DEVELOPMENT AND CHARACTERIZATION OF MICRO-CRYSTALLINE DIAMOND SYNTHESIZED BY HFCVD TECHNIQUE WITH DIFFERENT SEEDING POWDERS

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Abstract:

Synthesis of diamond films on carbide insert is a recent area of research in surface engineering. This research is carryout to know the effect of different seeding powders on diamond coating of WC tool by Hot Filament Chemical Vapor Deposition (HFCVD) method. Here, the formation of microcrystalline diamond (MCD) on SPUN tungsten carbide (WC-Co) cutting tool insert is carried out. Basically, before coating in HFCVD method, the substrate cobalt content should minimize by ultra-sonic etching. The uncoated tools are seeded ultrasonically by Diamond, Iridium, Platinum and Tungsten powder at the same coating condition to observe the growth of diamond crystals. X- ray diffraction gives clear results of diamond plane and adhesion of coating. The purity of diamond crystal after coating can be clear by observing the Raman shift in Raman spectroscopy (RS). The tool is seeded with diamond powder gives more nucleation density due to the presence of more sp3 bond as compared with sp2. Use of diamond and platinum powder as a seeding material gives fully developed crystal and uniform coating during diamond film deposition by HFCVD technique,, rather in case of other powder coating the discrete crystals were formed.

Keywords: Seeding, Hot filament CVD, Raman Spectroscopy, XRD

INTRODUCTION

The CVD diamond coating deposited on tungsten carbide insert has wide application in manufacturing industry. Basically nonferrous materials like aluminium and aluminium-silicon alloys are machined by diamond coated tools. In the CVD process nucleation of grains are much necessary to determine the morphology of diamond crystal. In the diamond deposition process the coating chamber environment also affects the crystal structure of diamond crystal. The formation of secondary nucleation of diamond occurs due to the residual grains implanted on the surface. [1- 4]. The cobalt content of the WC insert can be reduced by using various pre-treatment processes. The surface roughness of specimen can be increased by acid treatment which helps to embed seeding powder. Typically to get better coating adhesion many researchers used different techniques like itching with abrasive powders, biasing, etching ultrasonically and also combinations of these methods [5-7]. The surface morphology changes due to pre-treatment of specimen. The seeding powders are embedded into voids present on surface of substrate [8-10]. The biasing of substrate is a more advisable technique on the nucleation of diamond during coating. The benefits of the negative biasing of substrate are achieving high nucleation density.

The transition metal powder particles which are embedded into the etched surface will help during the growth of diamond crystal after nucleation [11].

The density of nucleation available on substrates abraded ultrasonically was found to be dependent upon the temperature of processing and adsorption. The temperature and pressure play a vital role during coating. The crystal morphology varies from pyramidal to cluster features with decrease in chamber temperature [12]. During the synthesis of nano-crystalline diamond films less chamber pressure is required compared to Micro-crystalline diamond [13-15]. The purity of diamond can be confirmed by knowing the sp3 hybridization rate during coating. D peak and G peak gives more clear results of diamond purity [16-19]. Nevertheless polycrystalline diamond has more impurities compared to single crystal due to more grain boundaries. CVD diamond provides diamond crystals with low defect density [20-23].

METHODOLOGY

The substrate is made up of tungsten and cobalt as a binder particle by powder synthesis process. The tool specification is SPUN 120308 6% wt. Co of WC insert. This is used for deposition of CVD diamond film by HFCVD method. The etchant is used for pre-treatment process as[$HCl+HNO_3+H_2O$ (1:1:1)] ratio for removal of cobalt percentage. Due to the presence of cobalt graphite crystal may arise in place of diamond. Pre- treatment process is carried out appropriately for the time period of 15 min. by using chemical etchant. This process was carried out using ultrasonic vibration vessel (45 KHz) at room temperature to reduce the cobalt percentage

Thereafter the insert was seeded with different powder ultrasonically, such that every seed would get into the voids to propagate nucleation of diamond rapidly at the time of deposition. The table 1 contains deposition parameters and table 2 gives brief idea regarding seeding powders which are used during HFCVD coating.

Table 1 Deposition parameters

Deposition Parameters	Specification
Substrate	WC(SPUN)type
Material of Filament	Tungsten wire(= 0.25 mm)
Filament temperature	2000^{0}C
Stand off distance	8mm
Substrate heater temperature	700^{0}C
Gas ratio	CH_4=1SCCM, H_2 =100SCCM
Reaction chamber pressure	20Torr
Time period of deposition	8Hr.

These following steps were carried out for seeding process.

a) Seeded with 4 different seeding powders by using iso-propanol in a borosil beaker.

b) The seeding process is carried out in the ultrasonic environment (Sonica, 45KHz frequency) for 5minutes. The solvent should not be containing any metal powder lumps and for that sufficient care was taken.

c) After pre-treatment the insert taken outside by the help of non-reactive plastic forceps. Then the insert is going for dry.

d) Again the ultrasonic cleaning is carried out for time period of 1min.withisopropanol alcohol only. The excess amount of metal powder during seeding process was removed from the substrate surface during this process. After that the insert was immediately kept inside the HFCVD chamber.

Table2 Seeding material

Serial No.	Type of seeding powders
1	Diamond powder(0.50m)99.9% pure, Sigma Aldrich
2	Iridium powder(0.6-1m)99.9% pure, Sigma Aldrich
3	Platinum powder(0.15-0.45 m) 99.9%pure, Sigma Aldrich
4	Tungsten powder(0.6-1m)99.9% pure, Sigma Aldrich

The reaction pressure of CVD chamber plays significant role in nucleation and growth of diamond crystals. The flow ratio of hydrogen and methane was kept as 100 SCCM and 1 SCCM respectively. The Mass Flow rate is regulated by using Mass Flow Controllers (Make- MKS). Methane gas flow in MFC having range of 20 SCCM and Hydrogen flow MFC having range of 500 SCCM. The purity level of hydrogen and methane gas is 99.995% and 99.9995% respectively. The pressure control in HFCVD chamber is consist of three important component they are Baratron pressure sensor (Range 1-100 Torr) and throttle valve with feedback control system. The crystal morphology was studied by using SEM (Model-SU3500,Hitachi made). The phases having their respected diffraction angle with crystal planes of different coated tools were studied by the help of X-ray diffraction (PAN analytical 3 kW X'pert Powder – Multifunctional XRD machine). The micro Raman spectroscopy (MODEL T64000, Argon-Krypton mixed ion gas laser) was used to know the purity of diamond coating and graphite present as impurity on coating.

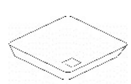
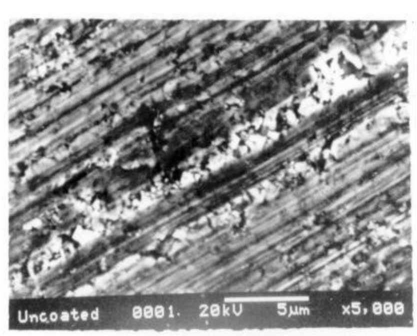
RESULTS AND DISCUSSION

As reserved and after chemical pre-treated substrate taken under SEM in figure 1 for knowing the difference in surface microstructure. The ED Sis taken to know the element affected by acid treated surface compared to as received surface. Generally by acid treatment the cobalt percentage reduced which helps to grow diamond crystal and gives more nucleation during coating which happens in Fig. 2. Fig 3 shows the SEM images of pre-treated inserts after seeding with the different powders. During the seeding process the seeding powders were properly entered into the cavity of the substrate. The X-ray diffraction graphs of as received and after coated substrate is showing in Fig 4.The presence of small, intense peak of diamond (111) slip plane confirms that diamond seeds are occurring in the valleys.

Diamond coated substrates which are seeded with different seeding powders characterized by SEM graphs are shown in figure 5.The substrate which seeded with diamond seeding powder showed cubo-octahedral, continuous and close packed crystals are present in SEM graph compared other powder seeded substrate. This suggests that the diamond crystals were not attacked by the surface cobalt. The diamond grains are projected upward, fully developed and having very good coating adhesion in nature. The secondary nucleation also occurs during the coating

Deposition, so that closed packed crystals are located. The iridium powder is not having a good crystal deposition and also having very small size crystal due to rapid transport of carbon in the substrate. The diamond nucleation rate is very less compared to others. The amorphous nuclei found during the coating due to the contamination of high heat resistance of iridium. Thus the formation of few crystals observes in case of iridium powder.

In case of platinum powder substrate the nucleation density slightly improved compared to tungsten powder. The crystal structure having (111) plane observed in platinum powder rather in case of tungsten powder agglomeration of crystal takes place. High amount of nucleation density is found in case of diamond powder seeded tools. The rake surface uniformly covered with diamond coating and having cutting edge with (111) facets. This is also confirmed by Raman spectroscopy result in Fig 7 with more sp^2/sp^3 content.

Carbide Inserts	 □5000
As received	

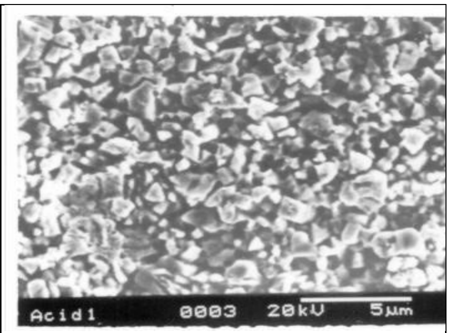
Pre- treatment (HCl+ HNO_3+ H_2O)	

Fig 1 SEM images of insert before treatment and after treatment.

WC inserts	Cobalt (%)
As-received	5.2
After pre-treatment	0.4

Fig.2.EDSofasreceivedandafterpre- treatment WC substrate

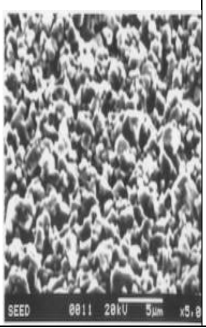
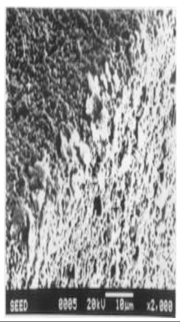
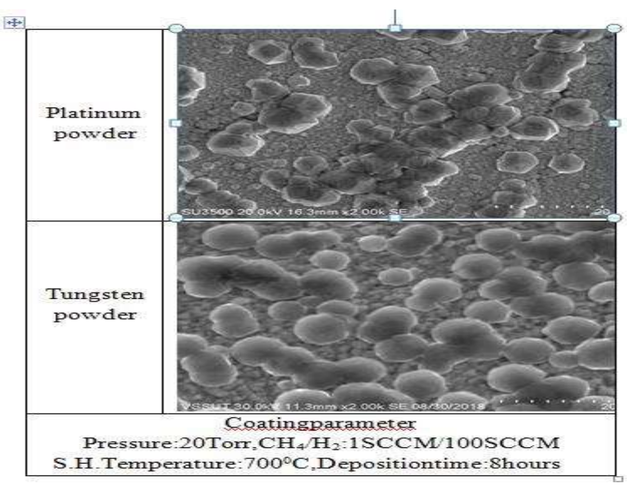
Treatment	□5000	 □2000
HCl+ HNO_3+ H_2O		

Fig. 3. SEM image of the substrate surface after seeding

Fig. 4. SEM images of coated inserts which showing the impact of metal seedingpowders on coating.



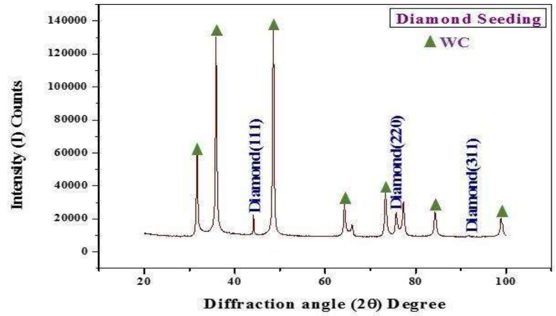


Fig.6.XRDpeaksofdiamondpowderseeded coated tool inserts

From the above Raman spectroscopy graph it can vbe noticed that metal powders did not have much impact on diamond nucleation. Use of diamond powder givescubo-octahedral shaped continuous crystals. This confirms that the micron seeding powdergenerally taken from transition material.

The X-ray analysis gives clear results in diamond plane present on a respective diffraction angle. XRD (X-Ray Diffraction) one of the best method for the tool characterization. In this insert the base materialisWCbyHFCVDprocessathinlayer coating is provided which give diamond peak. The XRD image shows that there are so many WC peaks due to mother material. Planes show the diamondpeakat44˚,75˚and91˚atplane(111), (220) and (311) respectively shown in Fig. 6. It is confirmed that the amount of diamond present in the cutting insert is very less.

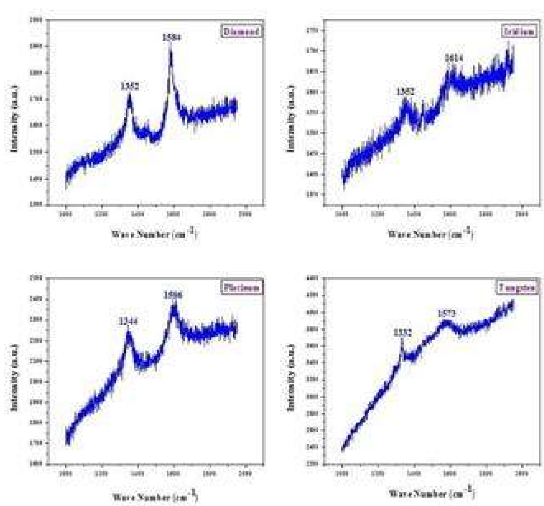


Fig. 7. Raman spectroscopy of coated diamond substrate with different powder seeded surface.

CONCLUSIONS :

In this research work, the WC cutting insert was coated with diamond layer by HFCVD technique using different transition metal powders. The variation of crystal size and coating adhesion with microstructural analysis is carried outbySEM.The purity of crystals after coating is performed by micro Raman spectroscopy. This work gives a new brief idea about diamond coating and itsapplication in various industrial field like manufacturing industry and automobile sector. Novelty of the research is simultaneously use of more seeding powder is rarely available inliteraturereview.

• After pre-treatment the cobalt percentage is reduced to 0.4% which help in better seeding and nucleation of diamond

•The nucleation density of diamond seeded powdersubstrategiveshighestcomparedwith otherpowder seeded substrate.Thesecondary nucleationalsotakesplaceincaseofdiamond powder seeded substrate and also having big crystal size. The rake surface uniformly covered with diamond coating and having cutting edge with (111) facets.

•From the SEM study it was found that the diamond seeded substrate has high coating adhesion and crystals are continues and fully developed in nature.

•The Raman spectroscopy shows very good intensity of diamond peaks in case ofdiamond powder seeded coating tools compared to other different powder seeded tool inserts. The purity of diamond is less in case of other three seeded substratecompared to the diamond seeded substrate.

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