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Diamond Thin Film Coating on WC Substrate by HFCVD Method using Different Seeding Powders and Its Characterization

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Abstract*: The formation of diamond thin solid film is studied by Hot Filament Chemical Vapor Deposition (HFCVD) by using different seeding powders on WC substrate. Here, we have deposited microcrystalline diamond (MCD) on SPUN cemented carbide (WC-Co) cutting tool insert using conventional HFCVD technique. The substrates were ultrasonically seeded with titanium, tungsten, molybdenum, diamond, combined diamond and tungsten powder at the same operation parameters to observe the difference in the growth of diamond by different seeding. Nucleation of diamond coating was studied after 40 minutes of coating with seeded substrate. The physical characteristics were studied by X-ray Diffraction (XRD).The Scanning Electron Microscope (SEM) was used to study the surface morphology. The diamond purity was studied with the help of Raman spectroscopy (RS). Reduction of cobalt percentage before and after pretreatment was studied by Energy Dispersive Spectroscopy (EDS). A very dense and uniform coating was deposited on the diamond powder seeded substrate. The nucleation density was found to be highest in diamond powder when compared with molybdenum and tungsten powder individually, because in initial stage the deposited material contains more sp^2 content as compared to sp^3 content. By using diamond and tungsten mixed powder the coating was uniform rather in case of only tungsten powder coating the discrete crystals were formed.

Index Terms*: HFCVD, *MCD, Raman Spectroscopy, Seeding, XRD.

I. INTRODUCTION

Nucleation process is important for determination of growth morphology along with quality of film for chemical vapour deposition of diamond. Different methods of nucleation rely on material and temperature of substrate, carbon species concentration along with atomic hydrogen produced by hot filament method. The nucleation of diamond may occur on residual grains implanted on the surface after scratching of the same with different powders [1-4]. The nucleation methods majorly rely on the different pretreatment processes for the substrate and also on the operating variables during different stages of the nucleation.

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Normally the substrate is exposed to different techniques like scratching or polishing by using abrasive powders, biasing, etching ultrasonically and also combinations of these methods [5-7].

Due to this pretreatment the surface is modified because of lower points, sharp edges including crest and also due to embedding of remaining powder inside the surface [8]. It is actually difficult to separate the impact of all mentioned factors in a particular mentioned experiment. Again the abrasive particles which are embedded, work like preferred areas for growth as here the nucleation stage is not required. The density of nucleation available on substrates abraded ultrasonically was found to be dependent upon the temperature of processing and adsorption. The surface diffusion also effects nucleation in great manner. The carbon surface diffusion is dependent on interaction of it with substrate. It is having three types which are

- Less or zero solubility or proper reaction type (Cu, Ag, etc.)
- Only C type of diffusion case (Pt, Pd, etc.)
- C type diffusion with formation of carbide (Ti, Fe, Cr, Mo, Ta, W, Co, Si, etc.)

As diamond is having higher surface energy, so nucleation on the substrates is being characterized because of lower densities of nucleation along with longer incubation time period. Hence there is need for surface pretreatment [9, 10].

Many researchers studied in detail about the effect of different metal powders which are to be seeded, abrasive slurry along with diamond powders at the time of nucleation and diamond crystal growth. The metal powders having transitional nature like tungsten, titanium and molybdenum were used to study nucleation along with growth. The materials having highest diffusion coefficient towards carbon atoms show the biggest induction stage for diamond nucleation. This shows clear indication about significance of carbonization stage for diamond nucleation with carbide forming materials [11, 12]. The catalytic action of metal and their specific reactions lead towards growth of diamond [13-15]. The enhancement of concentration for active hydrocarbon fragments in case of CVD diamond production process, alike sp^3 carbon bonding, may be accounted towards the observed increase in growth [16-19]. The reduction in concentration of hydrocarbons which are unsaturated (called as precursors towards graphite formation) and near surface area may be advantageous in diamond growth under the CVD conditions. The metal particles having highest enthalpies of chemisorption are expected to be the most active ones in case of unsaturated hydrocarbons [20-23].

II. Experimental Setup and Procedure

The turning inserts made of cemented carbide having geometry as SPUN 120308, ISO K10 grade with cobalt having 6% wt. were utilized as substrate to get deposition of CVD diamond. Before deposition, by using trichloroethylene and isopropyl alcohol the samples were cleaned for removal of contaminated ones from surface. Then the specimens were etched by using etchant [$HCl+HNO_3+H_2O$ (1:1:1)] solution properly for time period of 15 minutes each. The temperature was room temperature with ultrasonic vibration for removal of cobalt along with WC phases respectively. There after the insert was seeded by using metal and (or) diamond powder ultrasonically, such that every seed would get into the voids to work like site of nucleation at the time of deposition.

Table-1 shows about different deposition parameters along with conditions of HFCVD diamond formation on inserts (carbide)

Deposition Parameters	Specification
Substrate material	WC-6wt% ISO K10 Sandvik cemented carbide insert
Filament material	Carburized Tungsten wire(ϕ = 0.25 mm)
Temperature of filament	2000-2100^{0}C
Substrate to Filament distance	5-6 mm
Temperature of Substrate	700^{0}C
Gas composition values	H_2 =150 SCCM, CH_4 = 0.75 SCCM
Chamber reaction pressure	5 and 20 Torr
Deposition time period	40 and 480 minutes

These steps were carried out for seeding.

a) The suspension of 2-propanol and metal powder(s) was made by using a Borosil beaker of transparent type.
b) One ultrasonic vessel having 40 KHz ultrasonic vibration was used for preparation of the suspension. The time duration was for two minutes in order to obtain uniform mixture. The solvent should not be containing any metal powder lumps and for that sufficient care was taken.
c) By using plastic forceps with utmost care the insert (pretreated) was kept totally immersed within the prepared solution. Proper care was taken such that top (upper) surface of pretreated insert touched the bottom (lower) part of beaker. Because of this the insert contact with the solution increased. The agitation by ultrasonic means was done in continuous manner for a time period of 2 minutes.
d) Thereafter with the help of forceps the insert was taken out. Then it was dried by means hot air.
e) The same operation was once more continued for time period of 1 minute in 2-propanol only. The extra amount of metal powder was removed from the insert surface by means of this process. Thereafter the insert was immediately kept inside the HFCVD chamber.

Table-2 Seeding materials

Serial No.	Type of seed materials
1	Titanium powder(TiH_2) (1-2 μm) 99.9% pure, Fluka
2	Tungsten powder(0.6-1μm) 99.9% pure, Aldrich
3	Molybdenum powder(1-2μm) 99.9% pure, Aldrich
4	Diamond powder(0-2μm)
5	Combined diamond and tungsten powder

From these two stages it was confirmed that the seeds were uniformly embedded into the cavity of the carbide inserts. The initial nucleation and growth were varied with the addition of these seed powders.

For the crystal nucleation and then for diamond growth the reaction pressure plays important part. For both hydrogen and methane the flow rate were kept as 150 SCCM and 0.75 SCCM respectively. This flow rate was maintained by using Mass Flow Controllers (Make- MKS). The hydrogen and methane used were having purity level of 99.995% and 99.9995% respectively. The Baratron pressure sensor (MKS made, range from 1-100 Torr) and throttle valve with feedback control were utilized for the regulation of the pressure for the HFCVD chamber. The Talysurf (Talylor-Hobson Surtonic 3P) was used to measure surface roughness values of the concerned inserts. The Ra, Rz and Rmax. values were measured in μm by using a computer interface. The morphology of crystal was characterized by using SEM (No. of Model: JEOL 5800). The crystal planes of various phases of different materials were detected by the help of X-ray diffraction process using machine by Philips 1710 utilizing nickel-filtered Cu Kα(λ=01.54178Å) produced by 40kV/20 mA having speed of scanning as 3^0 per every minute. The JCPDS software was used for comparison of peaks. The micro Raman spectroscopy (Model Type: RENISHAW 20 mW Argon laser, wavelength value – 514.5nm, diameter of beam – 1.5μm) was used to analyze the diamond coating purity.

Experiments were conducted to know the effect of phase change by heating the metal powders Ti, Mo and W during deposition temperature of 700^{0}C. The X-ray peaks of the TiH_2 planes were shown in phase-I. The TiH_2 powder was kept in a dense ceramic crucible and heated to 700^{0}C in a vacuum furnace at a chamber pressure of 5×10^{-6} Torr. The temperature was maintained for 30 minutes. Then the powder was cooled to room temperature at a cooling rate of 10^{0}C/min. X-ray of this powder was done to detect the presence of different phases and shown in phase-II. Now this powder was heated again in hydrogen atmosphere at 700^{0}C in a ceramic crucible for 30 minutes at a pressure of 20 Torr in our HFCVD chamber. Now once again this powder was taken for X-ray analysis in phase-III to identify the presence of different phases. Mo powder was then taken for X-ray analysis and the different planes were shown in phase-I. The molybdenum powder was heated in a ceramic crucible in hydrogen atmosphere at 700^{0}C for one hour at a chamber pressure of 20 Torr. X-ray was done for this powder in phase-II to find out any deviation in the phase or formation of metal hydride.

The same procedures were followed for tungsten powder as well to find out the difference in phases on as received metal powder and after heating in hydrogen atmosphere. The experiments were conducted to find out the existence of metal hydride, oxide or combination of hydride and oxide during deposition. These experiments confirm the importance of transitional metal powder during nucleation of diamond and growth.

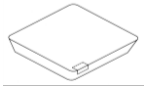
III. Result & Discussion

The Fig 1 is showing the SEM pictures of both as received substrate and pretreated substrate surface by etchant. Fig 2 shows EDAX of carbide substrates on as received substrate and pretreated with etchant .The SEM pictures in Fig 3 shows the pretreated inserts by etchant along with the diamond powder seeded inserts. Diamond powders were embedded inside the grooves and cavity. The X-ray peaks in Fig 4 showing the appearance of small peak of diamond (111) plane confirms that diamond seeds are retained inside the valleys. The SEM pictures in Fig 5 reveal few crystallites of diamond on the rake surface at chamber pressure of 5 Torr on both pretreated inserts after deposition of 40 minutes. Among these three powders the diamond powder showed nucleation density of highest value as compared with molybdenum and tungsten powder. The Raman peaks in Fig 6 after nucleation with different powders confirm the presence of amorphous peaks with equal portion of sp2 and sp3 content.

Fig 7 shows the SEM pictures of the diamond coating after deposition time of 8 hours on different substrates. The as received substrate showed cubo octahedral crystals and some part of the crystals were porous. This implies diamond crystals were attacked by surface cobalt. The pretreated insert by using etchant showed formation of few discrete crystals without the help of diamond seeds.

The titanium powder is not having any affect in formation of diamond due to formation of metal hydride during depositions. Because of rapid transport of carbon in the substrate diamond nucleation occurs rather late. The beginning of few nuclei survives due to the high rate of carbon dissolution into the Ti seeded substrate and forms titanium carbide. Thus it leads to formation of very few crystals.

Molybdenum powder showed slight improvement in nucleation density. Addition of tungsten powder also showed the similar kind of result. But using insert which was pretreated by etchant along with seeded by diamond powder, the density of nucleation was found to be highest and it also uniformly covered on the rake as well as cutting edge with (111) facets. This is also confirmed by Raman spectroscopy result in Fig 8 with more sp2/sp3 content. The specimen being pretreated by etchant and seeded by mixture of tungsten and diamond powder has showed slightly bigger crystals.

Carbide Inserts	 ×5000	 ×2000

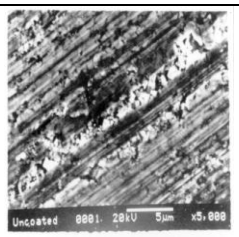
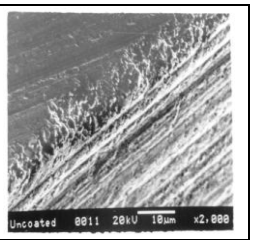
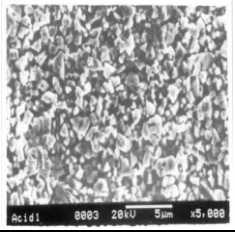
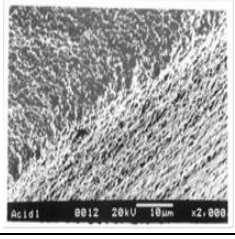
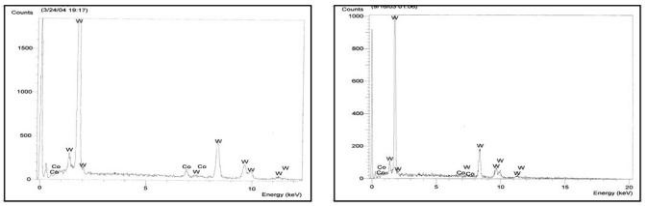
As received		
Treatment With Etchant (HCl+ HNO_3+ H_2O)		

Fig-1 SEM images of surface along with cutting edge morphology for insert before treatment &after treatment.



(As received) (After treat)

Fig-2 EDAX spectra of as received substrate surface and after treatment substrate surface.

Table-3 Cobalt percentage from EDAX spectra

Carbide Inserts	Percentage of Co
As received	5.2%
After treatment	0.4%

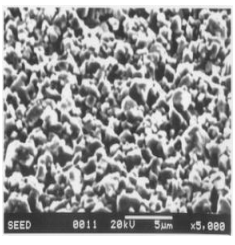
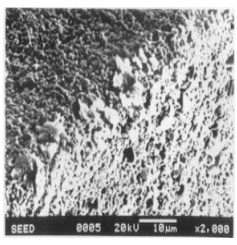
Treatment	 ×5000	 ×2000
HCl+ HNO_3+ H_2O		

Fig-3 SEM micrographs of the substrate surface after etching

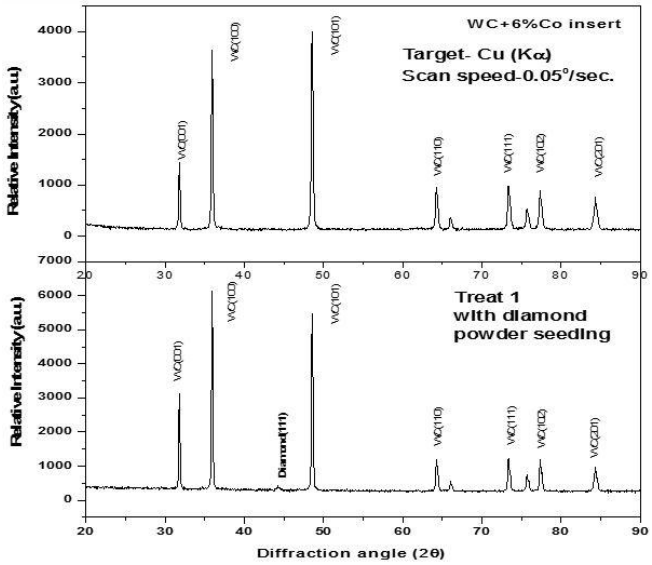


Fig-4 X-Ray Diffraction of as received carbide insert and diamond seeded carbide insert after pretreatment.

The Table 3 shows the cobalt content for as received and after pretreatment. This table shows decrease in percentage of cobalt up to 0.4%.

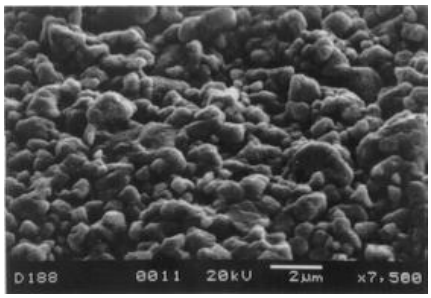
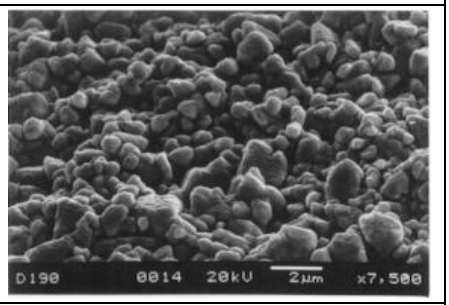
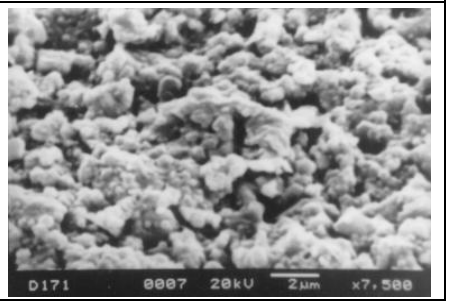
Types of seeding	Pretreatment ×7500
Mo seeding	
W seeding	
Diamond seeding	

Fig-5 SEM pictures showing nucleation of diamond crystallites after nucleation of 40 minutes.

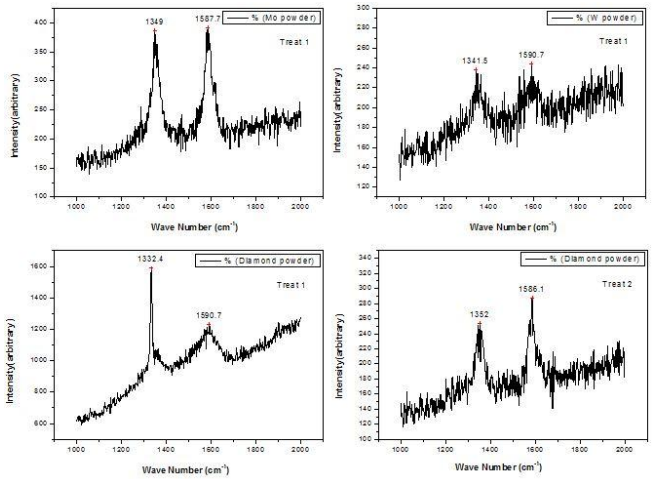
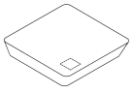
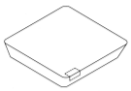
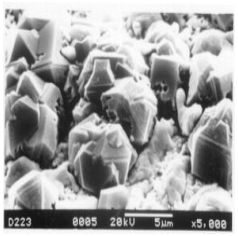
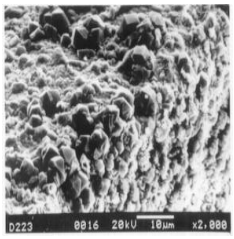
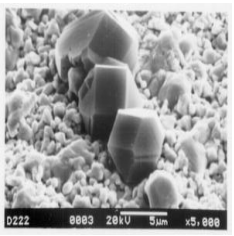
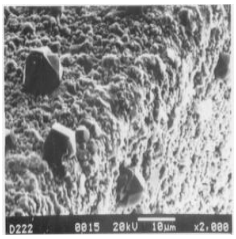
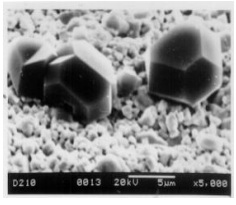
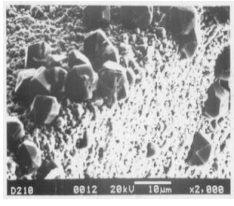
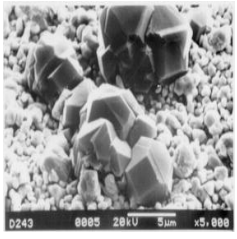
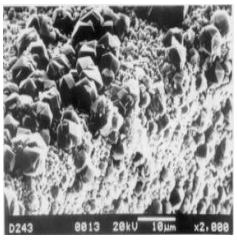


Fig-6 Raman spectroscopy peaks of diamond and amorphous carbon on nucleation for diamond after 40 minutes.

Type of seeding	 ×5000	 ×2000
As received No seeding		
Treated No seeding		
Treated Titanium powder		
Treated Molybde-num powder		

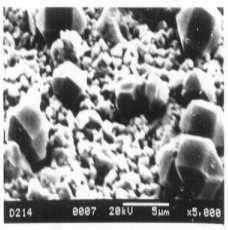
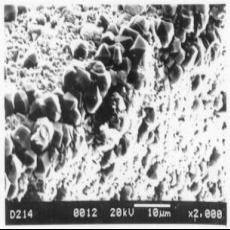
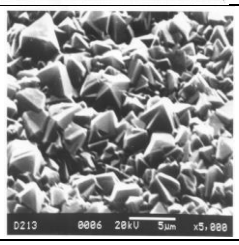
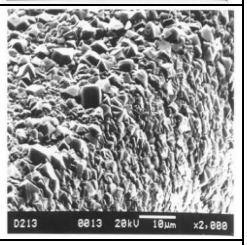
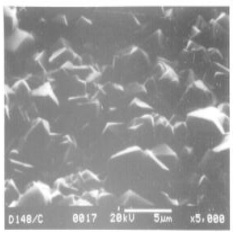
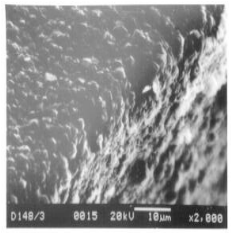
Treated Tungsten powder		
Treated Diamond powder		
Treated Tungsten And Diamond powder		
Deposition parameter Pressure:20 Torr,CH_4/H_2:0.75 SCCM/150 SCCM Substrate temperature:700^{0}C,Deposition time:8 hours		

Fig-7 SEM images for impact of seeding materials about nucleation and growth of diamond on carbide inserts

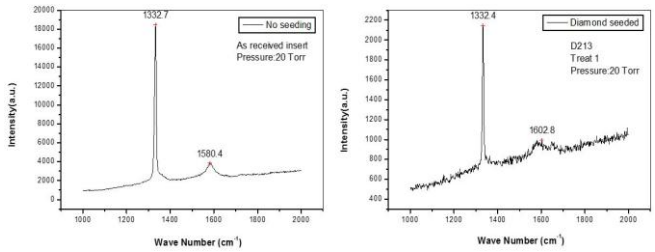


Fig-8 Raman spectroscopy of full grown diamond after deposition time of 8 hours.

All the results confirm that these metal powders did not have much impact on nucleation of diamond. Except use of diamond powder the inserts had cubo octahedral shaped discrete crystals. This confirms that the metal seeds did not have active part in retention of carbon phase/radicals on the grooves of the carbide insert.

The actual roles of metal powders were tried to be found out by X-ray analysis. During deposition in the presence of hydrogen, carbon and oxygen the metal powder might have changed to some intermediate phases. The changes of the X-ray planes of TiH_2 powder explains the titanium hydride powder has reduced to titanium (α phase) in heating in a high vacuum (5×10^{-6} Torr). However, all TiH_2 phases reappeared after heating once again in hydrogen atmosphere. This shows that titanium powder is not at all effective in diamond growth. These results were confirmed by X-ray analysis and are shown in Fig 9.

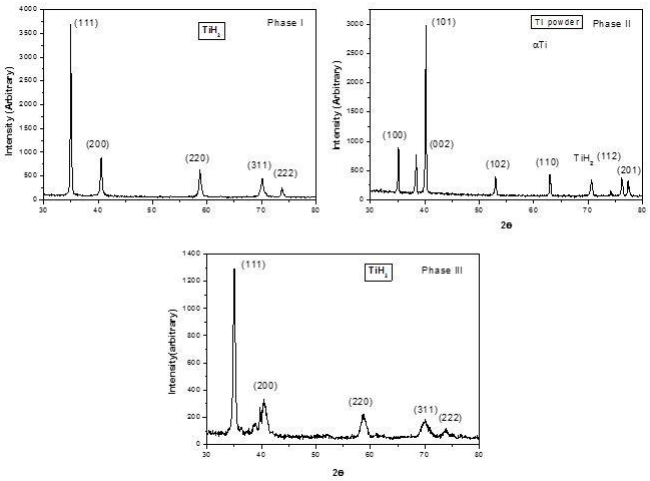


Fig-9 X-ray peaks of different phases of titanium, titanium hydride and titanium oxide at different stages.

Molybdenum powder did not show any change in crystal habits due to high melting point and high oxidation resistance at 700-800^{0}C in hydrogen atmosphere [1]. Tungsten powder also showed similar result as molybdenum powder and was confirmed by X-ray analysis shown in Fig 10.

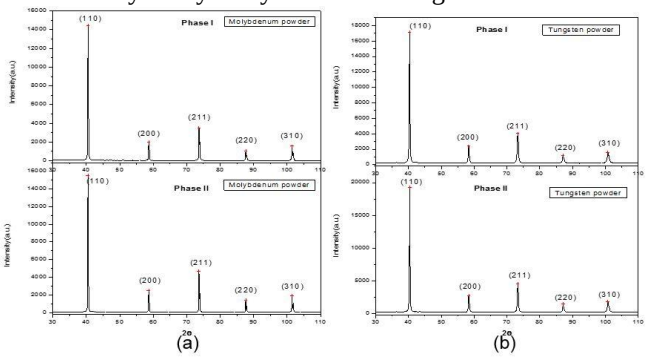


Fig-10 X-Ray peaks of molybdenum and tungsten powder with different crystal habits

IV. CONCLUSION

- The etchant could reduce the surface cobalt concentration of substrate (WC+Co) to lower value of 0.4%.
- Diamond powder showed the nucleation density as highest when compared with molybdenum and tungsten powder individually during the initial stage. In initial stage the deposited material contains more sp2 content compared to sp3 content.
- Among seeding powders used for nucleation of diamond, diamond powder was the most effective one.
- Titanium powders changed to TiH2 phase at 7000C and thus not suitable for diamond formation. There was no change in phases of molybdenum and tungsten powders at deposition temperature. Among different metal powders, tungsten powder exhibited slightly more nucleation density with small crystals.
- Tungsten and diamond powder together as seed could result in diamond coating with comparable morphology but increase in crystal size by about 10% was also observed.

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