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Murakami and H₂SO₄/H₂O₂ Pretreatment of WC-Co Hard Metal Substrates to Increase the Adhesion of CVD Diamond Coatings

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Abstract. Distinct improvement in adhesion of diamond coatings on hard metal substrates was achieved by following substrate surface pretreatment [1]:

First WC was removed from the substrate surface by etching with Murakami solution (K₃[Fe(CN)₆] in KOH), after which the Co binder network was etched with H₂SO₄/H₂O₂ solution. Then diamond coatings were deposited on the substrates by hot-filament CVD.

Apparently during the H₂SO₄/H₂O₂ treatment of the Co binder a thin CoO / CoSO₄ film forms, which prior to the diamond deposition would be reduced to CoS by the hydrogen and carbon species involved in the diamond synthesis. Since CoS is a stable compound at the diamond deposition temperatures, its Co vapor pressure and the Co surface mobility should be substantially lower than that for metallic Co. Thus the diamond/hard metal interface is no longer influenced detrimentally by the metallic Co binder. This explanation has however not yet been confirmed by analytical methods such as SIMS and XPS.

An alternative explanation would be the increased roughness of the hard metal surface resulting from the removal of the Co binder and the formation of deep grooves on the interface which could lead to the improved adhesion. This however does not explain why Co migration and other detrimental effects are not observed.

1. INTRODUCTION

CVD diamond coatings can be expected to significantly prolong the lifetime of coated tools during cutting and milling of non-ferrous materials such as Al(Si) alloys, graphite and plastics [2-6].

The Co in the hard metal binder phase can however detrimentally influence the chemical vapor deposition of diamond [7-10]. Co vapor pressure, surface migration, and carbon solubility are the main parameters influencing diamond nucleation and growth and coating adhesion [11-14].

The application of intermediate layers is one promising technique for the deposition of more adherent diamond films [15]. Pretreatment procedures are usually aimed at depleting the Co in the substrate surface by selective chemical etching [11,16-18]. A new approach to improve diamond coating adhesion involves the formation of Co compounds such as borides and silicides [19] which are stable under diamond deposition conditions.

In this paper the special surface pretreatment procedure reported in the patent [1] was investigated. After small amounts of WC are removed from the hard metal substrate surface by etching with Murakami solution (K₃[Fe(CN)₆] in KOH), the remaining Co binder network is treated with H₂SO₄/H₂O₂ solution. The effects of this surface treatment with respect to diamond growth rate, morphology and adhesion of the deposited coating on the substrates were investigated and SIMS depth profiles were used to characterize the substrate/coating interface.

2. EXPERIMENTAL DETAILS

2.1. Substrate surface pretreatment and diamond deposition apparatus

Indexable hard metal inserts from Teledyne Firth Sterling, La Vergne, TN, USA (grade SPGN 120308, quality H21; 94% WC, 5.5% Co, 0.5% (Ta, Nb)C [20]) were used as substrates. They were ultrasonically cleaned in acetone prior to pretreatment. The Murakami solution (10g $K_3[Fe(CN)_6]$, 10g KOH, 100ml H_2O) and the H_2SO_4/H_2O_2 (5% H_2SO_4 in 35% H_2O_2) solution were prepared just before the etching treatment. Between the etching steps the substrates were cleaned with water. No diamond scratching, bias treatments or other nucleation enhancements were applied.

The diamond deposition experiments were carried out in a hot-filament CVD reactor as described elsewhere [21-23]. A coiled tantalum filament was used and its temperature was measured by a two-color pyrometer (IRCON with Mirage OR 15 sensor).

The substrates were placed on the molybdenum substrate holder situated 10 mm from the filament. The substrate surface temperature was measured by a Ni/CrNi thermocouple positioned in a dummy substrate located about 0.2 mm under the substrate surface [23]. For each diamond deposition experiment two substrates were placed on either side of this dummy.

2.2. Examinations

2.2.1. Characterization of the diamond deposits

SEM was used to study the morphologies of the deposited layers and to measure the nucleation density when only individual crystals were obtained. The diamond growth rates were calculated from the weight differences of the substrates before and after deposition [22].

The adhesion of the diamond coatings was estimated from a Rockwell A test (test load 62.5 kg) [24] as well as from a manual scratch test with a diamond stylus [11].

Cutting tests were done by Teledyne Firth Sterling, La Vergne, TN, USA under the following conditions: Reynolds 390 alloy (18% Si), 1250 surface ft/min (380 m/min), 0.05 in (1.3 mm) depth of cut and 0.10 in/rev (2.5 mm/rev) feed.

2.2.2. SIMS analysis

SIMS measurements were performed using a CAMECA ims 3f ion microscope [25,26]. An O_2^+ or a Cs^+ primary beam was applied to sputter the samples. The rastered area varied between 300×300 and $500 \times 500 \mu m^2$ for an analyzed area $60 \mu m$ in diameter. Positive secondary ions of the masses 12 (C), 59 (Co), 182 (W), 184 (W) were detected with O_2^+ -bombardement, while negative secondary ions of the masses 16 (O), 75 (CoO) and 91 (CoS) were measured using Cs^+ ions.

The C signal was used as a reference for the diamond matrix and to locate the diamond/hard metal interface. Because of the high intensity of Co and W, energy filtering was applied to keep the signals in the dynamic range of the electron multiplier which was used as a secondary ion detector [27]. For W the offset was -75 V and two isotopes (masses 182 and 184) were measured to verify via the relative isotopic abundance that tungsten was detected.

In the case of Co only ions with a kinetic energy above 75 or 125 eV were detected. This was necessary because there is only one Co isotope at $m/e=59$. The observation of parallel signals indicated that Co was detected.

The nominal depth resolution was approximately 30 nm for flat samples. In practical operation however the depth resolution was limited due to the roughness of the specimens. The sputter rates of the relevant materials were determined via the measurement of the crater depth by a surface profilometer (Sloan Dektak IIA). For the applied measurement parameters the sputter rates were found to be 0.4 nm/s (O_2^+) and 3 nm/s (Cs^+) for diamond and 0.6 nm/s (O_2^+) for the hard metal substrate.

3. RESULTS

3.1. Substrate surface treatment by etching with Murakami and $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$

During the Murakami etching [1] WC particles are dissolved, leaving behind the Co network from the binder phase. In the second step the Co binder phase is attacked by $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ and in the 10 sec etching time Co is partially dissolved from the surface and can also react to form CoSO_4 .

Figure 1 shows the surfaces of the hard metal substrates after various etching treatments.

The WC etching effect by the Murakami solution was obvious after 5 minutes. During longer etching times the surface morphology did not change dramatically.

10 sec $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ etching hardly affected the original hard metal substrates. The Co binder phase was still present at the substrate surface. In the case of a prior Murakami treatment the etching for 10 sec with $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ produced fewer morphological changes in the substrate surface. Microprobe measurements showed that the Co content at the substrate surface decreased rapidly, but no S (from SO_4^{2-}) could be detected [28].

SIMS depth profiles measured by an O_2^+ primary beam (Figure 2) clearly showed an increase of Co at the substrate surface after Murakami etching and a strong decrease of Co after the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ etching. Because O and O compounds cannot be detected by an O_2^+ primary beam, measurements with a Cs^+ primary beam were also performed to obtain more information about the formation of CoSO_4 or oxides (Figure 3). With these measurements three regions could be identified: At the substrate surface low Co and CoO were observed which can be explained by the surface etching. Below the surface an area with maximal CoO concentrations was observed. Under this zone the hard metal bulk material began and all concentrations were constant. The CoS and S ions were also measured but due to the O_2 interference S could not be detected clearly.

Figure 1: The surfaces of the hard metal substrates after various etching treatments

1 μm

Figure 2: SIMS depth profiles of the hard metal substrates after various surface treatments (O_2^+ primary beam)

Figure 3: SIMS depth profiles of the substrates after different surface treatments (Cs^+ primary beam)

3.2. Diamond deposition

Following the various etching treatments the substrates were coated with diamond for 5 or 16 hours to investigate diamond nucleation, diamond growth rate, morphology and adhesion of each deposited diamond layer (Table 1, Figure 4).

Murakami etching: After this treatment and 5 h deposition the diamond particle density was very high (about $10^7/cm^2$) but among the diamond crystals, which were not always faceted, ballas-type particles were also observed. After 16 h deposition well-faceted diamond layers were deposited but the adhesion was very poor. These coatings flaked off during cooling so that it was impossible to measure the diamond growth rates.

10 sec H_2SO_4/H_2O_2 etching: The diamond particle density after 5 h was about $6 \times 10^6/cm^2$. The diamond crystals were already well faceted and no Co influences could be observed. For 16 h deposition the diamond growth rate was 0.54 mg/h. Although these coatings adhered after deposition, large patches flaked off after the Rockwell indentation tests.

Combined Murakami and H_2SO_4/H_2O_2 etching: The Murakami solution was applied between 0 and 80 min while the H_2SO_4/H_2O_2 step was uniformly 10 sec. The diamond particle density after 5 h deposition was $4 - 7 \times 10^6/cm^2$ on substrates etched for 0 - 30 min with Murakami. A strong increase in particle density up to $1.3 \times 10^7/cm^2$ was observed on substrates etched for 50 min in Murakami; for 80 min layer formation was observed after only 5 h deposition. The diamond growth rates measured after 16 h deposition showed a maximum for 20 min Murakami etching. Diamond adhesion was good: all of these diamond coatings survived the Rockwell test intact.

SIMS measurements: Figure 5 compares the SIMS depth profiles of diamond coatings on substrates given various pretreatments. SIMS profiles of diamond coatings on untreated hard metals [21] and on B- or Si-pretreated hard metal substrates [19] are not discussed here.

Depth profiles of C, W, and Co: Because of the different diamond growth rates on the substrates the layer thicknesses were not uniform. The varying surface roughnesses also influenced the profiles. The profiles indicated that the diamond / hard metal interface is reached when the W signal intensity increases and simultaneously the C signal decreases. The greatest differences were found in the Co signal, which did not reach its constant value at the interface, where it was much lower than in the hard metal bulk material. In two samples the Co signal was also observed in the diamond layer.

Table 1: Results of diamond deposition on WC-Co substrates pretreated with Murakami and $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ ($T_{\text{fil}}=2400^\circ\text{C}$, $T_{\text{sub}}=900^\circ\text{C}$, 1% CH_4 , $p=20$ torr)

etching Murakami [min]	etching $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ [sec]	5 h deposition			16 h deposition		
		diamond growth rate [mg/h]	particle density [$\times 10^6/\text{cm}^2$]	morphology	diamond growth rate [mg/h]	morphology	coating adhesion
5	0	0.54	8	fac.+ballas	--	faceted layer	poor
80	0	0.64	layer	fac.+ballas	--	faceted layer	poor
0	10	0.40	6	faceted	0.54	faceted layer	medium
5	10	0.44	6	faceted	0.56	faceted layer	good
10	10	0.32	4	faceted	0.68	faceted layer	good
20	10	0.28	5	faceted	0.79	faceted layer	good
30	10	0.36	7	faceted	0.69	faceted layer	good
50	10	0.38	13	faceted	0.63	faceted layer	good
80	10	0.52	layer	faceted	0.64	faceted layer	good

Figure 4: Diamond deposition on hard metal substrates after different etching treatments (5 and 16 h; $T_{\text{fil}}=2400^\circ\text{C}$, $T_{\text{sub}}=900^\circ\text{C}$, 1% CH_4 $p=20$ torr)

10 μm

Figure 5: SIMS depth profiles of the hard metal substrates after various surface treatments (16 h deposition; $T_{fil}=2400^{\circ}\text{C}$, $T_{sub}=900^{\circ}\text{C}$, 1% CH_4 , $p=20$ torr)

4. DISCUSSION

Diamond deposition on hard metals is of industrial interest for wear applications. However, for long tool life the well known detrimental influences of Co on the diamond morphology and adhesion must be overcome [7-10]. In the present work the Murakami - $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ etching procedure [1] was used to reduce the Co effects and to facilitate the study of diamond nucleation and growth.

4.1. The etching procedure

This method combining Murakami and $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ etching is necessary to reduce the metallic Co content on the surface and establish stable surface conditions.

Etching with Murakami alone merely increases the Co concentration at the substrate surface by removing WC.

$\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ alone results in much less etching due to the smooth substrate surface and less CoSO_4 and/or Co-oxide formation.

The Murakami etching as a first step however increases the substrate surface roughness, providing a large surface area which can be easily attacked by the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ solution. The Co network is dissolved by the acid and more Co is available to form CoSO_4 and Co oxides.

The SEM pictures (Figure 1) show mainly a rough substrate surface without well-faceted WC crystals since the Murakami etching removed any WC crystal facets that were present. The SIMS depth profiles also show a reduction of Co at the substrate surface, indicating that Co is etched from the substrate surface and transformed into CoSO_4 and/or Co oxides even below the substrate surface.

4.2. Diamond deposition

During diamond deposition the CoSO_4 and the Co oxides are quickly reduced by the (atomic) hydrogen, forming CoS and Co. As discussed earlier [19] Co compounds reduce both the Co vapor pressure and mobility during diamond deposition, leading to better diamond quality and better adhesion. This explanation has however not yet been confirmed by conclusive analytical methods as SIMS or XPS [28]. The increased roughness of the hard metal surface and the formation of deep grooves on the interface by the removal of the Co binder could also lead to improved adhesion. However, this alternate explanation does not account for the absence of Co migration or other detrimental Co effects.

Figure 6 illustrates the effects occurring during substrate pretreatment and diamond deposition.

Figure 6: Effects occurring during etching and diamond deposition

4.2.1. Diamond nucleation and growth

With the surface pretreatment diamond nucleation could take place as discussed for inert substrates [14]: The nuclei grow to individual crystals which later grow together to form a diamond layer. During this time the CoS protects the growing diamond. Both Co migration on the surface and the Co vapor pressure are reduced and no Co influences on the diamond coating could be observed. After the diamond coating has become continuous the growth rate is no longer influenced by the substrate, depending only on the diamond deposition conditions [14].

4.2.2. Adhesion between diamond layer and substrate

As already known [21] the Co binder phase is important for coatings since it fills the voids between the diamond crystals and so increases the adhesion. If these voids are reduced and the diamond / substrate interface becomes smooth the adhesion decreases [21]. The tendency of Co vapor to enhance the formation of non-diamond carbon at the interface also reduce the adhesion [9].

The influence of Co must however be suppressed during diamond nucleation and until a continuous layer has formed, after which Co should enhance the adhesion between the coating and the substrate.

The CoS formed during diamond deposition fulfills these requirements very well.

Rockwell indentation tests showed that the adhesion of the diamond layers deposited after the combined Murakami + $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ etching treatment was much better than on untreated WC-Co substrates. Short 3-minute cutting tests showed that the coatings have good wear resistance and adhesion.

5. CONCLUSION

Diamond deposition on hard metal substrates can be influenced by a surface pretreatment with Murakami and $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ etching. The detrimental influence of Co as observed on untreated substrates could be reduced. Diamond layers up to 16 μm thick showed better adhesion on pretreated substrates. The number of diamond crystals nucleated and the diamond growth rate were also higher on such substrates.

SIMS depth profiles confirmed changes in the Co binder phase composition during both the etching pretreatment and the diamond deposition. CoS formed from CoSO_4 should be the most stable Co compound in this system. CoS is very difficult to detect by SIMS and XPS but other analytical methods to identify it are being developed.

There are 3 common pretreatments for hard metals:

- (1) etching of the Co binder [10,16,17]
- (2) intermediate layers [15,29]
- (3) fixing the Co by forming stable compounds [19]

The present method combines (1) and (3), whereby the more significant aspect should be the formation of the stable CoS which reduces the Co effects.

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