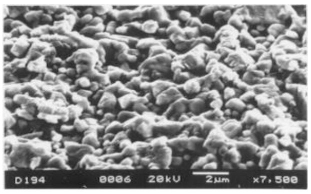
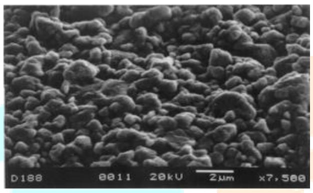
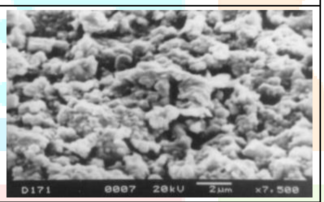
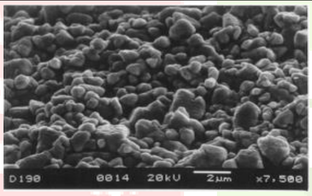
| | |
|---|---|
| Ti Seeding |  |
| Mo seeding |  |
| W seeding |  |
| Diamond seeding |  |
| Pressure=0.666 kPa<br>CH4 / $H_2$=0.5 / 100, Time:40 minutes | |

Fig.3.4: SEM pictures of diamond nanocrystals after nucleation of 40 minutes.

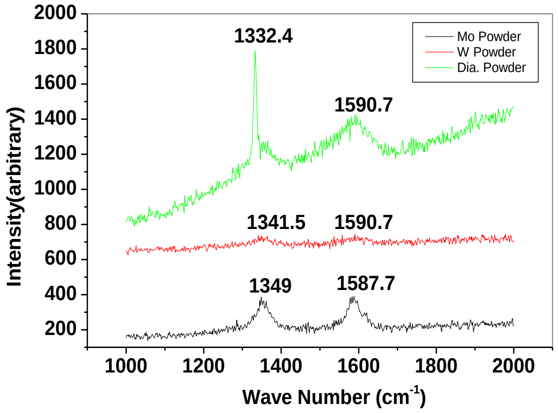



Fig.3.5: Raman spectroscopy peaks of diamond and amorphous carbon on nucleation for diamond after 40 minutes.

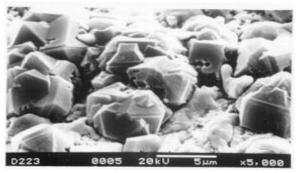
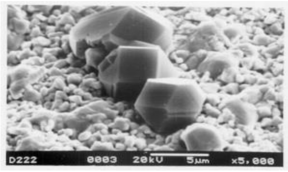
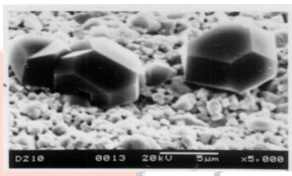
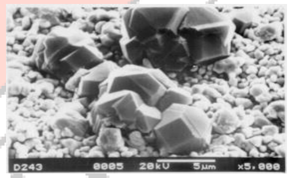
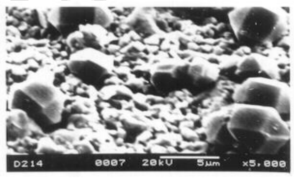
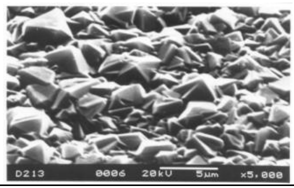
| | |
|---|---|
| As received<br>No seeding |  |
| Treat 1<br>No seeding |  |
| Treat 1<br>Titanium powder |  |
| Treat 1<br>Molybdenum powder |  |
| Treat 1<br>Tungsten powder |  |
| Treat 1<br>Diamond powder |  |
| Pressure:2.666 kPa,$CH_4$ / $H_2$:0.5 / 100,<br>Temperature:$700^0$C,Deposition time:8 hours | |

Fig.3.6: SEM micrographs showing effect of seeding materials on nucleation and growth of diamond on carbide inserts.

### 3.1 Effect of Titanium powder

During the deposition titanium powder did not play any role in diamond formation due to the formation of metal hydride. The actual roles of metal powder were found out from X-ray analysis. In the presence of hydrogen, oxygen and carbon metal powders might have changed to some intermediary phases which effect the formation of lattice defects during the deposition. Hence titanium powder is not at all effective in the formation and growth of diamond. These results were confirmed by X-ray analysis shown in Fig.3.7.

### 3.2 Effect of Molybdenum and Tungsten powder

The Mo and W powders did not show formation of metal hydride(s) and / or metal oxides due to stable at deposition temperature. Any changes in the crystal habit were not found for both cases due to high melting point and high resistance at 700-800 $^{0}$C in hydrogen atmosphere [2]. These results were confirmed from the X-ray analysis shown in Fig.3.8 and Fig.3.9.Molybdenum and tungsten have high melting points lead to lower carbon diffusion in the carbides compared to titanium. Simultaneously molybdenum forms more complex carbides compared to tungsten. The SEM pictures also corroborate that more diamond crystals were available in Mo and W powders compared to Ti powders.
But pretreated insert with treat 1 and seeded with diamond powder not only showed highest nucleation density but also uniformly covered on the rake face as well as cutting edge with (111) facets. All the results confirm that these powders did not have much impact on nucleation and growth of diamond. The inserts used without diamond powder seeding had discrete crystals with cubo-octahederal shape. This corroborates that metal seeds did not play active role in retention of carbon phase / radicals on the groove of the insert.

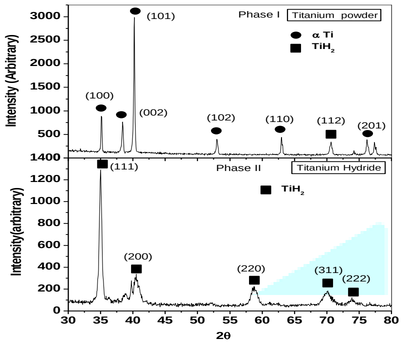



Fig.3.7: X-ray peaks of different phases of titanium and titanium hydride at two stages.

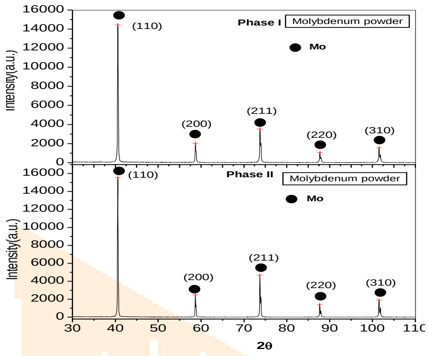



Fig.3.8: X-Ray peaks of molybdenum powder with different crystal habits at two stages.

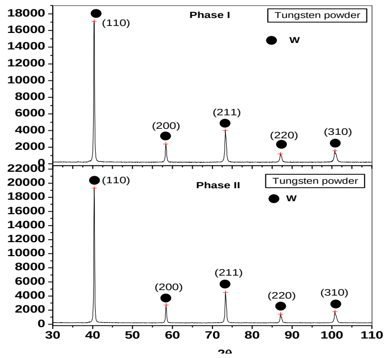



Fig.3.9: X-Ray peaks of tungsten powder with different crystal habits at two stages.

### 3.3. On Performance of Diamond Coated Tools

Fig.3.10 clearly reveals the fluctuation of both tangential ($P_z$) and axial ($P_x$) component of cutting force occurred over a broad band in comparison to what happened in case of a diamond coated tool (Treat 1, Pressure: 2.666 kPa, $CH_4$ / $H_2$= 0.5 / 100, Temp. = 700 $^{0}$C, Time: 8 hrs). The tangential and axial cutting force was always greater for the uncoated carbide tool compared to the diamond coated tool.

Diamond coated tools on the other hand exhibited their remarkable anti-welding characteristics during dry machining of Al as can be seen in SEM micrograph of Fig.3.11.No trace of built-up edge could be detected from the SEM micrographs. The cutting edge remained stable and intact during the span of the machining. The very anti-sticking characteristics of the diamond coating against aluminium resulted in lower surface roughness of the work-piece although roughness of the as coated surface is higher than roughness of rake and flank of the uncoated tool. It is strongly felt that by smoothening the diamond coating still lower surface roughness can be obtained on the work-piece.

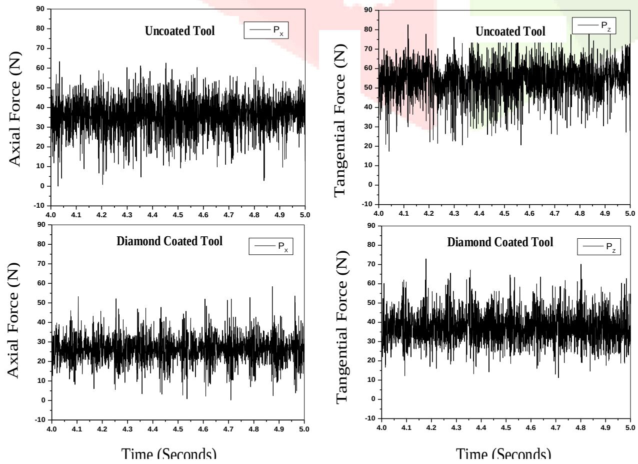



Fig.3.10: Comparison of cutting forces (axial and tangential components) of uncoated and diamond coated carbide insert (Treat 1, Pressure: 2.666 kPa, $CH_4$ / $H_2$= 0.5 / 100, Temp. = 700 $^{0}$C, Time: 8 hrs).

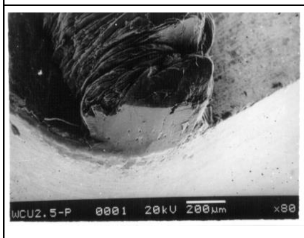
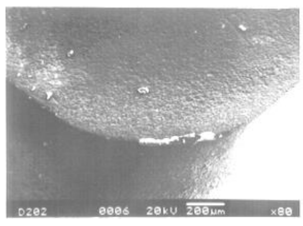
| | |
|---|---|
| Time(min.) | 4 |
| Uncoated | Treat 1(Diamond seeded)<br>Pressure: 2.666 kPa<br>$CH_4/H_2$=0.5/100<br>Temp.=700$^{0}$C |
|  |  |

Fig.3.11: SEM micrographs showing condition of tools after machining for 4 minutes.

## IV. CONCLUSION

- At the early stage diamond powder showed the utmost nucleation density compared to molybdenum and tungsten powder.
- In initial stage compared to $sp^3$ content coating material contains more amount of $sp^2$ content. Carbide inserts etched with Treat 1did not show any development in terms of nucleation or coating with respect to as received carbide surface.
- Among all seeding powders used for nucleation of diamond, diamond powder was the most effectual one. Titanium powders are not suitable for diamond formation. There was no change in phases of Mo and W powders at deposition temperature. Raman peaks corroborate the $sp^3$ / $sp^2$ content has increased with deposition time.
- During dry machining compared to uncoated tool, diamond coated tool displayed significant inertness towards aluminium leading to considerable reduction of cutting force and improved surface finish.

## REFERENCES

[1] TongLee, S. Zhangda, L. Jiang, X. 1999. CVD diamond films: nucleation and growth. Materials Science and Engineering: R: Reports, 25(4): 123-154.
[2] Haubner, R., Lindlbauer, A. and Lux, B. 1996. Diamond nucleation and growth on refractory metals using microwave plasma deposition. International Journal of Refractory Metals and Hard Materials, 14: 119-125.
[3] Liu, H. and Dandy, D.S. 1996. Nucleation kinetics of diamond on carbide-forming substrates during CVD-I, Transient nucleation stage. Journal of Electrochemical Society, 143:1104.
[4] Mahalingam, P. and Dandy, D. S. 1998. A quasi-equilibrium model for the prediction of interlayer chemistry during diamond chemical vapor deposition. Thin Solid Films, 32:108-116.
[5] Tang, C. and Ingram, D. C. 1995. The effect of ultrasonic pretreatment on nucleation density of chemical vapour deposition of diamond. Journal of Applied Physics, 78:5745-5749.
[6] Louchev, O.A., Dussarrat, C. and Sato, Y. 1999. Surface carburization and nucleation during chemical vapour deposition of diamond. Journal of Applied Physics, 86: 1736-1743.
[7] Avigal, Y. and Hoffman, A. 1999. A new method for nucleation enhancement of diamond. Diamond and Related Materials, 8:127-131.
[8] Denning, P. A. and Stevenson, D. A. 1991. Influence of substrate topography on the nucleation of diamond thin films. Journal of Applied Physics, 59:1562-1564.
[9] Lin, C. R. and Kuo, C. T. 1998. Improvement of Diamond Film Adhesion on Cemented Carbides (WC/Co) by Using Ti and Micro-Diamonds as Seeding Germination. Scripta Materialia, 38: 385-390.
[10] Tsubota, T., Ida, S., Okada, N., Nagata, M., Matsumoto, Y. and Yatsushiro, N. 2003. CVD diamond coating on WC–Co cutting tool using ECR MPCVD apparatus via electrophoretic seeding pretreatment. Surface and Coating Technology, 169-170:262-265.
[11] Wolter, S. D., Glass, J. T. and Stoner, B. R. 1995. Bias induced diamond nucleation studies on refractory metal substrates. Journal of Applied Physics, 77:5119-5124.
[12] Sein, H., Ahmed, W., Jackson, M., Polini, R., Hassan, I., Amar, M. and Rego, C. 2004. Enhancing nucleation density and adhesion of polycrystalline diamond films deposited by HFCVD using surface treatments on Co cemented tungsten carbide. Diamond and Related Materials, 13: 610-615.
[13] Chakk, Y., Brener, R.and Hoffman, A.1996. Mechanism of diamond formation on substrates abraded with a mixture of diamond and metal powders. Diamond and Related Materials, 5:286-291.
[14] Hay, R. A. (Ed.). 1994. The New Diamond Technology and its Applications to Cutting Tools. Ceramic Cutting Tools. Vol.11, William Andrew Publishing / Noyes, Norwich, NY: 305.
[15] Schwarz, J. Meteva, K., Grigat, A., Schubnov, A. Metev, S. and Vollertsen, F. 2005. Synthesis of diamond coatings on tungsten carbide with photon plasmatron. Diamond and Related Materials, 14 (3-7): 302-307.
[16] Ueng, H. Y. and Guo, C. T. 2005. Diamond-like carbon coatings on microdrill using an ECR-CVD system. Applied Surface Science, 249(1–4): 246–256.
[17] Chang, C. Liao, Y. Wang, G. Z., Ma, Y. R. and Fang (Eds) R. C. 2003. CVD Diamond Growth. Crystal Growth Technology, Springer, Heidelberg. 4:93.
[18] Jackson, M. J., Gill, M. D. H., Sein, H. and Ahmed, W. 2003. Manufacture of diamond-coated cutting tools for micromachining applications. Proceedings of IMechE Part L: Journal of Materials: Design and Applications, 217 (1): 77-83.
[19] Sein, H., Ahmed, W. Jackson, M. Woodwards, R. and Polini, R. 2004. Performance and characterisation of CVD diamond coated, sintered diamond and WC–Co cutting tools for dental and micromachining applications. Thin Solid Films, 447-448:455-461.
[20] Kobayashi, A. 2005. The features and applications of UPC nano-micro forming tools. Industrial Diamond Review, 4: 28-30.
[21] Sahu, D. K. 2013. Development of diamond coated cemented carbide inserts for machining of non-ferrous materials by HFCVD method. Ph. D. Thesis, Sambalpur University.