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DIAMOND DEPOSITION ON WC-Co CUTTING TOOLS AFTER PRE-TREATMENT IN REACTIVE SOLUTIONS

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We describe the influence of pre-treatment procedures on the adhesion of diamond films to WC-Co substrates. Annealing of substrates at 600 °C in vacuum and repeated etching in different reactive solutions ($Al(OH)_2$-COOH diluted in acetic acid, Murakami and $HCl:HNO_3$) were studied with respect to their effectiveness in suppressing C diffusion into Co on the WC-Co surface. Substrates were coated with polycrystalline diamond films by the dual plasma HF CVD method. Raman spectra confirmed the existence of the diamond phase on all samples. Film surface morphology varied with the pre-treatment method used. Adhesion strength was evaluated using the scratch test.

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1 Introduction

Coating cutting tools with a diamond layer improves their hardness and durability. Chemical vapour deposition (CVD) is nowadays a widely used technique of diamond layer deposition. The deposition of synthetic polycrystalline diamond films by the hot filament CVD (HF CVD) is an improved technique that attracts more and more attention and gives high quality diamond films [1]. For high quality diamond film growth an alternative to the HF CVD technology is the micro-wave plasma (MW CVD). Similar works and results were reached by our collaborating partners [2]. Both these techniques can be used to improve cutting tools.

The main problem which remains especially for materials like WC-Co is the rather poor adhesion of diamond over-coating to the cemented carbides due to the cobalt dissolution effect of diamond phase. The cobalt, which is used as a binder phase of the hard-metal substrate, strongly influences the diamond deposition and reduces adhesion between the diamond film and the hard-metal substrate. To improve the adherence and quality of the diamond layer, the cobalt has to be first removed chemically from the hard-metal surface. Next, the diffusion of cobalt from the interior to the surface must be suppressed. The diffusion of cobalt can also to be suppressed

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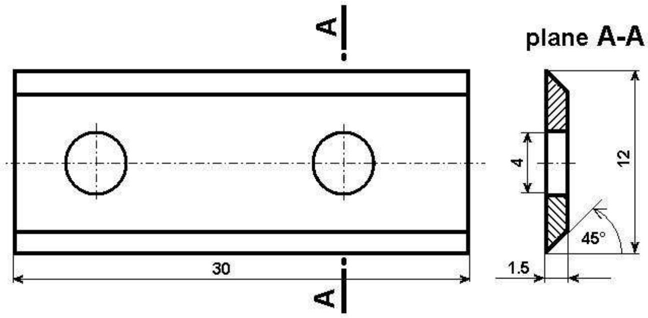

Fig. 1. WC-Co cutting tool.

by intermediate layers based on aluminium [3] or boron [4]. The best result for improving the adhesion was obtained by annealing and etching pre-treated the substrate surface. During the etching the Murakami (5 g $K_3[Fe(CN)_6]$ and 5 g KOH in 100 ml H_2O) or other solutions were used.

Another problem is the roughness of the tool. To machine a smooth surface with high precession the tool should have a smooth cutting edge. Nanodiamonds [5,6] are usually used to achieve this.

2 Experimental set-up

Figure 1. The cutting tool has a ribbon form and its cross-section has the form of an equilateral trapezium. Two holes serve for clamping. In the improved version the cutting edges were covered by the polycrystalline diamond film using HF CVD technology. The multitasking HF CVD reactor [7] that is used also for carbon nanotubes production, was used for growing the diamond film.

Three tungsten filaments (0.6 mm in diameter and 120 mm in length) were hung up at the distance of 7 mm above the substrate holder in the reactor, and their temperature was kept at $2000 \pm 50\ ^\circ$C, as measured by a two-colour pyrometer. The films were grown in a mixture of methane and hydrogen, with a total pressure of 3000 Pa. We used a flow of 300 sccm (standard cubic centimetre per minute) of hydrogen and 3 sccm of methane. A substrate temperature of 600 $^\circ$C was used for all these experiments. The DC plasma was created by applying of 100 V potential between the heated filaments and the plasma-grid placed over them. Two modes, the “nucleation mode” and the “growth mode” were used in the coating process. During the growth mode (after the nucleation) a positive bias of 100 V was applied. All the substrates were cleaned by a standard procedure (immersed in acetone with 3 minutes of ultrasound). Next, these substrates were etched in different reactive solutions and then were inserted into a vacuum chamber. Some of these treated substrates were annealed at 600 $^\circ$C in vacuum, others were coated with Al before insertion into the vacuum chamber. After annealing, these substrates were once more diluted in a reactive solution. Table 1 lists all the pre-treatment procedures used in the project. The samples were evaluated by Raman spectroscopy and the scratch test. The Raman spectroscopy is an advantageous method widely used to analyze the quality not only of diamond,

Tab. 1. Various pre-treatments of WC-Co substrates.

Sample number	**Etching**	**Coating**	**Annealing**	**Etching**
1	Not etched	Without	Unannealed	Not etched
2	$Al_2(OH)_2$-COOHdiluted in acetic acid	Without	Unannealed	Not etched
3	$Al_2(OH)_2$-COOHdiluted in acetic acid	Al	Unannealed	Not etched
4	Commercial etcher	Without	Unannealed	Not etched
5	Commercial etcher	Al	Unannealed	Not etched
6	$HCl:HNO_3$	Without	600° C	$HCl:HNO_3$
7	$HCl:HNO_3$	Without	600° C	$Al_2(OH)_2$-COOH diluted in acetic acid
8	Murakami solution	Without	600° C	Murakami solution

but also of other hard materials, such as the sapphire [8]

The scratch test is based on pulling a diamond stylus over the surface of a sample under a normal force, which is increased either stepwise or continuously until failure is obtained. In our case the diamond stylus has the Rockwell C geometry with a 120° cone and a 200 mm radius spherical tip defined in European Standards EN 10109-2. Scratch testing is widely used today by the coating industry for evaluating the tribological properties of coatings. This method is generally accepted as an appropriate and efficient technique for the quality assessment of coated surfaces and for assessming coating-to-substrate adhesion [9].

3 Results and discussion

Cobalt, which is included in the hard-metals as a binder (WC-Co), causes negative effects during deposition of the diamond layer. The reason is that cobalt causes the formation of sp^2 chemical bonds among the carbon atoms and during the deposition process creates a thin film of amorphous or graphitic carbon. This thin film strongly reduces the adhesion of the diamond layer. Migration of cobalt to the substrate surface and even its diffusion through the diamond layer is due to its high mobility. Because of the relatively high vapour pressure, a lot of the cobalt evaporates and influences the gas phase chemistry of diamond chemical vapour deposition, leading to the additional deposition of sp^2 carbon. The negative activity of the cobalt must be reduced to get a good adhesion of the diamond coating on the hard-metal substrate. Formation of Co-compounds with aluminium, which is stable under diamond deposition conditions, is one of many ways to achieve a better adhesion. Another way is to etch the sample in a reactive solution ($Al_2(OH)_2$-COOHdiluted in acetic acid, Murakami, or HCl and HNO_3) before the diamond deposition.

An aluminium layer was deposited on the substrate by evaporation in a high vacuum after etching in a commercial etcher. Fig. 2a shows the morphology of the diamond layer. The morphology was not very much dependant on the pre-treatment process. The quality of the dia-

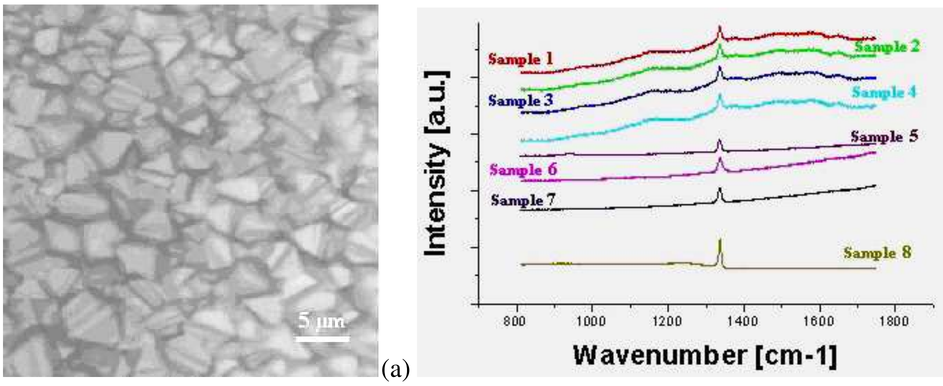

Fig. 2. (a) Morphology and (b) Raman spectra of diamond coatings deposited on WC-Co.

mond film deposited in the HF CVD reactor is expressed by the sharpness of Raman's maximum (Fig. 2b). The results of adhesion measurement are shown on the Fig. 3. They confirm that the adhesion was considerably higher on the pre-treated substrates than on the untreated substrates. Pre-treatment of the hard-metal substrates with various solutions and combination of etching with annealing gives different results. As seen in Fig. 3, the best diamond adhesion on WC-Co substrate was achieved by etching of substrate in Murakami solution, followed with annealing at 600 °C in vacuum. Diamond deposited in the HF CVD reactor after previous etching in Murakami solution and annealing at 600 °C showed a sharp Raman's maximum with good layer quality and best adhesion.

Tab. 2. Raman and Scratch-test results

Sample number	Raman shift [cm^{-1}]	FWHM [cm^{-1}]	Adhesion [relative units]
1	1335.6	7.0	6
2	1337.3	4.6	25
3	1337.3	6.8	less than 1
4	1337.8	8.2	63
5	1335.7	8.6	37
6	1336.7	11.9	56
7	1335.8	9.5	50
8	1336.3	6.4	118

4 Conclusion

The experiments presented in this paper prove that the pre-treatment influences the quality and the adhesion of diamond layers. The worst adhesion of the diamond layers occurred sample 3 (without pre-treatment) and for pre-treatment using coating with Al after previous etching in Al2(OH)2-COOH diluted in acetic acid. The treatment using HCl:HNO_3, or a commercial etcher

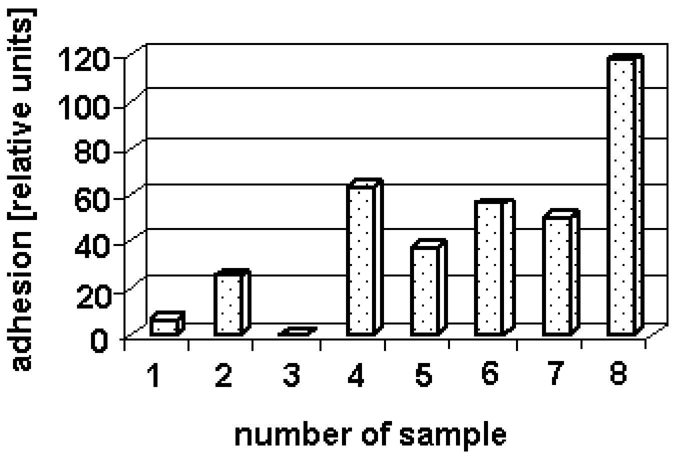

Fig. 3. Result of diamond adhesion on hard-metal substrates with various pre-treated of WC-Co substrates.

was promising for layer adhesion, but the diamond quality was rather poor. The best diamond adhesion occurred on sample 8. In the future we will continue in this work to match the demands of industry with our research.

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