Formation and characterisation of cobalt depleted outermost layer of WC–Co composite materials

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Abstract: The cobalt depleted layer of WC–Co composite materials was investigated after selective cobalt etching in diluted Caro’s acid. The time dependence of Co etching and the thickness of the etched layer was determined by using Glow Discharge Optical Emission Spectrometer (GD-OES) depth profiling as well as by calculation method based on determination of the dissolved Co by Atomic Absorption Spectrophotometric (AAS) measurement. The integrity of the modified outermost layer of the WC–Co composite materials were qualified using Rockwell C indentation test. This test methods were found usable for optimisation of the pre-treatment applied before the diamond thin film deposition.

1. Introduction

The cobalt sintered WC–Co composite material usually called hardmetals are frequently used as raw material of diamond coated machining tools. The formation of thin diamond layer onto the hardmetals is sensitive to the chemical nature of the substrate materials, since it has determined the form of the deposited carbon structure. For example, the Nb, Ta, Cr, Mo and W substrate materials promote the diamond formation, while the Fe, Rh, Ir, Ni, Pd or Pt substrates promote the graphite formation. Unfortunately, the Co component of the hardmetals belongs to the second group. Therefore, has detrimental effect on diamond formation during the CVD process. This fact can be explained by the good carbon solubility exhibits by the Co and the direction of catalyses which is promoted in case the sp\textsuperscript{2} bonded graphitic not the sp\textsuperscript{3} diamond deposit formation [1].

To eliminate this detrimental effect a commonly used method is the selective Co removal from the surface layer of the hardmetal by strong acid solutions which consist of different combination of H\textsubscript{2}SO\textsubscript{4}, H\textsubscript{2}O\textsubscript{2}, HNO\textsubscript{3} and HCl. A more sophisticated method is the so called two steps chemical treatment prior CV diamond deposition process. The first step of the treatment is the WC etching in K\textsubscript{3}[Fe(CN)\textsubscript{6}] and KOH containing aquatic solution, called Murakami’s reagent and the second step is the selective removal of part of the cobalt from the surface layer using strong acidic solution [2] [3] [4] [5] [6] [7].

However, the selective cobalt etching eliminates the detrimental effect of Co in case of the CV diamond deposition process but generate a negative outcome by weakening the outermost layer of the hardmetal leaving behind a few \textmu m thick unsintered porous WC skeleton on the surface. This antagonistic effect of the chemical pre-treatment require optimization to avoid the unnecessary weakening of the support layer of the Co sintered WC composite material [8] [9].

This research presented below focuses on: (i) determining the time dependence of the cobalt etching on different types of hardmetals; (ii) to find the relation between the dissolution rate and the thickness of the Co-depleted layer of the treated hardmetals; (iii) the qualification of the modified layer of hardmetals using Rockwell indention test method.
2. Materials and experiments
The Co dissolution experiment were carried out on five types of hardmetals. Some relevant data of the hardmetals are showed in Table 1. The samples were Ø 14 mm and 5 mm thick. The two flat sides of the samples were polished using metallurgical grinding unit. Then was selectively etched the WC of the sample surface in Murakami’s reagent containing 100 g K$_3[Fe(CN)_6]$, 100 g KOH, and 1000 ml H$_2$O for 25 minutes to get uniform surface condition before the cobalt etching.

The second, investigated step of the treatment was the cobalt etching in so called Caro’s acid aqua solution containing of c(H$_2$SO$_4$) = 0.29 mol/dm$^3$ and c(H$_2$O$_2$) 2 mol/dm$^3$. Each sample was treated in 100 ml acid solution then washed three times in distilled water and dried in hot air flow. The Co content of the used solution was measured with Atomic Absorption Spectrophotometer (AAS).

The layer thickness of the cobalt etched layer was determined depth profiling method using Glow Discharge Optical Emission Spectrometer (GD-OES). The sputtering speed was determined based of LASER profilometric measurement. The thickness of the Co depleted layers was also achieved using a calculation method based on the determination of the dissolved cobalt. More details from this method was presented in our previous work [10].

The cobalt etched layers were characterised using standard Rockwell C indentation test applying 1471 N loading force. This method was found applicable for the qualification of the modified, Co depleted layer of hardmetals [9].

Table 1. Characteristic data of the tested Hardmetals

| Hardmetal type, (WC grain size) | Nominal Co content, m/m % |
|-------------------------------|--------------------------|
| **Fine** (0.8-1.3 µm)        | 6.0                      |
| **Submicron** (0.5-0.8 µm)   | 6.0                      |
| **Submicron** (0.5-0.8 µm)   | 10.0                     |
| **Ultrafine** (0.2-0.5 µm)   | 8.2                      |
| **Ultrafine** (0.2-0.5 µm)   | 12.0                     |

3. Results and discussions

3.1. Dependence of the thickness of the Co etched layer from the treating time
The calculation method used to determine the thickness of the Co etched layer based on determination of the dissolved cobalt concentration in the etching solution. This measurement can also inform us about the rate of dissolution, Fig. 1. The measured data show that the time dependence of the Co dissolution depends on the type of the hardmetal. According the removed cobalt the thickness of the modified layer was calculated. The results are showed on Figure 2.

Figure 1. Cobalt dissolution comparison from different hardmetals in Caro’s acid. The mass ratio of liquid to solid were 130, temperature 20 ºC, static systems was used
Figure 2. Development of the thickness of the Co depleted layer on different hardmetals in function of etching time. Calculation based on the dissolved Co measurement with AAS method. Parameters same as at the Fig 1.

Other possibility to measure the thickness of the Co depleted layer is the GD-OES depth profiling method. One of characteristic curves of these measurements which are the emission signals of the sputtered elements in function of time are showed on Fig. 3. On the diagram well visible that the cobalt removal is effective since the Co signal is low in the modified layer but after a short transition zone it rises to the level characteristic for the bulk material. The GD-OES profiles were converted to thickness of the Co etched layer and compared with the calculated layer thickness. Comparison of the two methods are showed in Fig. 4. which has shown the methods conformity.

The Fig. 2. has shown that the Co etched layer developing with different rate on different type of hardmetals. The higher development of the modified layer is promoted by the higher average grain size of the WC and pressed back by the higher Co content.

Figure 3. GD-OES emission intensity profile of the carbon, tungsten and cobalt element in case of the “Ultrafine” hardmetal sample with 8 % nominal Co content, which was etched in aquatic solutions of Caro’s acid for 55 seconds.
Figure 4. The thickness of the Co depleted layer based on GD-OES measurement and calculated based on the dissolved Co, measured using AAS method in the case of the “Submicron 6 % Co” hardmetal samples. Sputtering time was transformed for sputtered thickness by LASER profile depth measurement

3.2. Cobalt etched layer characterisation using Rockwell indentation test

Rockwell indentation test was used to characterise the cobalt etched layer. This test is used for measuring the hardness of materials and appropriate to determine the adhesion of coatings. We showed that test is usable to characterise the Co depleted layer of hardmetals. If the cohesive force between the WC particles in the modified layer is too low, the layer delaminates around the imprint. This case the layer is not strong enough to hold and support the diamond coating. On Fig. 5 two type of this test results are presented. On picture (a) no delamination visible, despite on the (b) picture the modified layer is delaminated. This type of test was performed on all investigated samples. A comparison is given on Fig. 6, where no delamination occurred till the indicated highest Co depleted layer thickness. On the Fig. 7, we used the same logic but instead the Co depleted layer thickness the treating times are shown (the green bars present the highest “safe” treating time). For comparison the red bars show where the delamination occurs.

Figure 5. Rockwell indentation induced delamination onto “Submicron 10 % Co” samples. On the picture (a) no visible delamination around the Rockwell imprint. Picture (b) the Co depleted layer delaminated around the Rockwell imprint.

On Fig. 6. an Fig. 7. the green bars show the highest “safe” Co depleted layer thickness and treating time respectively which can be usable in case of optimising of the selective cobalt etching prior CV diamond deposition. These figures represent that the different hardmetal need quite different treatment which lead to strength enough support layer able to hold the CV deposited diamond layer during the applications.
4. Conclusions
The presented research highlighted the following aspects of the pre-treatment of hardmetals prior CV deposition of diamond:
- The thickness of the Co etched layer is measurable using GD-OES depth profiling method and can be calculated based on the measurement of the removed cobalt using AAS method. The two methods provide the same results.
- The Co depleted layer developing differently on different hardmetal types. The increasing WC grain size and the decreasing Co content promote the process.
- The Rockwell C indentation test is applicable and useful to qualifying the modified outermost layer of hardmetals by selective Co etching.
- In case of the investigated hardmetals the higher Co removal, i.e. the higher Co depleted layer thickness and treating time limits were determined and shown the optimising procedure of the pre-
treatment prior CV diamond deposition. The optimal treating time directly proportional to Co content of the hardmetals and inversely proportional to grain size of the hardmetals.

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