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WC-Co substrate preparation and deposition conditions for high adhesion of CVD diamond coating

Preparação do substrato de WC-Co e condições de deposição para alta adesão de revestimento de diamante CVD

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ABSTRACT

Different substrate surface pretreatments have been used to improve the adhesion of CVD diamond coatings on WC-Co substrates. This paper reports the results of a pretreatment method based on two-step chemical etching: first in Murakami solution and then in *aqua regia*. A systematic study was performed to evaluate the influence of the pretreatment on the composition and morphology of the WC-Co substrate. Furthermore, the effect of diamond nanoparticle seeding on the morphology and roughness of the substrate was also investigated. After these studies, diamond coating was deposited on seeded WC-Co substrate by hot-filament CVD. The sample was characterized by Raman spectroscopy, FEG-SEM and AFM. Rockwell C indentation test was used to evaluate the adhesion between the CVD diamond coating and the WC-Co substrate.

Keywords: CVD diamond; WC-Co substrate; Adhesion.

RESUMO

Diferentes pré-tratamentos têm sido utilizados para melhorar a adesão de revestimentos de diamante CVD sobre substratos de WC-Co. Este artigo relata um método de pré-tratamento químico baseado em duas etapas de corrosão: primeiro em solução de Murakami e depois em água régia. Um estudo sistemático foi realizado para avaliar a influência do pré-tratamento sobre a composição e a morfologia do substrato de WC-Co. O efeito do processo de semeadura com nanopartículas de diamante sobre a morfologia e a rugosidade do substrato foi também investigado. Após esses estudos, o revestimento de diamante CVD foi depositado sobre o substrato de WC-Co pela técnica de filamento quente. A amostra foi caracterizada por espectroscopia Raman, FEG-SEM e AFM. A adesão entre o revestimento de diamante CVD e o substrato de WC-Co foi avaliada por indentação *Rockwell C*.

Palavras-chave: Diamante CVD; Substrato de WC-Co; Adesão.

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INTRODUCTION

Coating of hard metal cutting tools with CVD (Chemical Vapor Deposition) diamond films has been the focus of much research in academia as well as industry. Such coatings can significantly prolong the durability of coated tools. Therefore they are of key importance in the fields of high speed cutting, dry machining or machining of special materials[1]. Apart from these advantages, a problem is the poor adhesion of diamond coatings to hard metals, like WC-Co, due to the Co-binder that catalyzes the formation of graphite[2-4]. Some methods have been developed to overcome this problem, two can be highlighted: (i) application of intermediate layers to act as a cobalt barrier and (ii) chemical pretreatment of the hard metal substrate in order to reduce the cobalt concentration on the surface to be coated[2].

It has been reported that the introduction of intermediate layers results in lower diamond nucleation rates and lower growth rates while that the use of chemical pretreatment is simple, cheap, efficient and more suitable for batch production[3-4].

In this work, a pretreatment of WC-9wt.% Co substrates based on two-step chemical etching (Murakami solution and *aqua regia*) followed by seeding with diamond nanoparticles was used to enable the study of CVD diamond nucleation and growth.

The contributions of this study to the literature include:

1. A detailed characterization of the WC-9 wt.%Co substrate. The majority of studies about adhesion of diamond coating to WC-Co tools has been concentrated on substrates with low Co concentration (3 or 6 wt. %). However, due to their higher strength and better ductility, WC-Co tools with high Co concentration (> 6wt.%) are required for difficult-to-cut material machining.
2. Reduction of the etching time in Murakami solution. Usually, this etching step is performed at least 30 min. Here it will be shown that 10 min are sufficient to attack the WC grains from the substrate surface and expose the cobalt to be removed during the second etching step using *aqua regia*.
3. Evaluation of the diamond coating adhesion after indentation test under a load of 150 kgf. Generally, the indentation tests are performed with a load of 60 or 100 kgf.

EXPERIMENTAL PROCEDURE

Substrate preparation

WC–Co disks (91% WC and 9% Co composition, 9 mm in diameter and 3 mm thick) commercially available were used as substrates. After the surface polishing procedures, these substrates were chemically pretreated by two etching steps. First, it was used a Murakami solution ($K_3(Fe(CN)_6)$ + KOH + H_20) for 10 minutes in an ultrasonic bath to etch the WC phase from the cemented carbide. The second etching step was performed using solution of *aqua regia* (HNO_3/HCl = 1:3) for 5 minutes to remove the cobalt from the surface. After each etching step, the substrates were rinsed with pure water. Prior to CVD diamond deposition, the substrates were characterized by FEG-SEM (field emission gun-scanning electron microscopy) with integrated EDS (Energy-dispersive X-ray spectroscopy) analysis in order to detect the cobalt concentration on the surface. Subsequently, the etched substrates were seeded in water slurry containing 4 nm diamond nanoparticles dispersed by PSS (sodium4-styrenesulfonate) polymer. More details about this process can be found in another publication[5].

CVD diamond deposition

Diamond film was deposited onto seeded WC-Co substrate in a conventional hot-filament system using a gas mixture of 2.0% methane (CH_4) and 98% hydrogen (H_2). The total flow rate was 100 sccm and the pressure inside the reactor was kept at 50 Torr. The substrate was placed at 7 mm from five tungsten filaments each one with 0.125 mm in diameter and 100 mm long. Table 1 summarizes the deposition parameters. Under these conditions, it was obtained a deposition rate of 1 μm/h.

Table 1: Deposition conditions used for diamond film deposition on WC-Co substrates.

Deposition conditions	Distance from filament top the substrate top (mm)	**7**
	Substrate temperature (ºC)	800
	CH_4 flow rate (sccm)	2
	H_2 flow rate (sccm)	98
	Filament current (A)	20.8
	Filament voltage (V)	24.2
	Pressure (Torr)	50
	Deposition time (min)	120

Characterization tests

Raman measurements of the CVD diamond film were performed using a Renishaw system 2000 Raman Spectrometer. The spectra were recorded in backscattering configuration at room temperature employing Ar^+ ion laser (λ=514 nm). The spectrometer was calibrated to the 1332 cm^{-1} band of natural diamond. The morphology and composition of the samples were examined with a scanning electron microscope (FE-SEM, Tescan Mira 3 FEG) coupled with Energy-dispersive X-ray spectroscopy (EDS or EDX). Surface roughness studies were done by an atomic force microscope (AFM) Veeco multimode. In order to evaluate the adhesion level of the CVD diamond coating, indentation tests using a diamond stylus Rockwell C with a conical diamond indenter (120º cone angle and 0.2 mm tip radius) were performed. The samples were tested by applying a load of 150 kg at the diamond indenter.

RESULTS AND DISCUSSION

Characterization of the WC-Co substrate

EDS analysis were performed in order to determine the Co content before and after pretreatment. Figure 1 shows the EDS mapping of the as-polished WC-Co substrate. Note in Fig. 1a that the Co binder is uniformly distributed on the substrate surface. Furthermore, as expected, W is the main constituent (Fig. 1a, b).

The EDS spectra of as-polished and pretreated WC-Co substrates are shown in Fig. 2.

Observing the data depicted in both graphics can be clearly seen that the substrate pretreatment was efficient reducing cobalt content to less than 1.0%.

In Fig. 3, it can be observed a significant change in surface morphology of the pretreated WC-Co substrate with respect to as-polished substrate. This occurs because the etching steps led to the corrugation of the WC-Co substrate surface. The mechanism is the following: (i) during the Murakami etching, WC particles are dissolved, leaving behind the Co network from the binder phase and (ii) in the second etching step, the Co binder phase is attacked by *aqua regia* and the Co is removed from the surface[6].

Seeded WC-Co substrate

As can be seen in AFM images shown in Fig. 4, the seeding process with diamond nanoparticles promoted an increase in the substrate surface roughness. The average roughness, R_a, of etched

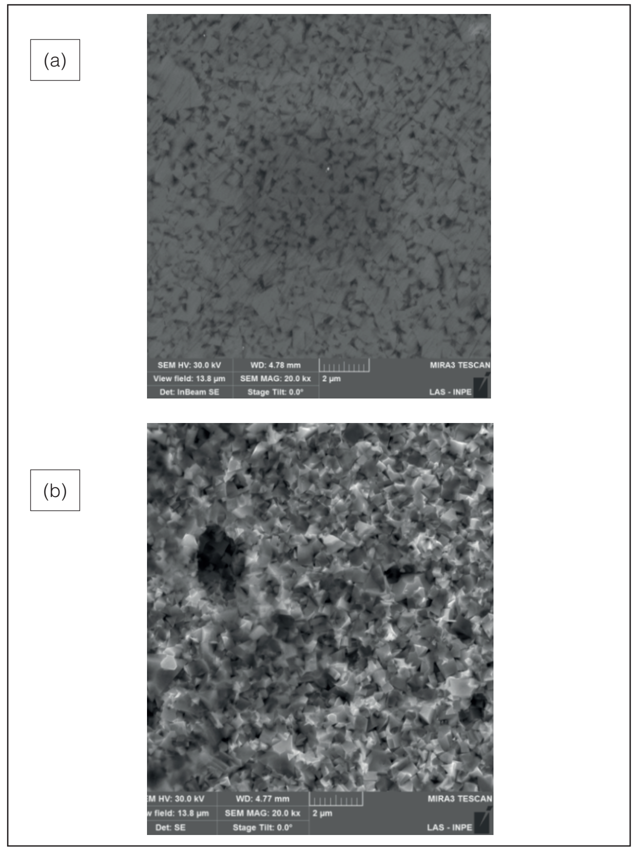

Figure 3: FEG-SEM images of the WC-Co substrate: (a) as-polished without pre-treatment and (b) after two-step etching

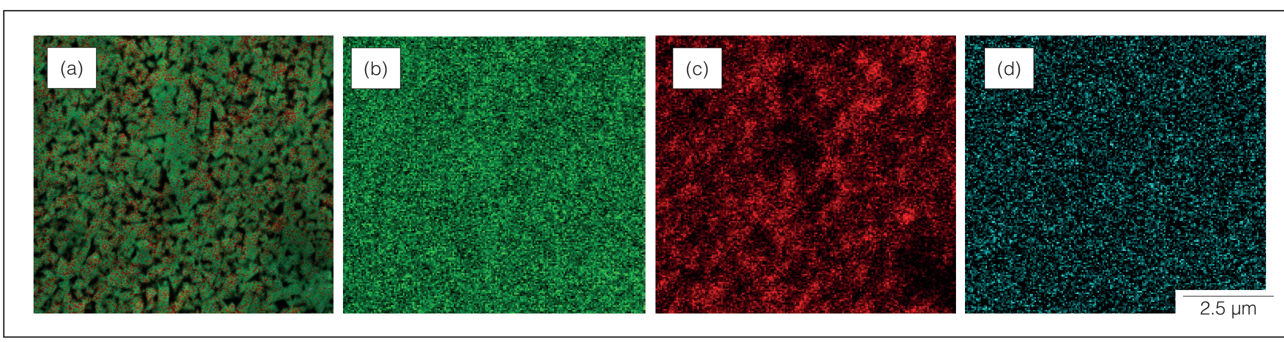

Figure 1: EDS mapping of the as-polished WC-Co substrate: (a) distribution of the elements on the WC-Co surface, (b) W element map, (c) Co element map, (d) C element map.

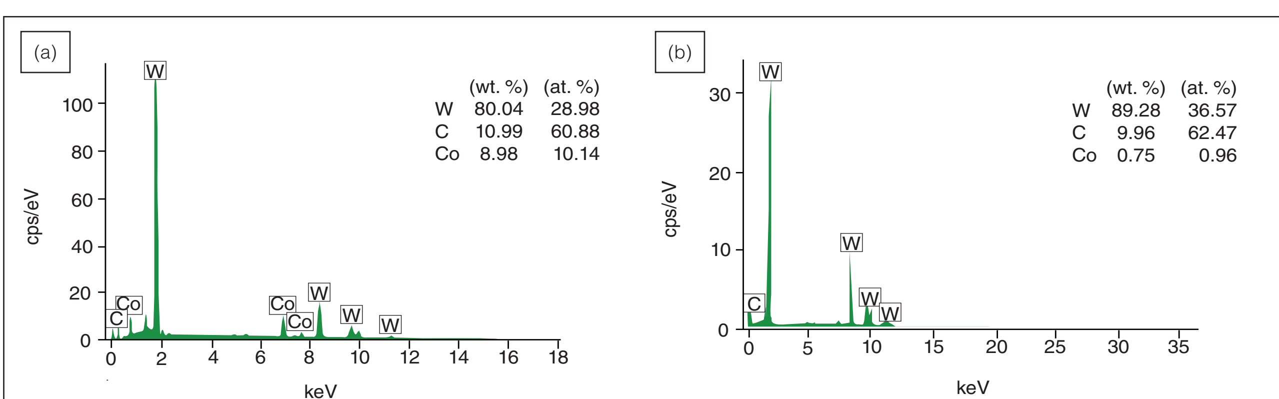

Figure 2: EDS of the WC-Co substrate: (a) without pretreatment and (b) after two-step etching

WC-Co substrate was 19.3 nm whereas the seeded substrate exhibited R_a of 46.5 nm.

This increase in surface roughness is crucial to increase the interface contact area and improve the diamond film nucleation, hence speeding up the formation of a continuous film which enhances the adhesion between the CVD diamond film and the WC-Co substrate(7). Figure 5 shows the FEG-SEM image of the seeded substrate.

Characterization of the CVD Diamond film

FEG-SEM image of the CVD diamond film grown on seeded WC-Co substrate is shown in Fig. 6a. The film is dense and continuous besides it is relatively uniform with crystal size of the order of 1 μm. Fig. 6b shows the AFM image of the same sample, depicting surface roughness of the diamond film. This microcrystalline diamond film has an average roughness of 48.9 nm.

The chemical quality of as-deposited CVD diamond film was evaluated by Raman spectroscopy. The Raman spectrum of the sample is shown in Fig. 7. It can be noted an evident diamond peak at 1340 cm^{-1} and a broadband centered around 1560 cm^{-1}, which is attributed to disordered graphitic carbons.

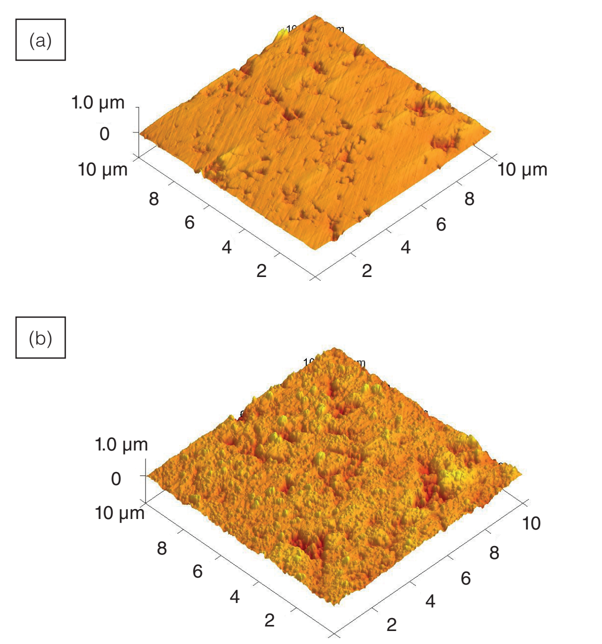

Figure 4: AFM images of the WC-Co substrate: (a) after two-step etching and (b) after seeding

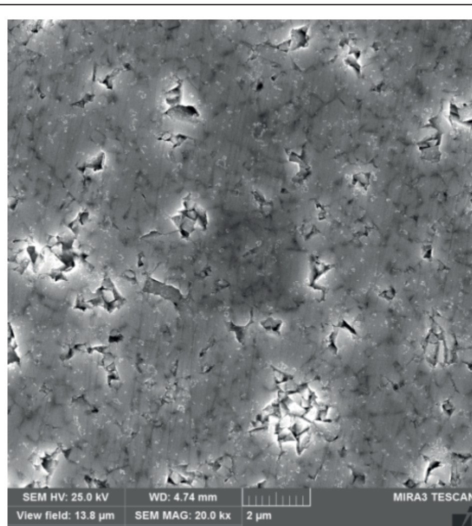

Figure 5: FEG-SEM images of the seeded WC-Co substrate

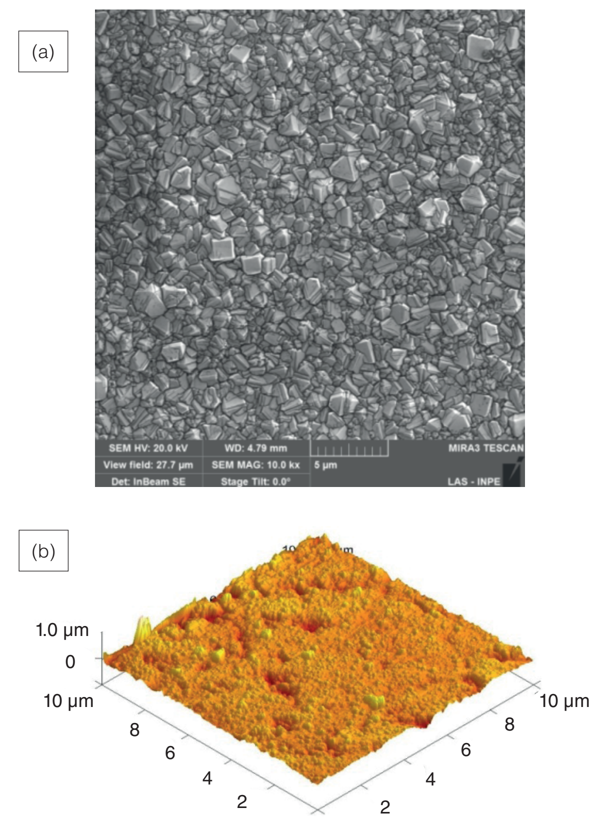

Figure 6: Images of the CVD diamond film grown on WC-Co substrate: (a) FEG-SEM and (b) AFM

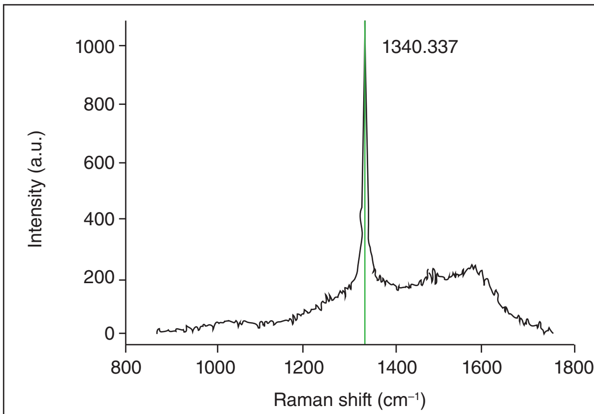

Figure 7: Raman spectrum of the CVD diamond film

The residual stress of CVD diamond film can be estimated from Raman spectra using the following equation[8]:

$$\sigma = -0.567\ (\nu_m - \nu_0)\ (\text{GPa}) \tag{1}$$

Where ν_0 is the characteristic peak of diamond (1332 cm^{-1}) and ν_m is the observed peak. Negative values correspond to a compressive stress.

From Raman spectrum shown in Fig.7, it was obtained a diamond film with a compressive stress of -4.7 GPa. It is known that a low residual stress of the coating, in the range of -2 GPa to -5 GPa, is one of the requirements for an good adhesion to the substrate.

Indentation test

The adhesion of the CVD diamond coating to WC-Co substrate was investigated by Rockwell C indentation test which is based on six levels of adhesion depending on the damages of the coating adjacent to the indentation boundary: HF1 to HF4 indicate adequate adhesion and no evident spallation around the boundary whereas HF5 and HF6 indicate severe delamination, i.e., inadequate adhesion between coating and substrate[9]. Fig. 8 compares the images of indentation WC-Co substrates with and without CVD diamond coating. In Fig. 8b, it can be observed a delamination (level HF5) indicating that there is no an appropriate adhesion between the diamond coating and the WC-Co substrate. On the other hand, a comparison between Fig.8 (c, d) shows that the WC-Co substrate exhibited a defined propagating crack, whereas the same was not observed for diamond coated WC-Co substrate.

Although the WC-Co pretreatment has been effective and the CVD diamond film has exhibited good chemical and morphological properties, the delamination observed in Fig.8b indicates that more studies are necessary in order to achieve a better adhesion between film substrate. One way is reducing the residual stress of the diamond coating increasing the nucleation rate. This can be achieved by improving the seeding and/or using bias assisted hot- filament CVD technique[10].

CONCLUSION

Two-steps etching pretreatment has removed almost completely the Co from the WC-9%Co substrate surface. Based on FEG-SEM and Raman spectroscopy results, it was observed that the CVD diamond film grown on seeded WC-Co substrate has good structural and morphological characteristics. However, Rockwell C indentation test revealed that the adhesion between film and substrate is still not adequate. More studies are necessary to achieve a high adhesion.

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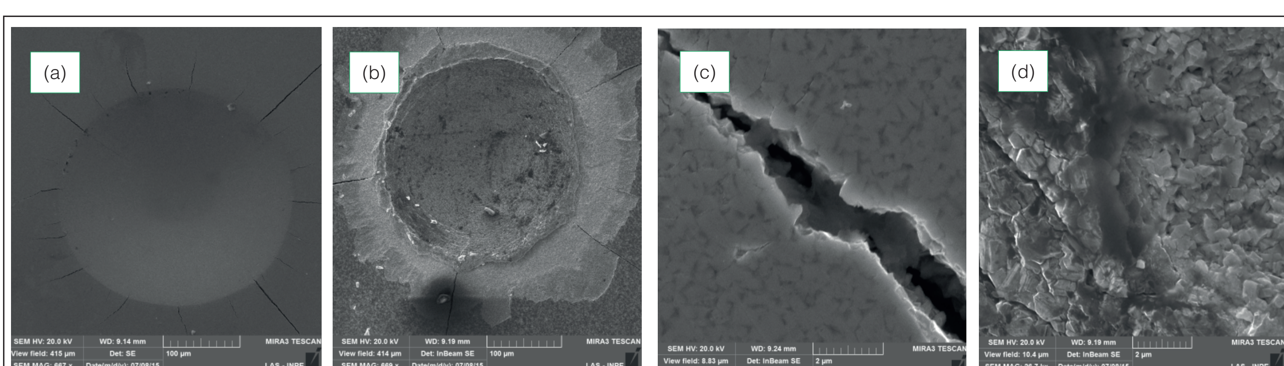

Figure 8: FEG-SEM images after indentation test: (a) and (c) WC-Co substrate, (b) and (d) diamond coated WC-Co substrate