SURFACE TREATMENT ON TUNGSTEN CARBIDE SUBSTRATE PRIOR TO HOT FILAMENT CHEMICAL VAPOUR DEPOSITION DIAMOND COATING

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Dedicated to my beloved wife, my children and my beloved father..

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ABSTRACT

Deposition of a large and uniform distribution of diamond grains with good adherent and high quality of diamond coating using chemical vapour deposition (CVD) technique is a challenge. Large diamond grains reduce the adhesion strength between the diamond coating and substrate material. The aim of this research is to develop a large and uniform distribution of grain size with high quality and good adhesion strength of diamond coating coated on WC–6wt% Co for grinding application. The research started with the determination of suitable etchant and etching time that can provide high surface roughness and lower Co content of WC substrate. The best concentration of SiC (174 µm) of 1, 5 and 10 g/l mixed with diamond (0.5 µm) powders with a concentration of 0.8 g/l for seeding was also determined. The diamond coating was performed for 30 hours using hot filament CVD unit. The field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and Raman spectra results indicate that all the coated samples have well faceted grains of (111) and (220) morphologies with high quality (>99% purity) of diamond coatings. The atomic force microscopy (AFM) shows the grain size formed was in the range of 1-6 µm with a density of above 10^8 grains/cm^2. Sample treated with HNO_3 + H_2O_2 for 60 seconds however had the highest adhesion strength measured by sand blasting. It is due to the lowest surface Co content and highest diamond grain density. The WC substrates etched with this etchant then seeded with 1 g/l of SiC mixed with 0.8 g/l of diamond powders was found to have diamond coating with sharp peaks with uniform height and gaps between diamond grains when observed using FESEM and AFM. This condition fulfilled the requirement for grinding application and at the same time having the highest quality (99.496% purity) and adhesion strength. To determine the grinding performance, WC grinding wheels were fabricated and treated with HNO_3 + H_2O_2 for 60 seconds, seeded with 1 g/l of SiC mixed with 0.8 g/l of diamond powders and diamond coated for 30 hours. The grinding process was performed on WC-2wt% Co work piece using ultra-precision grinding machine at different feed rates of 0.015, 0.030, 0.045, 0.060 and 0.075 mm/min respectively. The diamond grain sharpness of the wheel was found unaffected after analysed using FESEM while the surface finish (*Ra*) of the work piece was finer from 0.020 µm to 0.007 µm. When compared with the commercial diamond bonded wheel grinding at 0.20 mm/min, the work piece surface finish is almost the same. However, the diamond bonded wheel was severely damaged with clogged grinding chips, broken-off and dislodged diamond particles. Meanwhile, at the diamond coated wheel, only clogging was observed. As a conclusion, mix seeding of diamond (5 µm, 0.8 g/l) and SiC (175 µm, 5 g/l) has produced good diamond coating properties for grinding application which is at par with the diamond bonded wheel.

ABSTRAK

Menghasilkan salutan intan dengan saiz bijian yang besar dan seragam, daya rekatan dan kualiti yang tinggi menggunakan kaedah pengenapan wap kimia (CVD) adalah satu cabaran. Bijian intan yang besar mengurangkan daya rekatan antara salutan intan dan bahan substrat. Kajian ini bertujuan untuk menghasilkan bijian salutan intan yang besar dan seragam, daya rekatan dan kualiti yang tinggi ke atas WC-6% berat Co untuk kegunaan proses canaian. Kajian bermula dengan menentukan larutan dan masa punaran yang sesuai untuk menghasilkan kekasaran permukaan yang tinggi dan kandungan Co yang rendah pada substrat WC. Konsentrasi campuran serbuk SiC (174 µm) terbaik di antara 1, 5 dan 10 g/l di campur dengan serbuk intan (0.5 µm) dengan konsentrasi 0.8 g/l bagi tujuan pembenihan juga ditentukan. Salutan intan dilakukan selama 30 jam menggunakan unit filamen panas CVD. Analis dari mikroskop imbasan elektron pancaran medan (FESEM), pembelauan sinar-X (XRD) dan Raman spektrum menunjukkan semua salutan intan mempunyai segi bijian yang jelas dengan morfologi (111) dan (220) dan berkualiti tinggi (>99% ketulenan). Analisis mikroskopi daya atom (AFM) menunjukkan saiz bijian adalah dalam julat 1-6 µm dengan ketumpatan melebihi 10^8 bijian/sm^2. Sampel yang dipunar dengan HNO_3+H_2O_2 selama 60 saat, didapati mempunyai daya rekatan tertinggi bila diuji secara pembagasan pasir. Ini disebabkan oleh kandungan Co terendah serta ketumpatan bijian intan tertinggi pada permukaan substrat WC. Substrat WC yang dipunar dengan larutan ini yang kemudiannya di lakukan pembenihan dengan campuran serbuk 1 g/l SiC dan 0.8 g/l intan didapati mempunyai salutan intan dengan puncak yang tajam, ketinggian dan jarak antara bijian yang seragam apabila di analisis menggunakan FESEM dan AFM. Keadaan ini memenuhi keperluan aplikasi proses canaian dan pada masa yang sama mempunyai kualiti (99.496% ketulenan) dan kekuatan rekatan tertinggi. Bagi menguji prestasi canaian, roda pencanai WC dihasilkan, dirawat dengan HNO_3+ H_2O_2 selama 60 saat dan dibenihkan dengan campuran serbuk 1 g/l SiC dan 0.8 g/l intan serta disalut intan selama 30 jam. Proses canaian telah dilakukan ke atas benda kerja WC-2% berat Co menggunakan mesin canai ketepatan ultra dengan kadar suapan berbeza iaitu 0.015, 0.030, 0.045, 0.060 dan 0.075mm/min. Ketajaman bijian intan didapati tidak terjejas apabila di analisis menggunakan FESEM dan kemasan permukaan (*Ra*) benda kerja adalah lebih halus dari asalnya 0.020 µm kepada 0.007 µm. Perbandingan canaian pada 0.20mm/min menggunakan roda intan terikat komersial menunjukkan kemasan permukaan benda kerja adalah hampir sama. Walau bagaimanapun roda komersial didapati rosak teruk dengan tatal canaian yang tersekat serta partikel intan yang pecah dan tertanggal. Sementara pada roda salutan intan, hanya tatal canaian tersekat berlaku. Sebagai kesimpulan, campuran bahan pembenihan serbuk intan (5 µm, 0.8 g/l) dan SiC (175 µm, 5 g/l) telah menghasilkan salutan intan dengan sifat yang sesuai untuk kegunaan canaian serta ia setara dengan roda canaian terikat intan.

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LIST OF SYMBOLS

A	-	Ampere
Al_2O_3	-	Aluminium oxide/Alumina
α	-	Diamond growth factor
^{O}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
HOPG	-	High Oriented Graphite Phase
IR	-	Infrared
PACVD	-	Plasma Assisted Chemical Vapour Deposition
SEM	-	Scanning Electron Microscope
UV	-	Ultraviolet
XRD	-	X-RAY Diffractometer

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CHAPTER 1

INTRODUCTION

1.1 Background of the Research

Since the introduction of first coating and coating process, it has been recognized by the industry that the tool's performance and its lifetime could be extended by applying a hard surface to a cutting tool. Further gains in performance and tool life have been achieved each time advancement in equipment and technology has made it possible to develop new coatings. Today, there are several coating processes and numerous types of coatings being used on a wide range of tools.

One of the main coating materials that held a special interest in the hearts and minds of the scientists, researchers and engineers is diamond. Diamond which derived from the Greek word "*adamas*", meaning "invincible" is a very impressive material as it is the hardest known material with the lowest coefficient of thermal expansion, chemically inert and wear resistance, offers low friction, has high thermal conductivity, electrically insulating and is optically transparent from the ultraviolet (UV) to the far infrared (IR) (Asfold *et al*, 1997). It is formed naturally deep in the earth under extreme conditions of very high temperature and pressure and the only known source of diamond for centuries.

With the introduction of high pressure high temperature (HPHT) method in 1950s (May, 1995), the first artificial diamond was crystallized through metal solvated carbon at pressure of about 80 kBar and temperature around 2000^{O}C. For more than three decades, “industrial diamonds” have been produced commercially by this method. With the discovery of a various types of chemical vapour deposition (CVD) techniques in 1960s by Spitsyn *et al* (1991) in Moscow, has sparked more interest of scientific nature in this material. It involves the gas phase chemistry mainly between hydrocarbon and hydrogen gaseous within the vicinity of the surface which causes diamond deposition onto that surface.

Given all the many positive properties together with the availability of various CVD techniques, diamond already finds use in many diverse applications as the optical windows operating in severe environment, heat sinks in electronic devices, semi conductors applications (field effect transistors, diodes, high voltage-high current switch, radiation and gas detectors) as well as in mechanical applications which are commercially available (abrasives, coating on cutting tools such as inserts, drill bits, end mills, reamers and counter sinks) (Alix Gicquel *et al*, 2001).

One of the major considerations for the development and production of high quality diamond coating on cutting tools using CVD techniques is the choice of appropriate hard material substrates. These hard substrate materials should have optimal thermal and mechanical properties such as heat conductivity, thermal expansion coefficient, hardness and toughness as well as having good adaptation to the CVD coating process. Hard cemented carbide mainly tungsten carbide (WC) that was normally used as cutting tools was found to be the most suitable material as it has all the required properties for diamond coating using CVD (Haubner, 1996). The most widely used of WC for diamond coated cutting tools is WC-6 wt% Cobalt (Co) which has been manufactured in various complex shapes such as inserts (Arumugam *et al.,* 2006), (Davim and Mata, 2008), end mills (Gomez *et al.,* 2012), drill bits (Hanyu *et al.,* 2003), (Chen *et al.*, 2002) and grinding tools (Chou *et al.*, 2010), (Butler-Smith *et al.*, 2012).

However, the successful diamond coating using CVD technique onto the WC-6 wt% Co substrate in terms of well faceted crystals, good adhesion, high quality, uniform coverage and grain size depends on these factors:

(a) Co content and the surface roughness of the WC-6wt % Co

(b) Diamond nucleation density

Co binder used in cemented carbide causes the diffusion and dissolution of carbon during coating process which reduces the diamond nucleation rate and promote the formation of graphite. This will results in poor coating quality as well as weaker coating adhesion strength (Jan Gabler and Westermann, 2000; Miao *et al.*, 2004). During diamond deposition on cemented carbides a surface with only a minimum Co concentration will allows good diamond deposition (M. Alam, 1997). This is particularly important for the industrial formation of diamond coatings on cutting tools. WC substrate surface roughness is essential in promoting high diamond nucleation density. Amirhaghi (1999) has proved that the scratched area on WC substrate surface produce high nucleation density as compare to non-scratched area and this factor promote high adhesion strength, uniform coverage and grain size.

Various methods and techniques have been successfully employed to prepare the WC substrate surface prior to diamnd coating such as introduction of Co inter-diffusion barrier interlayer (Amirhaghi *et al.*, 1999; Chou *et al.*, 2008), biasing (Chiang and Hon, 2008; (Saito *et al.*, 2009) as well as chemical pretreatment (Saito *et al.*, 2009; Raghuveer *et al.*, 2002). Two-step chemical pretreatment (Sien *et al.*, 2004; Volker Buck et al., 2002) followed with diamond seeding (Xu *et al.*, 2013; Wei *et al.*, 2011) is however, simple, effective and widely used to roughen, minimized surface Co concentration as well as creating better diamond nucleation sites.

1.2 Problem Statement

Successful diamond coating on cemented WC requires solutions to the problems of adequate diamond nucleation and most importantly poor adhesion. The poor adhesion between diamond coating and the WC substrate results from the thermal expansion mismatch between the diamond coating and the substrate, which lead to large thermal stresses at the interface, and the presence of binder materials such as Co in the substrate, will enhance the graphite formation. Currently the most effective, simple and cheap technique employed by most researchers to improve the adhesion strength and nucleation density of diamond on WC substrate is through the combination of two-step chemical pretreatment and diamond seeding process (Almeida *et al*, 2011). The adhesion strength is further improved by mixing other small particles such as Ti (Bujinster *et al*., 2009) and SiC (Avigal and Hoffmann, 1999) with diamond powder during seeding. However, this technique mostly applied to produce not only high adhesion strength but also high diamond nucleation density which means small and uniform grain size. This condition is only suitable for cutting tools (inserts, end-mill and drill bits) in order to maintain the cutting point or cutting edge of the tools as well as to provide wear resistant properties. However, for abrasive application mainly for grinding, the rough surface finish of diamond film is necessary where the entire diamond grains will act as cutting points for minute material removal. At the same time it also provides clearance between the grains to accommodate the grinding chips (Kopac and Krajnik, 2006). The smooth surface of diamond film with very fine, uniform and high density of diamond grains is however not suitable for grinding application as there will no cutting action take place. Currently, most of the CVD diamond coated grinding wheels have been produced by machining of solid CVD diamond pieces (Butler-Smith *et al.*, 2012) or by laser patterning the diamond grains (Butler-Smith *et al*, 2009) which is very costly processes. The application of chemical pretreatment and seeding which is a viable process and cheaper on WC grinding tools was however minimally reported. A thought of applying smaller diamond powder size mix with larger size of second type of powder on WC grinding wheel substrate surface during seeding that may produce rough surface finish with larger grains of diamond coating and its grinding performance which is unknown is worth to be investigated.

1.3 Objectives of the Research

The main objective of this research is to establish the hot filament chemical vapour deposition (HFCVD) diamond coating film with high adhesion strength and quality with appropriate grain size and distribution suitable for grinding application. The specific objectives for this research are as follows:

1. To determine suitable chemical pretreatment process and seeding parameters that can produce high quality of diamond coating for grinding application..

2. To evaluate and compare the grinding performance in terms of the condition of the wheels and the surface finish of the work piece between fabricated diamond coated WC and the commercial diamond bonded WC wheels.

1.4 Scopes of the Research

The research scopes are as follows:

1. The cemented tungsten carbide (WC-6 wt% Co) was selected as a substrate material.
2. Two-step pretreatment was chosen as the method to prepare the WC substrate surface with the first step was fixed using Murakami solution for 20 minutes. For second step of treatment, three different chemicals were used with three different etching times.
3. Seeding process was conducted using fixed size and concentration of diamond powder mixed with fixed size (174 μm) and different concentrations (0, 1, 5 and 10 g/l) of SiC powders
4. Diamond coating was conducted using hot filament CVD (HFCVD) with fixed parameters for 30 hours.
5. Surface characterizations on the chemically treated substrates were analyzed by using FESEM, EDX and surface roughness tester for element, morphology and surface roughness respectively.

6. Surface characterization on the diamond coated substrates were analyzed under FESEM, XRD, Raman Spectrometer, AFM for morphology, quality and surface roughness
7. The adhesion strength of diamond films was determined through the size of diamond flake-off area and time to flake-off using blasting technique.
8. Grinding was performed on WC-2 wt% Co work piece using ultra-precision cutting and grinding machine with varying feed rate as other parameters are fixed.
9. Analysis of grinding was conducted on the grinding wheels in terms of grinding edge conditions as well as on the WC samples in terms of finishing surface morphology and roughness using FESEM and surface profiler respectively.

1.5 Significance of the Research

This research is expected to provide an alternative method to produce suitable CVD polycrystalline diamond on WC substrate for abrasive application which should be comparable with diamond bonded wheels. With the application of simple and cheap conventional two-step pretreatment process combine with mix seeding to provide proper substrate conditions, should open up further research in producing different grain sizes of diamond coating for different grinding applications.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

5.1 Conclusions

Various methods have been employed to increase the adhesion strength of CVD diamond film on to the WC substrate. Two-step pretreatment followed with diamond powder seeding are found to be very effective in increasing the diamond nucleation density with the purpose of increasing the adhesion strength adhesion strength. Seeding using mixture of diamond powder with large size of second material powders has been proved more effective in increasing the diamond nucleation density. However, most of the reports published used Si as a substrate. Employing even larger powder size of second material during seeding with the intention of producing larger diamond grain size and at the same time having high adhesion strength was still not reported. This experimental study was conducted to determine the effect using large second material powder size on the adhesion strength of diamond film and the diamond grain size. The grinding tests were conducted to determine the effectiveness of the produced diamond grains. This experimental study is concluded with following findings:

1. Application of large SiC powder with small diamond powder size during seeding has produced large HFCVD diamond grains with the same structure consist of mixture of (111) and (220) structures

regardless of the different second step pre-treatment. It is suspected due to the same seeding condition conducted on all the samples. However, the adhesion strength were varied, due to various factors and such as high surface Co content, high residual stress as well as lower density of diamond grains. Sample treated with HNO_3 + H_2O_2 for 60 seconds has the highest adhesion strength due to lowest surface Co and highest grain concentration. This indicates that the concentration of substrate surface Co and the diamond nucleation density are the major factors in determine the adhesion strength.

2. The adhesion strength of the diamond film was also found to be depend on the amount of large second material powders used during the seeding. With the same pretreatment conducted on the samples, it is clearly indicates that with a certain ratio of mix seeding, will produce a certain adhesion strength. In this particular experiment, sample seeded with diamond and 1 g/l has the highest adhesion strength due to highest diamond grain concentration and diamond quality. This selected seeding condition also produced almost uniform height and distribution of diamond grain and on top of that sharp peak of the grains which is suitable for grinding application. The diamond grain concentration was lower as compare to sample seeded with only diamond powder. This is expected as with only diamond powder used, there was no restriction of the powders to be embedded into the WC substrate surface. The adhesion strength of sample seeded with only diamond, however was lower due to no hammering effect of large SiC powder onto the diamond powder during seeding.

3. The mirror image surface finish with the minimum roughness, Ra of 0.007 µm of the WC work piece was achieved with no indication of any defect occur to the diamond coated grinding wheel. When grinding performance was compared with diamond bonded wheel, the surface finish of the work piece was at par. However, the problem of grinding chips clogging is obvious which commonly found in

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