MECHANICAL PROPERTIES OF HFCVD MICROCRYSTALINE DIAMOND COATED ON SEEDED WC SUBSTRATE

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To

My Beloved Family

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ABSTRACT

The mechanical properties and adhesion strength of a diamond film coated on cemented carbide has great significance in its performance as a cutting tool. Many studies have been conducted to improve the mechanical properties through the careful optimization of a variety of substrate pretreatment techniques. In this study, a two step chemically pretreated WC-6% Co was seeded with a solution of diamond powders (0.5µm) having fixed concentration (0.8 g/l) mixed with varying SiC powders (175µm) concentration of 1.0, 5.0 and 10.0 g/l respectively so as to produce different microcrystalline diamond film surface roughness. Diamond films were grown on the pretreated tungsten carbide (WC) substrates using hot filament chemical vapour deposition (HFCVD) technique for 30 hours with fixed parameter. Field emission scanning electron microscope (FESEM) images and x-ray diffraction (XRD) spectrums results indicates that all the diamond films have well faceted grains of (111) and (220) morphologies. The WC substrates etched and seeded with 1g/l of SiC mixed with 0.8g/l of diamond powders was found to have diamond coating with sharp peaks with uniform height and gaps between diamond grains when observed using atomic force microscope (AFM). Sand blasting technique was employed to determine the adhesion strength of the coated diamond film, where the sample seeded with a mixture of diamond with 5 g/l SiC powder concentration was found to have the highest diamond film adhesion strength. Nano-scratch tests show that all the diamond films have excellent adhesion with the mode of deformation found to be cohesive chipping rather than adhesive failure. Nano-indentation tests using Berkovich indenter revealed that the substrate seeded with diamond mixed with 5 g/l concentration of SiC powders was found highest in hardness (104.3 GPa) and modulus(1115 GPa) which is comparable to natural diamond properties.

ABSTRAK

Sifat mekanik dan daya rekatan salutan lapisan intan ke atas permukaan karbida tersimen mempunyai kesan yang besar kepada prestasinya sebagai alat pemotong. Banyak kajian telah di jalankan untuk meningkatkan sifat mekanik ini melalui proses pengoptimuman berhati-hati pelbagai teknik pra-rawatan substrat karbida. Dalam kajian ini, tungsten karbida (WC-6wt% Co) substrat yang telah di pra-rawat kimia dua langkah telah dibenihkan dengan campuran serbuk intan (0.5µm) dengan konsentrasi yang telah ditetapkan (0.8 g/l) dan serbuk SiC (175µm) berkonsentrasi masing-masing 1.0, 5.0 dan 10.0 g/l dengan tujuan untuk menghasilkan kekasaran permukaan salutan intan habluran yang berbeza. Salutan lapisan intan ke atas substrat WC telah di hasilkan melalui kaedah pengendapan wap kimia filamen panas (HFCVD) selama 30 jam dengan parameter salutan yang telah ditetapkan. Imej mikroskop imbasan electron pancaran lapangan (FESEM) dan spektra pembelauan sinar-x (XRD) menunjukkan bahawa semua saluatan intan mempunyai bijian yang bersegi dengan campuran morfologi (111) dan (220). Substrat WC yang di pra-rawat dan di benihkan dengan campuran serbuk 1g/l SiC dan 0.8 g/l serbuk berlian didapati mempunyai salutan intan dengan puncak yang tajam serta ketinggian dan jarak anatara bijian yang seragam apabila di analisa menggunakan mikroskop tenaga atomic (AFM). Teknik letupan pasir telah di guna untuk menentukan kekuatan daya rekatan lapisan salutan intan dimana sampel yang dibenihkan dengan campuran serbuk 5 g/l SiC dan serbuk intan didapati mempunyai daya rekatan yang tertinggi. Ujian calar-nano menunjukkan bahawa semua lapisan intan mempunyai daya rekatan yang baik dengan hanya menunjukkan mod ubahbentuk serpihan tanpa sebarang kegagalan rekatan. Sementara ujian pelekukan-nano menggunakan pelekuk Berkovich mendedahkan bahawa substrat yang dibenihkan dengan campuran serbuk intan dan yang serbuk 5 g/l SiC mempunyai nilai kekerasan (104.3 GPa) dan modulus (1115 GPa) tertinggi yang setanding dengan sifat intan yang asli.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

A	-	Ampere
Al_2O_3	-	Aluminium oxide/Alumina
α	-	Diamond growth factor
°C	-	Degree Celcius
CH_3	-	Methyl
CH_4	-	Methane
cm^{-1}	-	Per centimeter
cm^2	-	Centimeter square
cm^{-2}	-	Per centimetre square
Co	-	Cobalt
g/l	-	gram per liter
H	-	Atomic hydrogen
H_2	-	Hydrogen
H_2O	-	Water
H_2O_2	-	Hydrogen peroxide
H_2SO_4	-	Sulphuric acid
HCl	-	Hydrochloric acid
HNO_3	-	Nitric acid
hr	-	hour
K	-	Kelvin degree
$K_3[Fe(CN)_6$	-	Potassium ferro-cynide
KOH	-	Potassium hydroxide
Mbar	-	Milibar
µm	-	Micrometer
μmhr_{-1}	-	Micrometer per hour
ml/min	-	milliliter per minute
mm/min	-	Milimeter per minute

Mo	-	Molybdenum
nm	-	Nanometer
Ra	-	Average roughness
sccm	-	Standard cubic centimeters per minute
sec	-	second
Si	-	Silicon
SiC	-	Silicon carbide
Ta	-	Tantalum
θ	-	Theta
Torr	-	Unit pressure
W	-	Tungsten/Wolfrum
WC	-	Tungsten Carbide
wt%	-	Weight percentage
ZrO_2	-	Zirconia

LIST OF ABBREVIATIONS

AFM	-	Atomic Force Microscope
CTE	-	Coefficient of Thermal Expansion
CVD	-	Chemical Vapour Deposition
FESEM	-	Field Emission Scanning Electron Microscope
HFCVD	-	Hot Filament Chemical Vapour Deposition
PACVD	-	Plasma Assisted Chemical Vapour Deposition
SEM	-	Scanning Electron Microscope
XRD	-	X-RAY Diffractometer

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Diamond is among the main coating materials that have attracted interest due to its tendency to improve the tools performance and ultimately the lifetime as a result of its wide range of extreme unique properties. These unique properties of natural diamond which include its extreme hardness, high thermal conductivity, chemically inert and wear resistance as well as its rarity motivated researchers to attempt to synthesize diamond since it was found out that diamond is an allotrope of carbon.

Various techniques have been developed to synthesis diamond which includes high temperature and high pressure (HTHP) process, physical vapor deposition (PVD) and chemical vapor deposition (CVD) from carbon based compounds. Harnessing these extreme properties of carbon in its crystalline diamond structure was achieved mostly by the better understanding of the formation of diamond and the significant development of the chemical vapor deposition (CVD) technique, which was designed specifically for better deposition of diamond.

Polycrystalline diamond films which are synthesized by various types of CVD techniques available are used in many diverse applications that include coating on cutting tools, heat sink in electronic devices, optical lenses and biomedical components among others. The performance of the coated diamond film depends on the properties of diamond, quality of diamond deposited, and the adhesion strength between film and the substrate and also on the substrate surface characteristics to be deposited on. As such, substrate selection plays a vital role in the quality of diamond film produced using CVD technique. A hard material substrate which has optimum mechanical and thermal properties as well as good adaptation to the CVD technique is required. The most widely used substrate material for diamond films deposition on cutting tools is hard cemented carbide WC, which are normally enriched with cobalt binder (3-13 wt %) to provide fracture strength has all the required properties for diamond coating using CVD.

When diamond film is deposited on these substrates, the strong catalytic effect of the cobalt binder promotes diffusion of carbon in cobalt thereby producing a weak non diamond phase (graphite) that results in the reduction of the diamond nucleation rate, low adhesion strength and low quality of diamond. Therefore cemented carbide with a minimum concentration of surface cobalt is required to suppress the detrimental effect of cobalt and improve the mechanical properties of the coated diamond film. To overcome these problems, a two step ultrasonically chemical pretreatment methods is reported as the effective and most common method used. First step of the chemical pretreatment involves etching the substrate ultrasonically in Murakami solution to roughen the surface and attack the WC particles; this is followed with a second step etching that involves the use of acid solution to remove the substrate surface Co (Wei *et al*., 2010).

Seeding is another ultrasonic pretreatment process that is commonly done with diamond powder suspension that effectively increases the diamond nucleation density. This process can also be done by mixing together diamond powder of different size or with other particles of different size in order to determine the optimum diamond size combination. It has also been proved that by mixing suspension of diamond powders with different grain size particles of SiC, B_4C and SiO_2 increases the diamond nucleation density much more than when using diamond powders alone (Avigal and Hoffman, 1999).

Mix seeding of diamond powder with other larger particles has been reported to further improve diamond nucleation density, significantly affects mechanical properties of diamond film (Buijnsters *et al*., 2009, Neto *et al*., 2012). However, mechanical properties and interfacial adhesion strength of a coated diamond film plays an important role in its application. Recently, nanoindentation technique has been widely used in probing the mechanical properties of material on the submicron level. This is due to its depth sensing and dynamic loading ability, which enables the monitoring of the indenter penetration (h) during the phases of loading and unloading (Oliver and Pharr, 1992).

1.2 Problem Statement

A wide variety of solutions have been developed in order to improve the mechanical properties of the diamond films deposited on hard cemented carbide substrate and ultimately improve the cutting tools quality.

Many studies have been done so as to improve the mechanical properties through the careful selection of the various substrate pretreatment techniques as well as diamond growth conditions. However, studying the mechanical properties of diamond such as film hardness and adhesion is very limited due to the difficulties associated with plastically deforming films that may have hardness near that of diamond indenters or scratch tester tips, which themselves could yield during testing.

Current research shows that combining substrate chemical pretreatment methods with diamond seeding process is effective method of improving the diamond nucleation density. However, the effect of mixed small sized diamond powder (0.5µm) with large sized SiC particles (174µm) during seeding on WC substrates to determine its effect on the mechanical properties is minimally reported. Therefore, the focus of this study was on the effect of mixed seeding fixed concentration of diamond powders (0.5µm) with varying concentration of SiC particles (174µm) on the mechanical properties of HFCVD diamond film layer deposited on WC-6% Co substrates.

1.3 Objectives of the Work

Recently cutting tools produced all over the world are targeted to meet the requirements of both having optimum adhesion strength between the film and the substrates and high diamond quality with minimum impurity. The objectives of this study are to:

1. Study the suitable chemical pretreatment process and seeding parameters that can produce high quality of diamond coating.

2. To determine mechanical properties, adhesion, morphology and grain size of the diamond film coated on different microcrystalline diamond surface roughness.

1.4 Scope of the Work

The scope of the work includes:

1. The cemented WC-6%Co will be used as the substrate surface.
2. The pretreatment process of the WC-6%Co substrate will be fixed. 2 steps chemical pretreatment.
3. Different conditions of seeding will be employed in order to produce different MCD film surface roughness.
4. The coating characteristics and analysis will be conducted using FESEM, XRD, and AFM for morphology, grain size, topography, surface roughness of the diamond film and film thickness.
5. The coating mechanical properties and adhesion will be determined using the nano-indentation and sand blasting technique.

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