Comparative investigations of the selective Co etching from hardmetal support layer of diamond coating

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Abstract. Selective cobalt etching from WC–Co composite usually carry out prior diamond deposition was investigated. Diluted Caro’s acid as primarily utilized etching reagent was used. The cobalt and tungsten dissolution from hardmetals (HM) were determined as a function of time and a comparison were done in case of different grade hardmetals. For comparison beside the hardmetals the pure metallic cobalt and binderless, plasma sprayed tungsten carbide dissolution also has been tested. Hot filament chemical vapor deposition (HFCVD) technic was used to investigate the diamond nucleation on the differently pre-treated samples. The investigation highlighted for that: a) the selective cobalt etching can due to the different rate of dissolution of the two components, however the dissolution of the WC was not zero, b) the dissolution rate governed by the composite substance structure by the pore size which has formed during the selective dissolution process, therefore the dissolution rate of both components was found to be influenced by the grain size of WC and the cobalt content of the hardmetal. c) The removed cobalt quantity from the hardmetal surface has strong effect on the diamond nucleation during HFCVD method. Based on this research a better understanding of the mechanism of the pre-treatment and a chance for optimizing the selective cobalt etching from hardmetals prior diamond deposition will be achieved.

1. Introduction
Diamond is an attractive material in a wide range of technical applications due to its exceptional optical, chemical, and mechanical properties. This generates a huge needs of synthetic diamond production now days. The methods available for producing synthetic diamonds luckily let the producers to tailor the produced formations to the demands. One of the typical cases of this is the production of diamond on hardmetals to get wear resistant drilling and cutting tools.

The hardmetal which in this case works as a support of the deposited diamond is a metal matrix composite: consisting of different size tungsten carbide particles sintered by cobalt.

The hot filament diamond deposition method beside of the instrumental conditions as the gas composition, the gas flow, the temperature of the filament and the substrate sensitive to the chemical nature and the elemental composition of the substrate. Hwang et al. [1] has demonstrated that in the same CVD condition different carbon forms can be produced if the metallic substrate is different, e.g. silicon, iron or palladium. Diamond could form only on the silicon, graphite soot will deposit on the iron while nanotubes on the palladium. This means that the chemical nature of the substrate determines the structure of the deposited carbon form during CV deposition. Based on the literature it can state the preferred carbon forms is graphite if the substrate is Fe, Co, Rh, Ir, Ni, Pd or Pt, despite in case of Ti, Nb, Ta, Cr, Mo, W, Cu, Ag, Au or Si the diamond deposition is possible and preferred [1]. Not only the pure metals but metallic compounds and composites as well can be used as support. Researches
The samples were polished using 3 different samples. The integrity of the modified outermost layer of the treated hardmetal samples were investigated using Rockwell C indentation adhesion test applying 1471 N pressing force. The test pieces were the same as which were used to the Co and W dissolution experiment.

The diamond nucleation was investigated using the ultrafine hardmetal type in form of Ø 6 mm rods. The samples were treated in the same way than the samples used for the dissolution rate investigation.
and the dissolved cobalt was calculated according that measurement data. The diamond deposition of the samples was performed in the HFCVD diamond coating unit of the Fraisa Hungária Kft using the company’s standard deposition parameter for diamond coating, but the deposition was stopped after one hour. Then to determining the diamond nucleation density the individual diamond crystals were counted on the SEM made pictures where the magnification was 10’000x.

### Table 1. Characteristic data of tested materials

| No. | Commercial name | WC grades, (typical grain size) | Co binder, m/m % |
|-----|----------------|--------------------------------|------------------|
| HM1 | CTF12E (Ceratizit GmbH) | Fine (0,8-1,3 µm) | 6,0 |
| HM2 | CTS12D (Ceratizit GmbH) | Submicron (0,5-0,8 µm) | 6,0 |
| HM3 | TSF22 (Ceratizit GmbH) | Ultrafine (0,2-0,5 µm) | 8,2 |
| Co  | Co metal       | -                             | 100              |
| WC  | WC (plasma sprayed) | (1-2 µm)                     | 0                |

### 3. Results and discussions

#### 3.1. Dissolution rate of Co and W from hardmetal and reference materials

The dissolution rate of the cobalt and tungsten are presented in Fig. 1. The dissolution rate of Co is higher in the case of the Fine hardmetal (HM1) than the Submicron hardmetal (HM2). The most probably cause of the higher solubility of HM1 is the higher average grain size of WC in the HM1. The two HM has the same initial Co content. The higher WC grain size mean higher space between the grains filled with Co. Since the HM1 and HM2 hardmetal have the same of WC to Co ratio and the higher grain size of WC mean lower specific surface area. Hence, in HM1 the same volume of Co cover lower surface of WC particles than the average Co film between the WC grain must be thicker compared to HM2 (in so far as the shape distribution of WC particles have the same in the two HM). During the Co dissolution larger pores has formed which more favourable for the transport processes.

The Ultrafine HM (HM3) has the highest Co content and this shows the highest dissolution rate. Our finding is that the higher WC grain size and the higher initial Co content of HM result higher dissolution rate of the cobalt. However, this picture can be more complex since it is known that the Co content of HM during the HM sintering process solute some W and that can modify the solubility of Co. Further investigation needed to clarify the effect of the dissolved W in Co at the contacting layer.

Determine the tungsten concentration in the etching solutions it shows that the tungsten solubility from the hardmetal in Caro’s acid does not zero. Even the binderless plasma sprayed WC has shown some W solubility. Based on this it can state the selective Co etching in Caro’ acid can due to the large difference of the solubility of the two components. If someone can improve this difference the selective Co removal will be more pronounced.

#### 3.2. Cobalt dissolution mechanism from composite materials

According to the presented data of the Fig. 1, the cobalt dissolution rate shows great difference in case of HM compared to pure Co. It can be explained by supposing different dissolution mechanism take palace in the compared two cases. Concerning the dissolution of a piece of pure metal or its powder it is obvious the surface will govern the rate of dissolution. The rate is goeverned how fast the solvent and the dissolved ions can move towards the surface from the solution phase. But in case of HM composites the solution can access to the cobalt in the developed pores formed during the dissolution as it showed on Fig. 2. The rate difference of the transport in pores and free space can create this low solubility for the composites compared to the pure metals.
Figure 1. Cobalt and tungsten dissolution rate comparison from different materials in Caro’s acid. The ratio of liquid to solid: in case of HM, pure Co and plasma spray made WC were 130, 500, 150 respectively, temperature 20 °C, static systems.

Figure 2. Different mechanism of the cobalt dissolution. In the left side the cobalt powder dissolution in solvent. The right-side cobalt dissolution between tow WC particle, in that case the accessibility of the solvent to the Co is limited by the WC particles.

3.3. Diamond nucleation enhancement during CVD process
The diamond nucleation were tested on hardmetal probes etched differently which means increasing amounts of Co was removed from the boundary layers where the diamond can formed and deposited. The Fig. 3. shows this in the case of two samples. On this SEM pictures it can be seen the coverage is different with diamond which equal the different manner of the diamond nucleation. The Fig. 4. presents the found nucleation density of diamond as a function of etched Co from the sample surface. These data prove that better quality diamond film can form if more Co removed from the boundary layer.

Figure 3. SEM pictures of the early stage of CV diamond deposition onto ultrafine hardmetal samples on the left-side poor diamond nucleation density cause of the higher Co content of the surface, on the right-side higher diamond nucleation density cause of the more removed cobalt from the surface. (Left-side sample: 0,33 mg cm$^{-2}$ dissolved Co, 2,4 μm$^{-2}$ diamond nucleation density; the right-side sample: 0,57 mg cm$^{-2}$ dissolved Co, 3,9 μm$^{-2}$ diamond nucleation density.)

3.4. Integrity of the modified outermost layer of hardmetal
The Rockwell indentation test usually used to determine the adhesion of coatings [16]. We found that test is suitable to characterise the modified Co-depleted or Co etched layer of HM prior diamond
deposition. The Fig. 5. shows the outermost Co-depleted layer of hardmetal which is weakened because the Co was removed from it during the pre-treatment. In the section 3.3. and Fig. 4. it was shown that larger amount of Co removal helps the diamond nucleation, but the Fig. 5. shows another considerable fact must relate to Co removal, this is the strength of the boundary layer which function is to support the deposited diamond.

Using the Rockwell indentation test we have found that the Co-depleted outermost layer of the HM exceeded a certain removed cobalt become instable and around the imprint of the indenter delaminate. In other words, the modified layer after too much etched Co behave like a coating having bad adhesion. The Fig. 6. shows that delamination effect. [17]

Figure 4. Nucleation density of diamond during HFCVD process onto differently Co etched samples.

Figure 5. SEM picture of CVD diamond coated HM3 type hardmetal. The Co-depleted layer of the hardmetal is well visible between the bulk hardmetal and the diamond film. The polished sample was etched during 10 s in 3% of Nital solution.

Figure 6. Light microscope pictures of the Rockwell imprints on two steps treated ultrafine hardmetal samples. The sample (b) around the imprint it can be seen delamination of the outermost Co-depleted layer as a cause of the too much dissolved cobalt; the sample (a) don’t show the delamination phenomena due to the less removed cobalt than the sample (b). Magnification: 200x. [17]
4. Conclusions

The presented research highlighted the following aspects of the CV deposition of diamond onto hardmetal substrate:

In point of the engineering of a proper diamond coating onto the hardmetal support need to find the balance between removing cobalt from the surface to enhance diamond nucleation but left enough Co in the modified hardmetal layer which able to fix the WC particles and strongly hold the diamond film.

The Co dissolution rate in case of hardmetal is affected by the grain size and the Co content of hardmetals, but to establish correlation between the dissolution rate and the grain size of hardmetal are needed furthermore investigation which considers the effect of the dissolved tungsten in the WC sintering metallic Co.

The Co dissolution mechanism in the case of composite materials was found different from that of the bulk or the powder-like sample.

The selective Co etching from hardmetal has based on that the Co dissolution rate is much higher than the W dissolution rate from WC, however the W dissolution rate is not zero.

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