EFFECT OF TWO-STEP PRETREATMENT ON COBALT CONTENTS AND SURFACE ROUGHNESS OF TUNGSTEN CARBIDE SUBSTRATE PRIOR TO DIAMOND COATING

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Dedicated to my beloved spouse, my little son, my beloved parents and mother in law

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ABSTRACT

Cemented tungsten carbide is the most widely used material for cutting tools. Due to extreme demands higher tool life several types of coating have been introduced to prolong the service time which include diamond coating. However cobalt binder in tungsten carbide prevents diamond to adhere well on the substrate and its content at the outer surface should be reduce to below 1%. Single step and two-step pretreatments have been studied by many researchers. But to date poor adhesion of diamond coating still an issue. In this work a two-step pretreatment was used to etch tungsten carbide with 6% cobalt (WC-6% Co) at the surface of the substrate in order to solve poor adhesion problem. First step with Murakami's reagent (2, 3, 6, and 20 minutes) and the second step of the process were carried out by etching in a solution of hydrochloric acid (30, 45, and 60 seconds) or a solution of sulfuric acid (10 seconds). The effect of them on Co cemented tungsten carbide samples in term of surface morphology, surface roughness, and cobalt removal from the surface were examined. It is found the longer Murakami etching time produces a slightly rougher surface than the shorter exposing time. Both acid solutions were used in the second pretreatment step able to reduce cobalt content to below 1% at all conditions regardless of etching time. The best combination of pretreatment process is 20 minutes Murakami etching and 45 seconds exposure time of hydrochloric acid that yields the higher surface roughness and the lowest cobalt content on the substrate surface.

ABSTRAK

Tungsten karbida semen adalah bahan yang paling banyak digunakan dalam alat-alat pemotongan. Disebabkan oleh permintaan yang tinggi terhadap alatan pemotong yang berjangka hayat lama, kaedah saduran diperkenalkan untuk meningkatkan masa penggunaannya termasuklah saduran berlian. Walaubagaimanapun, pengikat kobalt di dalam tungsten karbida menghalang berlian daripada melekat dengan sempurna pada substrak dan kandungannya perlu dikurangkan kepada bawah daripada satu peratus. Kaedah langkah tunggal dan dua-langkah pra-rawatan telah dipelajari oleh ramai penyelidik sebelum ini. Tetapi masalah berlian yang tidak melekat dengan baik masih menjadi isu. Didalam kajian ini, kaedah dua-langkah pra-rawatan digunakan untuk menghakis tungsten karbida dengan 6 peratus kobalt (WC-6% Co) pada permukaan substrak dalam usaha menyelesaikan masalah perekatan yang tidak sempurna ini. Langkah pertama adalah dengan reagen Murakami (2, 3, 6 dan 20 minit) and langkah kedua dalam proses ini ialah pengakisan menggunakan asid hidroklorik (30, 45 dan 60 saat) atau asid sulfurik (10 saat). Kesan daripada eksperimen ini terhadap tungsten karbida semen dikaji dari segi morfologi permukaan, kekasaran permukaan dan penyingkiran kobalt dari permukaan. Didapati bahawa lebih lama masa pengakisan Murakami, ianya memberi kesan yang lebih kasar terhadap permukaan dan lebih singkat masa untuk pendedahan. Kedua-dua larutan asid yang digunakan untuk langkah kedua pra-rawatan ini mampu mengurangkan kandungan kobalt sehingga kurang daripada satu peratus untuk semua keadaan tanpa mempedulikan masa pengakisan. Kombinasi yang terbaik terhadap proses pra-rawatan ini ialah 20 minit pengakisan Murakami dan 45 minit pendedahan masa asid hidroklorik dimana ianya menghasilkan permukaan yang lebih kasar dan kandungan kobalt yang paling sedikit terhadap permukaan substrak.

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LIST OF SYMBOLS

°K - Kelvin degree

Ag - Silver

Al_2O_3 - Aluminum oxide

Au - Gold

CH_4 - Methane

Co - Cobalt

CrC - Chromium carbide

Gm - Gram

GPa - Giga Pascal

H_2 - Hydrogen

H_2O - Water

H_2O_2 - Hydrogen peroxide

H_2SO_4 - Sulfuric acid

H_3PO_4 - Hydro phosphoric acid

HCl - Hydrochloride acid

HF - Hydrofluoric acid

HNO_3 - Nitric acid

m - Weight

Mg - Magnesium

Mo - Molybdenum

Nb - Niobium

Ni - Nickel

NiCr - Nickel chromium

Nm - Nanometer

Pt - Platinum

Ra - Average roughness

Ry - The peak-to-valley height

Rz - Ten-point height

S - Area

Sa - Section area

Si3N4 - Silicon nitride

SiC - Silicon carbide

Ta - Tantalum

TiAlN - Titanium aluminum nitride

TiC - Titanium carbide

TiCN - Titanium carbide-nitride

TiN - Titanium nitride

V - Volume

WC - Tungsten carbide

WC-Co - Co-cemented tungsten carbide

ZrN - Zirconium nitride

Δ - Delta

μm - Micrometer

ρ_{wc} - Bulk density of tungsten carbide

$\rho_{wc\text{-}co}$ - Bulk density of Co cemented tungsten carbide

LIST OF ABBREVIATIONS

a-C	-	Amorphous carbon
BEN	-	Bias Enhanced Nucleation
CVD	-	Chemical Vapor Deposition
DOC	-	Depth-Of-Cut
HFCVD	-	Hot Filament Chemical Vapor Deposition
HP-HT	-	High Pressure High Temperature
MCD	-	Microcrystalline Diamond
MMCs	-	Metal Matrix Composites
MPECVD	-	Microwave Plasma Enhanced Chemical Vapor Deposition
NCD	-	Nano-Crystalline Diamond
PACVD	-	Plasma Assisted Chemical Vapor Deposition
PCBN	-	Polycrystalline Cubic Boron Nitride
PCD	-	Polycrystalline Diamond
PVD	-	Physical Vapor Deposition
SEM	-	Scanning Electron Microscope
TMCVD	-	Time-Modulated Chemical Vapor Deposition
TRR	-	Thickness Removal Rate
XRF	-	X – Ray Fluorescenc

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Improvement in materials by hard Chemical Vapor Deposition (CVD) and Physical Vapor DepositionPVD coatings are widely used today (Lux *et al.*,1992) Super hard high pressure products (i.e. polycrystalline diamond (PCD) and polycrystalline cubic boron nitride (PCBN)) currently have a well-established market. Their properties and performance under severe working conditions are generally considered to be outstanding and highly competitive. They are the ultimate standard to be reached or, if possible, even to be exceeded by the new low pressure diamond products now being developed. Both PCD and PCBN are sintered products with appropriate amounts of a binder, and compacted at high temperatures and ultrahigh pressures. Frequently, the PCD or PCBN layers are bonded directly to a cemented carbide substrate.

The candidate work materials are some of the difficult-to-machine materials, such as abrasive aluminum–silicon alloys, glass fiber reinforced composites as well as high-speed machining of cast iron. Without a hard coating such as diamond, the cemented tungsten carbide tools wear rapidly when machining these materials. Consequently, polycrystalline diamond tools made by the high pressure–high temperature (HP–HT) process are used for this application. However, these tools are rather expensive in view of the high cost of the HP–HT process as well as the high cost of shaping and finishing of the tool by diamond grinding and polishing. By coating the cemented carbide tools in its final form with low-pressure CVD diamond, it is not necessary to finish the coated tool. This along with the less expensive coating process makes these less expensive and more attractive for this application (Mallika and Komanuri., 1999). Two approaches are followed for the CVD diamond coatings on cutting tools. One is to grow thick (1–1.5 mm) free standing polycrystalline diamond slab, cut it to size, and braze it on to the cemented carbide substrate. However, the tools have to be finished to shape before use. In concept, this type is not very much similar to the polycrystalline diamond tools made by HP–HT process in that the tools have to be finished by expensive diamond grinding and polishing. Further, brazing of diamond on to the carbide substrate is an additional operation. The other approach is to develop thin diamond coatings (2–5 μm) on cutting tools. This, in fact, is unique to the CVD diamond process as it is not possible and/or economical to produce thin coatings by the HP–HT process. Microwave CVD, hot-filament CVD, combustion synthesis, and plasma arc are some of the techniques used either individually or in combination to deposit diamond coatings on cutting tools.

Diamond is attractive as an ideal coating material for hard metal cutting tools for its unique combination of excellent properties, i.e., the highest hardness and elastic modulus, very low friction coefficient, the highest thermal conduction coefficient, high strength and the chemical inertness (Lu *et al.*, 2006). PCD tooling having complex shapes, i.e., taps, drill bits, and cannot be formed using any known techniques. Numerous attempts have been made to provide diamond coated tools which have performance approaching that of PCD tools because they would be less costly to manufacture and use, and because diamond coated tools having more complex shapes than are possible with PCD tools are theoretically manufacturable employing substrates such as cemented tungsten carbide.

Bad adhesion is frequently strongly associated with interfacial stress, which depends primarily on the different expansion coefficients of layeand substrate. Excessive internal layer stress is also important (Lux *et al.*, 1992). It was shown that lowering the surface temperature during diamond deposition on cemented carbide tools can improve adhesion of the coating.

1.2 Statement of problems

A significant challenge to the developers of diamond-coated tooling is to optimize adhesion between the diamond film and the substrate to which it is applied, while retaining sufficient surface toughness in the finished product (Michael and Robert, 1996). Sintered tungsten carbide (WC) substrates without cobalt or other binders have been studied but can be too brittle to perform satisfactorily as tooling in machining applications. Cemented tungsten carbide substrates with 6% cobalt have the required toughness and thus show the greatest long-term commercial promise for tooling applications. Cemented tungsten carbide can be formed into a variety of geometries, making it a potential material for drilling operations, die manufacturing, and other applications of value to the automobile and other industries. It is therefore desirable to provide a way to coat cemented tungsten carbide substrates with a layer of diamond film having adequate adhesion to the substrate for use as a machine tool.

A well-known problem is the poor adhesion of diamond films on tungsten carbide due to the Co-binder that catalyzes the formation of graphite. A two step of the chemical pretreatment is the most effective method to etch tungsten carbide at the surface of the substrate in order to solve poor adhesion problem. first step with Murakami's reagent and the second step of the process are carried out by an etch in a solution of hydrochloric acid and hydrogen peroxide in deionized water or a solution of sulfuric acid and hydrogen peroxide. Surprisingly pretreatment with agents such as Murakami’s solution is the most effective pretreatment in term of quality and adhesion of diamond coating on WC-Co substrate due to mechanical interlocking. But until now it is not declare the most effective etching time and also it was not reported using a solution of hydrochloric acid and hydrogen peroxide in deionized water as a second step of the process.

1.3 Objective of the Study

The objectives of this research were:

1. To analyze the effect of Murakami etching time on Co cemented tungsten carbide surface roughness as well as cobalt content.
2. To evaluate the effect of different acid solution (HCL and H_2SO_4) in second step etching in terms of cobalt removal, surface roughness on Co cemented tungsten carbide.

1.4 Significance of the Study

The most suitable substrate material for producing diamond coated tools is Co-cemented tungsten carbide (WC-Co). In fact, given a limited thickness of the deposition, mechanical stresses are transmitted to the substrate. Diamond coating on hard metal (WC-Co) tools exhibit wear resistance comparable to or even better than polycrystalline diamond tools (PCD). The pretreatment of the substrate plays an important role in determining the adhesion of the diamond coating onto hard metal and the final properties of coated parts. This serves as an useful information for other researchers and manufacturers as evaluation on the diamond adhesion strength which can significantly improve the performance of cutting tool and has great potential to reduce the manufacturing cost.

1.5 Scopes of the Study

The scopes of this study were limited as follows:

1. The substrate material was limited to WC with 6wt% of Co.
2. The study was focused on the two step pretreatment process.
3. Etchant used in this work were Murakami's solution, sulfuric and hydrochloric acids at specific concentration.
4. Response parameters that were evaluated include surface roughness, weight losses and cobalt contents.
5. All experiments were conducted at room temperature.