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Integrity of CVD-Diamond Coatings on Cemented Tungsten Carbide Substrate: Mathematical Analysis carried out for Calculating the Force of De-lamination and Load Bearing Capacity of Coating-substrate System

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ABSTRACT

Smooth and adhesivenanocrystalline diamond (NCD) and microcrystalline diamond (MCD) coatingshave been achieved on a chemically etched cemented tungsten carbide (WC-6%Co) substrates, using hot filament chemical vapor deposition (HFCVD) technique. Structural and micro-structural characteristics of these coatings were compared using X-ray diffraction (XRD), Raman spectroscopy and Scanning electron microscopy (SEM) techniques.The parameters affecting the integrity of these coating-substrate systems were studied and mathematical analysis was carried outfor calculating the force of de-lamination and load bearing capacity.

Introduction

Natural diamond is known for itshighest hardest with high elastic modulus, good chemical inertness, prominent thermal stability, less coefficient of friction and having a large projected wear life [1]. Due to its high wear resistance, enough adhesion strength (on substrates)and to withstand high amount of mechanical load makes the diamond a promising candidate for the industrial applications [2]. Cemented tungsten carbide (WC-Co) is the commonly used hard material for cutting tools and tribological components because of its high wear resistance and high elastic modulus.

Hot filament chemical vapor deposition (HFCVD) is now today’s best technique used for the deposition of synthetic diamond coatings on tungsten carbide material. CVD-diamond coatings are now usedfor improving the mechanical and tribological behavior of WC-Co tools because of high hardness and low friction coefficient [3]. CVD-diamond has drawn great attention of the researchers through years of development because of its unique mechanical, thermal, electrical and tribologicalproperties with excellentindustrial applications [4]. Extensive research has led to the successful application of CVD-diamond coatings on WC-Co hard material by controlling the % weight of cobalt, tungsten carbide grain size and different surface treatment processes [5, 6].

Growth of CVD-diamond Coatings

Cobalt (Co) in WC-Co material acts as binder and increases its hardness, but the presence of surface Co resists the nucleation of diamond coating and permits the formation of the graphitic carbon phases, which decrease the strength of adhesiveness [7]. Hence, the removal of surface cobalt by chemical etching method is very necessary to enhance the force of adhesion of coating-substrate system [8].Thermal stresses which are produced during the deposition and cooling down processalso affect the adhesiveness[9].These thermal stresses are reduced by choosing the proper grade of WC-Co material with minimum cobalt content, which decreases the change in thermal expansion coefficient of coating-substrate system [10].

Methane concentration and chamber pressure are adjusted to control the grain size of the diamond coatings [11]. Smooth nanocrystalline diamond (NCD) surfaces are developed by reducing the grain size to the order of nanometers, which are suitable for practical applications, but intrinsic stresses within a layer increase with a decreasing grain size [12].

NCD coatings have larger number of grain boundaries that contain maximum amount of graphitic carbon phases which decrease the crystallinity of diamond films and therefore affecting the mechanical properties [13]. Surfaceroughness, morphology and microstructures play important role in enhancing the adhesion between the coating and substrate system [14].The adhesive properties between theinterfacesof diamond coatings also depends onmicrostructure, therefore MCD coatings show high hardness, high coefficient of friction and low adhesiveness (on substrates) due to more grain size in comparison to NCD coatings [15].

There are various methods to evaluate the adhesive strength of the coating-substrate interface. Indentation test is a qualitative technique to analyze the adhesion characteristics of the coatings, whereas dynamic scratch test method is a potentially quantitative procedure to assess the adhesion characteristics of the coatings [16, 17]. Raman line-width is linearly related to the thin film growth rate and linearly related to the inverse of the particle size, measured by X-ray. Thus, the film growth rate is also linearly related to the inverse

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of the particle size [18].

Increasing the coating thickness increases the grain size and will increase the residual stresses at the coating–substrate interface but will only increases the load bearing capacity [19]. The adhesive strength can also be improved by increasing the contact area between coating and substrate [20].

Toachieve the advantages of both NCD and MCD layersmultilayer coatings system is one of the new techniques used recently.Multilayer composite diamond coatings system consisting of alternate layers of MCD and NCD are reported with low friction, improved surface roughness, good adhesion and mechanical properties. However, using transition layer between MCD and NCD increases the strength of adhesiveness between these coatings. Because of the difference in residual stresses among the layers and higher degree of graphitic content at the interface of NCD layer, there may be separation during practical applications [21].

In the present study, smooth and adhesive (∼3μm thick)nanocrystalline andmicrocrystalline diamond coatings have beensuccessfully achieved on two WC-Co substrates, using hot filament CVD technique.The analysis revealed the high phase purity, well oriented crystalline and columnar growth of both types of coatings. The parameters affecting the integrity of coating-substrate system were studied and also two mathematical expressions were derived for calculating the force of de-lamination and load bearing capacity.

Experimental Details

Cemented tungsten carbide substrate material (WC-Co, Ceratizit-CTF12A) with 6% Co and 0.8–1.3μm WC grain size was selected. Samples (cubed shape) of size 1cm×1cm×0.3cm were first cleaned in ethyl alcohol with ultrasonic agitation to remove the surface impurities from the substrate.Substrates were chemically treated with Murakami's reagent (10 g KOH+10 g K_3 [Fe (CN) 6] +100 ml water) for 10 min using ultrasonic agitation followed by cobalt etching for 10s with Caro's acid (3ml (96%) H_2SO_4+88 ml (30%) H_2O_2). Then the samples were seeded with nano-diamond particles (4-6 nm) dispersion for 10 min by ultrasonic agitation to increase the nucleation density and to fill the cavities. Finally samples were treated with isopropyl alcohol for 2 min to remove the loosely bound nano-diamond particles from the surface.

Hot Filament Chemical Vapor Deposition Process

Hot filament CVD system (Model 650 series, sp3 Diamond Technologies) with enhanced process control system was used for the diamond growth. Chamber pressure and methane concentration can be controlled dynamically during deposition by using throttle valve and mass flow controllers respectively. An array of tungsten wires (ø 0.12 mm) were used as hot filaments for the activation of gaseous phase. The filament to substrate distance of 15 mm was maintained for all the experiments. Hydrogen (H_2) and methane (CH_4) were used as the precursor gases and their gas flow rates were controlled using mass flow controllers. Grain size of the diamond films can be changed by changing the methane concentration and chamber pressure during process. By increasing the methane concentration and decreasing the chamber pressure will enhance the secondary nucleation and therefore decreases the grain size from microcrystalline diamond (MCD) to that of nanocrystalline diamond (NCD) [22].

Results and Discussions

Physical Characterization

The surface morphology and microstructure of the NCD and MCD coatings were studied using High Resolution Scanning Electron Microscope (Quanta 3D, FEI). Coating crystallinity was studied using grazing incidence X-ray diffraction (PANalytical) technique with Cu Kα (λ=0.154 nm). Raman microscope (Alpha 300, WITec) with a 488 nm wavelength of laser light was used for the study of quality, nature and study stress state analysis.

X-ray Diffraction (XRD) Technique

The XRD patterns of MCD and NCD coatings are shown in fig.1. (a) and (b) respectively. Sharp and intense peaks of cubic diamond coating corresponding to (111) crystal and (220) crystal planes were observed at 44° and 75.5° respectively for both these coatings, along with the substrate (WC) peaks. These peaks confirm the crystallinity of these coatings [23]. The variations in these peaks show that there are differentinterferences at different planes and the highest peaks of WC substrate show that its grain size is more than nano/micro-diamond coating.

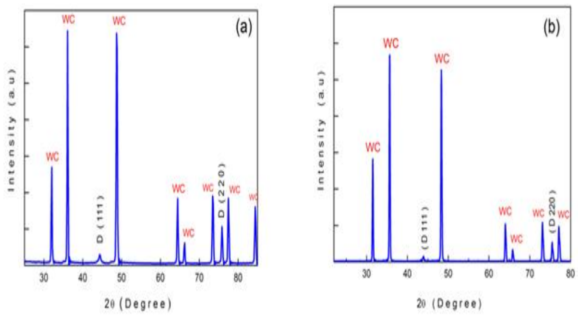

Fig 1. X-ray diffraction patterns of (a) MCD and (b) NCD coatings

Raman Spectroscopy and Residual Stress Analysis

Fig.2. (a) and (b) show the Raman spectra of MCD and NCD diamond coatings respectively.Raman spectroscopy was used to checkthe chemical structure, crystalline quality and stress state analysis of the diamond coatings. Therefore, free stress crystalline diamond coating shows fundamental Raman peak at 1333 cm^{-1}, confirms that the coating is diamond in nature [24]. First order Raman peak shift towards higher side centred at 1333 $cm^{-1}$is indicative of the presence of residual compressive stress in both the coatings. Mainly, these compressive residual stresses are due to the difference in thermal expansion coefficients between substrate and coating system[25]. Residual stresses can be calculated from σ = -0.348 (v_m – v_0) G Pa for the un-split Raman peak at v_m, where v_0 =1332 $cm^{-1}$and v_m = 1333 cm^{-1}. Thus, each deposited diamond films accommodate a compressive stress of 0.348 G Pa. [26]. Two other peaks ν_1 = 1143 cm^{-1} and ν_3 = 1431 cm^{-1}, are characteristics of in-plane (C-H) and stretching (C=C) vibrational modes, respectively. The presence of these modes wasdue the formation of transployacetylene (TPA) chain in the grain boundaries of NCD coatings [27].

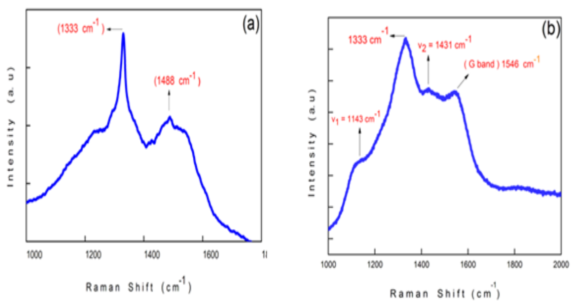

Fig 2. Raman Spectra of (a) MCD coating and (b) NCD coating

Scanning Electron Microscopy Technique (SEM)

SEM technique was used to study the surface morphology, microstructure and grain size of coatings. Fig.3(a),(b) and (c) show SEM images of 3μm thickNCD coating, with grain size lying in the range of 0.2–0.6μm on its surface. Fig.3 (d) shows the histogram of SEM image, where the average grain size is 0.35μm.Nano-characteristics were observed over the whole surface, otherwise there is most chance of abnormal grain growth with thick (>3μm) NCD coatings [28].Fig.4 (a), (b)and (c) show HRSEM images of the3μm thickMCD coating, with grain size lying in the range of 0.3–0.7μmon its surface. Fig.4 (d) shows the histogram of SEM image, where the average grain size is 0.50μm. MCD always shows faceted form of surface morphology whereas; a cauliflower type of surface morphology is generally seen with the NCD coatings. The comparison between the characteristics of WC-Co and CVD-diamond coatings are shown in table 1.

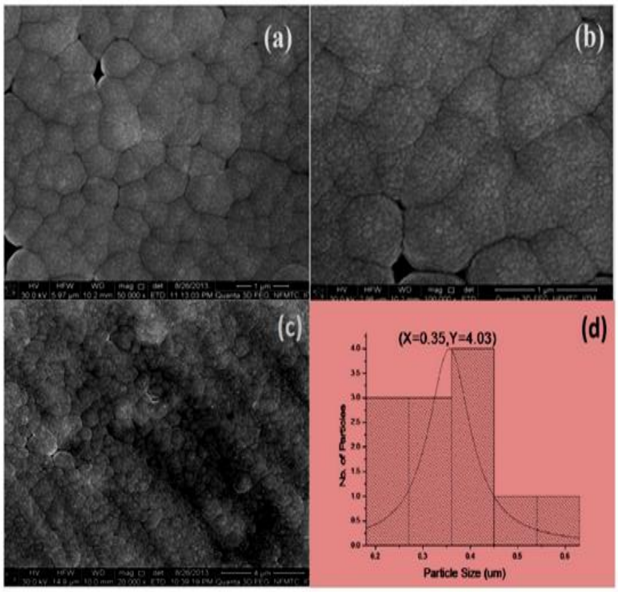

Fig 3. (a), (b), (c) SEM images of single layer NCD coatingand (d) histogram of SEM image

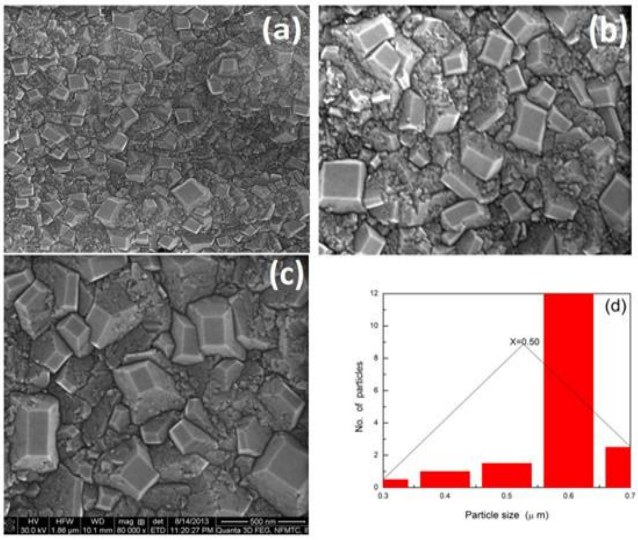

Fig 4. (a), (b), (c) SEM images of single layer MCDcoating and (d) histogram of SEM image

Parameters Affecting the Integrity of Coating-substrate System

The parameters on which the strength of adhesiveness between coating and substrate system mainly depends are: (1) Surface roughness of substrate before deposition (2) Elastic modulus of substrate (3) Contact surface area between coating and substrate (4) Coating thickness (5) Grain size of coating and (6) Compressive thermal stresses at the interface of coating-substrate system.

Compressive thermal stresses (σ) cannot be eliminated, as they were produced during the deposition and cooling down process of coating in HFCVD. These stresses mainly depend on temperature of substrate during diamond growth, presence of graphitic carbon at grain boundaries and thickness of coating.

Consider a CVD- diamond coating of thickness $t(\mu m)$. Suppose S (cm^2) be the contact area between substrate and coating and σ(Newton/cm^2) be the compressive thermal stresses at the interface of coating-substrate system. Let x (nmor μm) be the average grain size and N be the number of grain particles (appox.) on NCD surface, as both can be calculated from the histogram of SEM image. Therefore total size of all grain particles on NCD surface is equal to NX.

Force causingthe De-lamination of Coating-substrate System

If F (Newton/cm^3) represents the force per unit volume causing de-lamination between coating and substrate system, then it mainly depends on: σ, t, NX and $\frac{1}{S}$.

Combining above equations, therefore $F \propto \frac{\sigma \times t \times (NX)}{S}$

Suppose NX= A, then $F \propto \frac{\sigma \times t \times A}{S}$

Or $F = k\frac{\sigma \times t \times A}{S}$ (1)

Where k is a constant of proportionality and it depends inversely on the roughness factor, Ra (μm or nm)of WC-Co surface before deposition i.e. $k \propto \frac{1}{Ra}$.Since the strength of adhesiveness between coating and substrate increases with the increase in value of Ra, therefore the force of de-lamination decreases with the increase in value of Ra. This clearly suggests that why chemical etching is necessary for the surface of WC-Co substrate before diamond deposition. During chemical etching the surface roughness has been increased and more cavities were produced in order to increase the integrity of coating-substrate system.

From eq. (1),

$$F = \frac{1}{Ra}\left[\frac{\sigma \times t \times A}{S}\right] \quad (2)$$

Or F (Newton/cm^3)

$$= \frac{1}{Ra\,(\mu m)}\left[\frac{\sigma(Newton/cm^2) \quad \times t\,(\mu m) \times A\,(nm) \times}{S\,(cm^2)}\right.$$

$[10^{-7}]$…………….. (3)

The eq.(3) shows that F mainly depends on Ra, t, S and A, which describes that the adhesiveness of coating-substrate system can be only improved by increasing value of Ra and S or by decreasing value of A and t.

Thus the force of de-lamination, F can be decreased by decreasing the grain size of diamond film, which can be maintained by changing the process parameters during HFCVD process. This equation clearly suggests that nanocrystalline diamond layer has good integrity with WC-Co substrate than microcrystalline diamond layer because of smaller grain size, but presence of graphitic carbon at grain boundaries decreases adhesive force. Also using thick NCD ($> 3\mu m$) coating decreases its adhesive strength with WC-Co substrate because increasing thickness increases the grain size.

Table 1. Characteristics of WC-Co and CVD-diamond coatings

Material	Roughness Factor (R_a)	Average Grain Size	Surface Area (S)	Thermal Residual Compressive Stresses (σ)	Thickness (t)	Elastic Modulus (E)
WC-Co	~0.35 µm	1.05 µm	$1 cm^2$		0.3 cm	~550GPa
NCD	~0.19 µm	0.35 µm	-	0.348 G Pa= 34800 N/cm^2	3 µm	
MCD	~0.25 µm	0.50 µm	-	-	3 µm	

Calculation of Force of de-lamination for WC-Co/NCD

Usingeq. (3), F ($Newton/cm^3$)

$$= \frac{1}{Ra}\left[\frac{\sigma(Newton/cm^2)\times t(\mu m)\times A(nm)}{S(cm^2)}\times[10^{-7}]\right.$$

$$= \frac{1}{0.35\,(\mu m)}\left[\frac{34800\left(\frac{Newton}{cm^2}\right)\times 3(\mu m)\times\{4\times 0.35\times 10^{-3}(\mu m)\}}{1\,(cm^2)}\right.\times$$

$[10^{-7}]=4.17600\times10^{-5}$**,** Where for NCD surface, A= NX= 12× 0.50 (µm).

Calculation of Force of de-lamination for WC-Co/MCD

Using eq. (3), F ($Newton/cm^3$)

$$= \frac{1}{Ra}\left[\frac{\sigma(Newton/cm^2)\times t(\mu m)\times A(nm)}{S(cm^2)}\times[10^{-7}]\right.$$

$$= \frac{1}{0.35\,(\mu m)}\left[\frac{34800\left(\frac{Newton}{cm^2}\right)\times 3(\mu m)\times\{12\times 0.50\times 10^{-3}(\mu m)\}}{1\,(cm^2)}\right.$$

$\times[10^{-7}]=17.89715\times10^{-5}$**,** Where for MCD surface, A= NX= 12× 0.50 (µm).

Based on the above calculations, the adhesiveness of NCD is more than MCD on WC-Co substrate due to less force of de-lamination between interface of coating-substrate system, thus eq. (3) is validated.

Expression for Load Bearing Capacity

For the design of coating-substrate system for mechanical applications, this system can be separated into three components such as (i) coating, (ii) interface and (iii) substrate.

The coating is expected to have high wear resistance, high hardness, low friction coefficient, good surface finish, high oxidation resistance, high fracture toughness, high thermal conductivity and enough thickness for load-bearing applications. The Interface should have good adhesion and shear strength. The substrate should have high elastic modulus for load-bearing applications, high temperature strength and high thermal conductivity [29].

Thus the load bearing capacity per unit length for the design of coating-substrate system mainly depends on: (1) Elastic modulus of substrate (2) Coating thickness and (3) Grain size of coating.

Let Es ($Newton/cm^2$) = the elastic modulus of substrateand for WC-Co, Es = 550GPa.If F (Newton) per unit length,be the amount of load bearing capacity for the design of coating-substrate system, it mainly depends on: Es, t and A

Combining above equations, therefore F $\propto$ Es $\times$ t $\times$ A

Or $F = zEs \times t \times A$ (4)

Where z (mm) is the propertyof coating-substrate system, called adhesive critical failure regionand can be calculated experimentally during scratch adhesion testing.These adhesive critical failure regions can be identified by simplemicroscopic analysis and it was found that the NCD and MCDcoatings were failed at a scratch distance of about 0.75 and 1.57mm i.e. z_{NCD} = 0.75mm, z_{MCD}= 1.57mm [30].

From eq. (1),

$$F\,(Newton) = z\,(mm)\times Es\left(\frac{Newton}{cm^2}\right)\times t\,(\mu m)\times A(nm)$$

Or

$$F\,(Newton) = z\,(mm)\times Es\left(\frac{Newton}{cm^2}\right)\times t\,(\mu m)\times A(nm)\times[10^{-12}] \quad (5)$$

Thus the above equation clearly shows that, using thick NCD or MCD coating on WC-Co substrate increases only its load bearing capacity.

Calculation of load bearing capacity for WC-Co/NCD

Using eq. (5),

$$F\,(Newton) = z_{NCD}\,(mm)\times Es\left(\frac{Newton}{cm^2}\right)\times t\,(\mu m)\times A(nm)\times[10^{-12}]$$

$$= 0.75\,(mm)\times\{550\times10^5\left(\frac{Newton}{cm^2}\right)\}\times 3(\mu m)\times\{4\times0.35\times10^{-3}(\mu m)\}\times[10^{-12}].$$

$$= 1732\times10^{-10}.$$

Calculation of load bearing capacity for WC-Co/MCD

Using eq. (5),

$$F\,(Newton) = z_{MCD}\,(mm)\times Es\left(\frac{Newton}{cm^2}\right)\times t\,(\mu m)\times A(nm)\times[10^{-12}]$$

$$= 1.57\,(mm)\times\{550\times10^5\left(\frac{Newton}{cm^2}\right)\}\times 3(\mu m)\times\{12\times0.50\times10^{-3}(\mu m)\times[10^{-12}].$$

$$= 15543\times10^{-10}.$$

Based on the above calculations, the load bearing capacity of MCD coating is more than NCD coating on WC-Co substrate, thus eq. (5) is validated.

Conclusions

The integrity of NCD and MCD coatings on WC-Co substrate can be enhanced by maintaining the parameters like coating thickness, grain size of coating and surface roughness of substrate.The adhesiveness of NCD coating is more than MCD coating on WC-Co substrate, due to less force of de-lamination between interface of coating and substrate system. Hence, increase in thickness of these coatingsincreases only load bearing capacity and the load bearing capacity of MCD coating is more than NCD coating.Therefore, usingdual layer (MCD-NCD) coatings on WC-Co with 3µm thickness, low friction coefficient, high hardness and good interfacial integrity would certainly be important for many engineering applications.

Competing interests

The authors declare that they have no competing interests and are unanimously agreed upon the submission of this article.

Authors' contributions

K. A. Najar, M. A. Shah and N. A. Sheikhcontributed in the synthesis and characterization and drafted the manuscript. All authors read and approved the final manuscript.

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