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Chemical pretreatments at surface of WC-6 % Co for diamond coatings ①

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[Abstract] The WC-6 %Co (mass fraction) substrate surfaces were chemically pretreated with the two-step etching method, using Murakami reagent for 3～7 min, and then an $\varphi(HNO_3):\varphi(HCl) = 4:1$ solution for 1～15 min. Diamond films were deposited on the substrates by a hot-filament chemical vapor deposition reactor. The results show that the Co content of the substrate surfaces can be reduced from 6 % to 0.12 % within the etching depth of 5～10 μm, the surface roughness of the substrates is increased up to $R_a = 1.0$ μm, as well as the substrates hardness is decreased from HRA 89.5 to HRA 84.2 after the two-step etching. A slight preference towards {111} orientation can be observed from the XRD patterns and SEM micrograph of diamond film on WC-6 %Co sample. The morphology of small rice-like ballas diamond was observed on the WC-6 %Co substrates. A typical Raman spectrum with a sharp peak at 1 332 cm^{-1} for the diamond film indicates that the deposited films are good-quality polycrystalline diamond. The indentation testing shows that the adhesion between diamond film and the substrate after HF CVD deposition is good.

[Key words] cemented carbides; diamond coatings; chemical pretreatment

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1 INTRODUCTION

Diamond is known to be the hardest and most wear resistant material in the world. Therefore, one of its applications is to use as a protective coating for cutting tools. However, the major problem with this application is the poor adhesion between the film and the substrate due to great internal stress in the films and the presence of Co in the substrate that brings about the transformation of diamond to amorphous and graphitic carbon[1]. Several methods have been adopted to enhance the adhesion of the diamond films on WC-Co substrates. These methods can be divided into two categories: removal of Co at the diamond-carbide interface using different etching agents and the deposition of an interlayer as a diffusion barrier[2～10]. Since the etching method is simpler, lower cost, and more suitable to the industrial production, therefore, surface etching to minimize Co content on the substrate surface before diamond deposition is generally adopted. As it is known, the result of removal Co from the carbide substrates depends on the kind of etching composition and etching time. It is very important to systematically investigate the effects of the kind of etching composition and etching time on the removal Co from the carbide substrates.

An attempt was made in this investigation to develop the suitable chemical surface pretreatments matched with HF CVD deposition conditions for adherent diamond coatings on the cemented carbides. The goal is to determine the optimal condition of the chemical surface pretreatments at cemented carbides (WC-6 %Co) for achieving a good-quality diamond film on the substrates.

2 EXPERIMENTAL

The substrates used in the study were WC-6 % Co of dimension 9.0 mm × 5.5 mm × 3.0 mm. After the samples were ground to the surface roughness of $R_a = 0.2$ μm, the substrates were pretreated with the two-step etching methods, using first Murakami-solution ($\varphi(K_3[Fe(CN)_6]):\varphi(KOH):\varphi(H_2O) = 1:1:10$) for 3～7 min, and afterwards an $\varphi(HNO_3):\varphi(HCl) = 4:1$ solution for 1～15 min, then they were ultrasonically cleaned in acetone and weighed in an electronic balance for measuring the mass loss due to etching. The electronic balance could measure mass loss up to 10^{-5} g. A hot-filament reactor as described elsewhere[11] was used for the deposition of diamond film. The substrate bottom temperature (700 ± 5 ℃) was measured by a Ni-Cr-Ni thermocouple placed on

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the bottom of substrate. Further experimental conditions are: total pressure = (4～8) ×10^3 Pa, $\phi(CH_4)$: $\phi(H_2)$ content = 0.5 %～1 %, deposition time, 6 h. After etching, the surface roughness and hardness of the substrates were measured by SE-30C and Rockwell testers, respectively, as well as the depth and content of the substrate Co-depleted region were detected by SEM with integrated EDX (Finder 1000) analysis of cross-section of the samples. The morphologies of the diamond film were examined by a scanning electron microscope KYKY-2800. A Rockwell indenter was used to apply discrete loads to the diamond film until surface cracks could be observed. An X-ray diffractometer (Siemens D-5000) was applied to examine the crystal structure. A SPEX 1403 macro- Raman spectrometer was used for chemical quality evaluation by Raman characterization.

3 RESULTS AND DISCUSSION

The changes of mass loss and hardness of the substrates after the two-step etching are shown in Fig. 1.

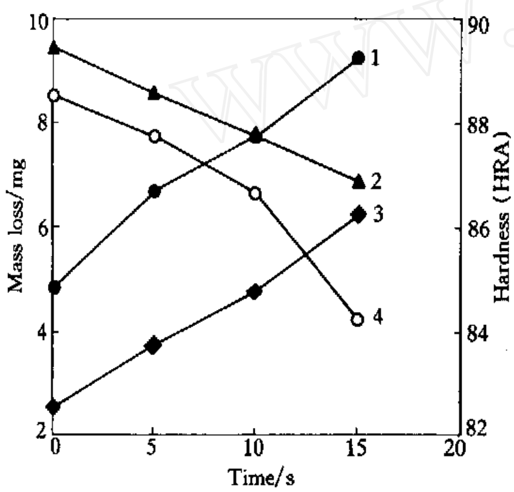

Fig. 1 Relationship of mass loss and hardness with etching time of second step in solution of $\phi(HNO_3)$: $\phi(HCl)$ = 4 : 1
1 —Mass loss, 7 min; 2 —Hardness, 3 min; 3 —Mass loss, 3 min; 4 —Hardness, 7 min

It is clear that the mass loss is increased and hardness is decreased with increasing etching time whether in the first or second step, it is because that the etching reaction lead to a loose structure of the substrates, but the first step etching has less affection as compared with the second one due to a weak reaction with the substrates in Murakami solution. The increase of surface roughness from R_a = 0.2 to 1.0 μm is observed for the same reason.

Fig. 2 shows that the Co contents of the substrate surface are obviously decreased from 6 % to 0.12 %～3.56 % within the etching depth of 5～10 μm with increasing etching time in the second step. As it is known, the substrates consist of Co and WC phases, and the WC content is as high as about 94 %. Although the Co phase in the substrates is easy to be etched by various acids, WC phase is highly resistant to the acids. If only using the one-step etching method to deplete Co, WC grains would hinder the Co phase to be etched in the depth of the substrate[12]. Hence, the two-step etching method should be used to effectively remove Co, first using the Murakami reagent which is found to be ideal as it attacks only WC grains leaving the cobalt unaffected, then the various acids to deplete Co phase[3].

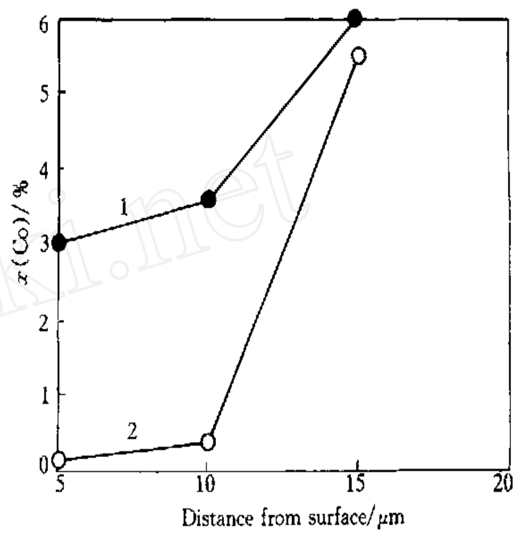

Fig. 2 Relationship of Co content with distance from surface
1 —1 min; 2 —15 min

Fig. 3 shows the XRD patterns of diamond film on WC-6 %Co sample. A slight preference towards {111} orientation can be observed in Fig. 3, which can also be confirmed by SEM micrograph, as shown in Fig. 4. The preference towards {111} orientation

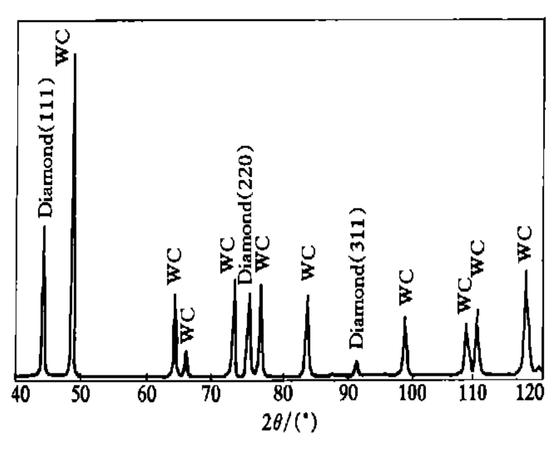

Fig. 3 XRD patterns of diamond film on WC-6 %Co sample

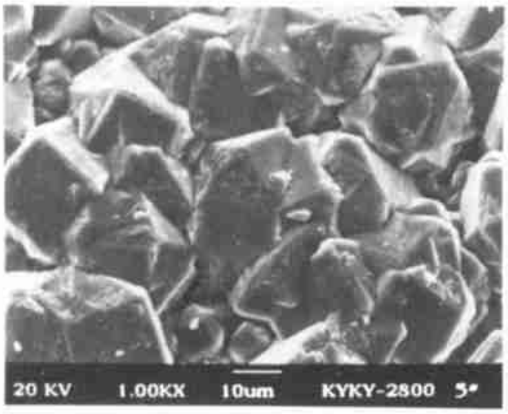

Fig. 4 SEM micrograph of diamond film on WC-6 %Co sample

of diamond films can be explained by the surface free energy (γ) of diamond crystal which is expected to be anisotropic because of the orientation of the bonds and is calculated by the following equation[13]:

$$\gamma_{hkl} = 3E\lambda / (8 d_0^2 \sqrt{h^2 + k^2 + l^2})$$

where E and d_0 denote the energy and the length of the C—C bond in diamond respectively, while λ represents the maximum of the Miller indices of h, k and l, especially $\gamma_{100} : \gamma_{110} : \gamma_{111} = 1 : 1/\sqrt{2} : 1/\sqrt{3}$, where γ_{100}, γ_{110} and γ_{111} represent the surface free energy of {100}, {110} and {111} facets, respectively. The ratio is the kind of equilibrium form, according to this, the {111} surface of diamond has the smallest surface free energy.

The SEM image of small rice-like ballas diamond was observed with the pretreatment of short etching time after the deposition, as shown in Fig. 5. The small rice-like ballas diamond is called amorphous carbon or DLC (diamond like carbon). It is the higher concentration of carbon around the substrate surface that leads to forming of the morphology of small rice-like ballas diamond, which is concerned

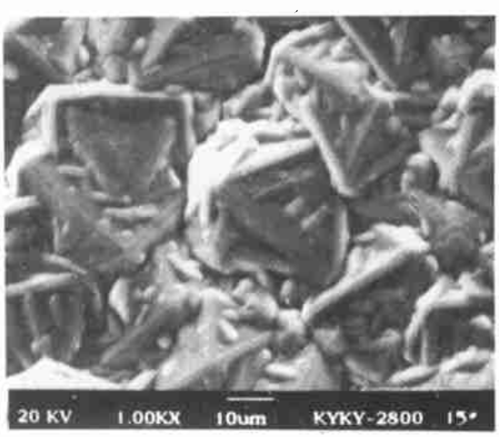

Fig. 5 SEM image of small rice-like ballas diamond film on WC-6 %Co sample

with the higher Co content left at the substrate surface and the deposition conditions.

Fig. 6 shows a typical Raman spectrum for the diamond film obtained in this work. A sharp peak at 1 332 cm^{-1} indicates that the deposited films are good-quality polycrystalline diamond.

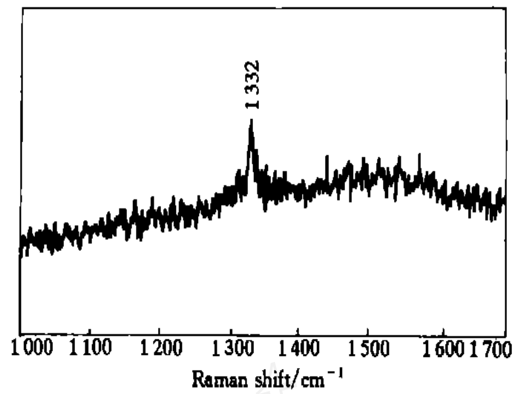

Fig. 6 Raman spectrum with a sharp peak at 1 332 cm^{-1} for diamond film on WC-6 %Co sample

The indentation tests allow the evaluation of film adhesion in terms of the coating-substrate interface toughness[14]. Indentation test results were interpreted by analyzing the SEM images of the damage produced in the diamond films. The smallest load necessary to produce the first cracks was used as a measurement reference of film adhesion[15]. Fig. 7 shows the SEM micrograph of the imprint obtained by Rockwell (60 kg) indentation of the diamond film grown on the WC-6 %Co substrate, which did not result in any cracking expansion and indicated a good adhesion between the diamond film and the substrate.

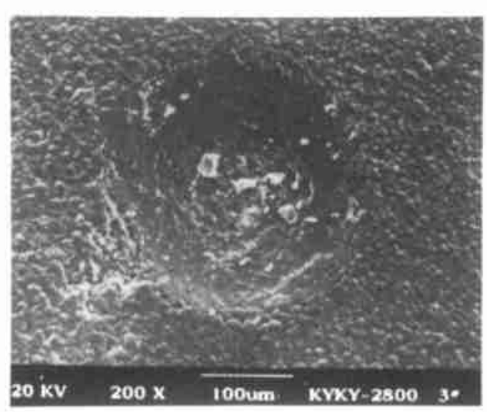

Fig. 7 SEM micrograph of imprint obtained by Rockwell (60 kg) indentation of diamond film grown on WC-6 %Co substrate

4 CONCLUSIONS

1) After the two-step etching, it is indicated

that the Co content of the substrate surfaces can be reduced from 6 % to 0.12 % within the etching depth of 5~10 μm, the surface roughness of the substrates is increased up to R_a = 1.0 μm, and the substrates hardness is decreased from HRA 89.5 to HRA 84.2.

2) A slight preference towards {111} orientation can be observed from the diamond film on WC-6 %Co sample, and the deposited films are good-quality polycrystalline diamond.

3) The morphology of small rice-like ballas diamond is observed on the WC-6 %Co substrates.

4) The indentation testing shows that the good adhesion between diamond film and the WC-6 %Co substrate after HF CVD deposition can be obtained.

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