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HF-CVD법에 의한 세라믹스 기판에의 다이아몬드박막 합성과 그 밀착성 평가

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Diamond Film Deposition on Ceramic Substrates by Hot-Filament CVD and Evaluation of the Adhesion

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초 록 Ta(TaC) 필라멘트를 이용한 HF-CVD법에 의하여 Si_3N_4, SiC, WC, Al_2O_3를 기판으로 다이아몬드 박막을 증착하고, 그 밀착특성을 평가하였다. 로내의 CH_4농도를 5%이하로 낮추었을 경우에는 기판종류에 상관없이 다이아몬드만의 박막이 증착됨을 알 수 있었다. 그러나 CH_4농도를 10%로 높게 하였을 경우에는 막중에 graphitic (amorphous) carbon이 생성됨을 확인할 수 있었다. 박막을 12㎛ 정도까지 두껍게 하면, WC기판에서는 부분적 박리형상이 관찰되었으나, Si_3N_4를 기판으로 하였을 경우에는 안정한 박막을 얻을 수 있었다. Indentation test결과로부터 grinding에 의한 기판표면처리가 밀착성 향상에 효과적이라는 것을 알 수 있었다. 또 compression topple test에서는 박막의 두께는 밀착성과 반비례의 관계를 가지는 것을 알 수 있다.

Abstract Diamond thin films were deposited on Si_3N_4, SiC, WC, TiC and Al_2O_3 substrates by the CVD method using Ta(TaC) filament, and the appearance of the diamond films and their adhesion properties were examined by SEM, optical microscopy, indentation test and compression topple test. Diamond films were deposited at lower CH_4 concentration than 5%CH_4 for all kinds of the substrate material, but graphitic (amorphous) carbon was observed at 10%CH_4. The diamond film of about 12㎛ thickness on WC substrate partly peeled off, but the film on Si_3N_4 substrate held good adhesion. The indentation test showed that roughly ground surface was very effective for adhesion of diamond films to substrates. The topple test revealed that film thickness was an important factor governing the adhesion of the diamond film.

Key words : Hot-filament CVD, TaC filament, diamond thin film, ceramic substrate, and adhesion.

1. Introduction

The techniques for diamond film deposition under a low pressure have been extensively studied for many industrial applications.[1,2] The hot-filament CVD is one of the most promising techniques since it can easily produce diamond films and the equipment itself is less expensive than the others.[1~10] Recently, the filament materials for diamond CVD have been studied to improve the deposition rate and the stability. The use of Ta as a filament instead of W has shown high deposition rate and excellent stability for high temperature in the diamond deposition.[11]

Ceramic substrate materials are useful for the CVD coating because it needs high temperature treatment during the deposition and for the application of hard materials like cutting tools and wear resistant parts. In addition to optimize the deposition conditions for diamond film on ceramic substrates by CVD, the practical techniques for evaluating the adhesion of the diamond films are required. However, more knowledge and information are needed concerning these issues.

In this study, optimum conditions for diamond film deposition by the hot filament CVD using Ta(TaC) were obtained for various ceramic substrate materials. Then, the appearances of diamond films deposited on the ceramic substrates were examined. Finally, the adhesion between diamond films and substrates was evaluated by two different techniques.

2. Experimental procedure

Fig. 1 shows a schematic drawing of the deposition system used in this study. Commercial Ta wire of 0.5mm diameter was used for the filaments. Before the deposition experiments, the Ta filament was sufficiently carburized to TaC at 2673K in H_2-5%CH_4 gas

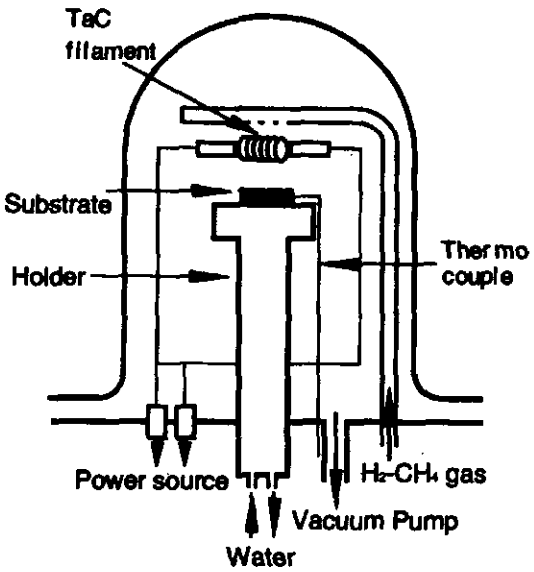

Fig. 1. Schematic drawing of the apparatus for diamond deposition by thermal CVD using a TaC filament.

Table 1. Conditions for chemical vapor deposition.

Conditions	Values
Gas composition	H_2-(3-10)%CH_4
Total gas pressure	4kPa
Total gas flow rate	20ml/min
Filament temperature	2873K
Substrate temperature	1173K
Distance between filament and substrate	5mm
Deposition time	1-4hr

mixture. The conditions for diamond deposition are listed in Table 1. The diamond depositions using the TaC filamemt were carried out under CH_4 concentrations from 1 to 10%. The deposition time was in the range from 1 to 4 hr depending on the film thickness. The other parameters were fixed at constant as seen in Table 1. The ceramic substrates used were Si_3N_4, SiC, WC, TiC and Al_2O_3. The substrate surface was prepared by either grinding with a diamond wheel, or polishing with diamond powders.

The diamond films were observed by optical microscopy and by scanning electron microscopy (SEM). Raman spectroscopy was used to identify the diamond phase. The adhesion of diamond films was evaluated by two methods. These were indentation and compression topple tests.[12] Fig. 2 shows a schematic drawing of the compression topple tests. The toppled bar with a mass of 25g is pasted onto the deposited film. The deposited films were peeled from the substrate by increasing

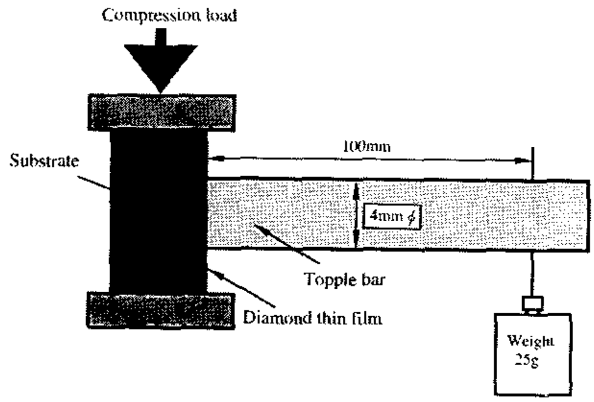

Fig. 2. Schematic drawing of compression topple test.

the compression load. The critical load for peeling was measured as a function of the film thickness.

3. Results and discussion

Fig. 3 shows SEM micrographs of the diamond films on Si_3N_4, SiC, WC, TiC and Al_2O_3 with polished surfaces. The CH_4 concentration during deposition was fixed at 3%. The deposits show a little difference in morphology depending on the substrate material, but all show highly facetted grains.

Fig. 4 show a SEM micrograph of the surface of the deposit on a WC substrate under 10%CH_4 concentration. It is seen that the deposit has a finer grain structure than that of 3%CH_4 and does not show the facetted grain shapes. A similar appearance was observed for the films on other substrates at high CH_4 concentration.

Fig. 5 shows the Raman spectra of the films on WC substrates deposited under various CH_4 concentrations. For concentrations from 3% to 5%, a sharp peak at 1334cm^{-1}, which is characteristic of diamond[2] is observed. The spectra for the films deposited with the CH_4 concentration from 7 to 10% have broad peaks at around 1560cm^{-1}. The broad peaks may arise from graphitic carbon, which has finer microstructure than diamond films. From these results (SEM micrographs and Raman spectra), it was found that the optimum CH_4 concentration for the diamond film formation is less than 5%. The CH_4 concentration was fixed at 3% for all subsequent depositions.

Fig. 6 shows the optical micrographs of diamond films of about 5μm in thickness. The diamond films on Si_3N_4 and WC are essentially homogeneous, with free of peeling, while the films on the TiC and Al_2O_3 have not adhered well to the substrates. Fig. 7 shows the appearance of the films about 12μm in thickness on WC and Si_3N_4 substrates. The film on WC was partly peeled off,

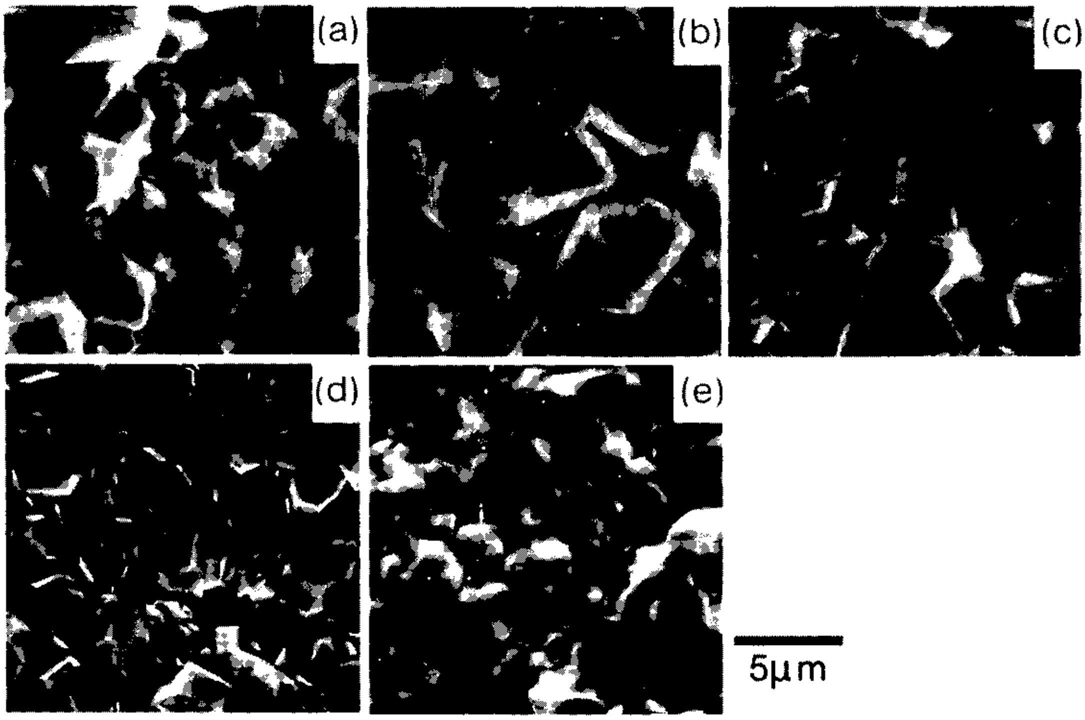

Fig. 3. SEM micrographs of diamond film surface deposited on ceramic substrates in H_2-3%CH_4: (a) Si_3N_4, (b) SiC, (c) WC, (d) TiC, (e) Al_2O_3.

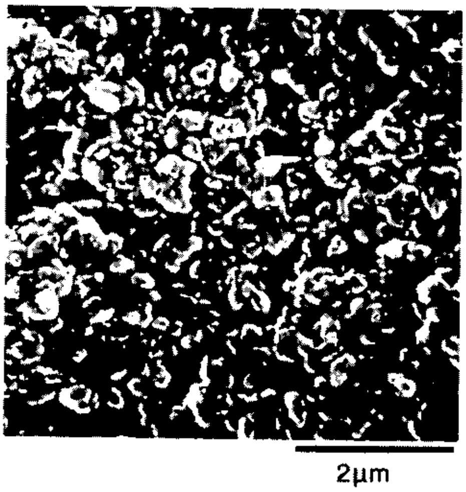

Fig. 4. SEM photographs of surface deposited on the WC substrate in H_2-10%CH_4.

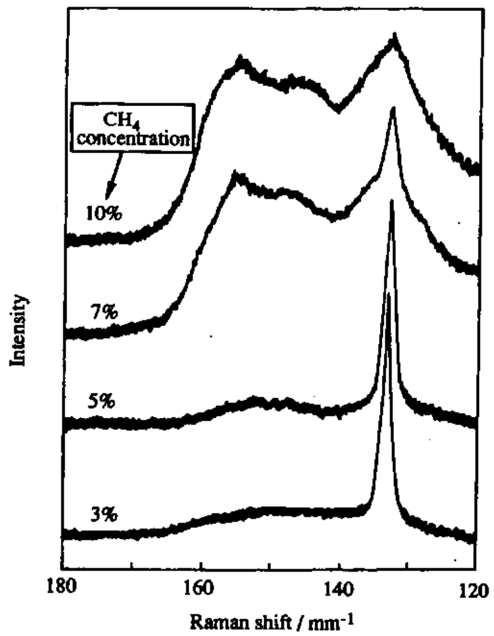

Fig. 5. Raman spectra of deposited films formed under various CH_4 concentrations.

but the film on the Si_3N_4 substrate was adhered.

The film peeling is believed to be due to the thermal stress, which is from the difference in contraction rates between the diamond films and substrates. The thermal expansion coefficients of diamond, Si_3N_4, WC, TiC and Al_2O_3 are 3.0, 3.3, 4.0, 8.0 and 8.0(10^{-6}/K), respectively.[13,14] The thermal stress, σ, of the films can be approximated by the following equation : $\sigma = (\rho_D - \rho_S) \times \Delta T \times E_D$, where ρ_D and ρ_S are the thermal expansion coefficients of diamond and substrate, respectively. ΔT is difference between at deposition and room temperature. E_D is the Young's modulus of diamond (1TPa).[13] The calculated values of σ for the films on WC and Si_3N_4 substrates are about -0.9 and -0.3GPa, respectively.

The residual stresses in the films were measured by means of an X-ray method. The stress in the films with 5µm thickness deposited on WC substrate was found to be about -0.9GPa, which agrees with the calculated

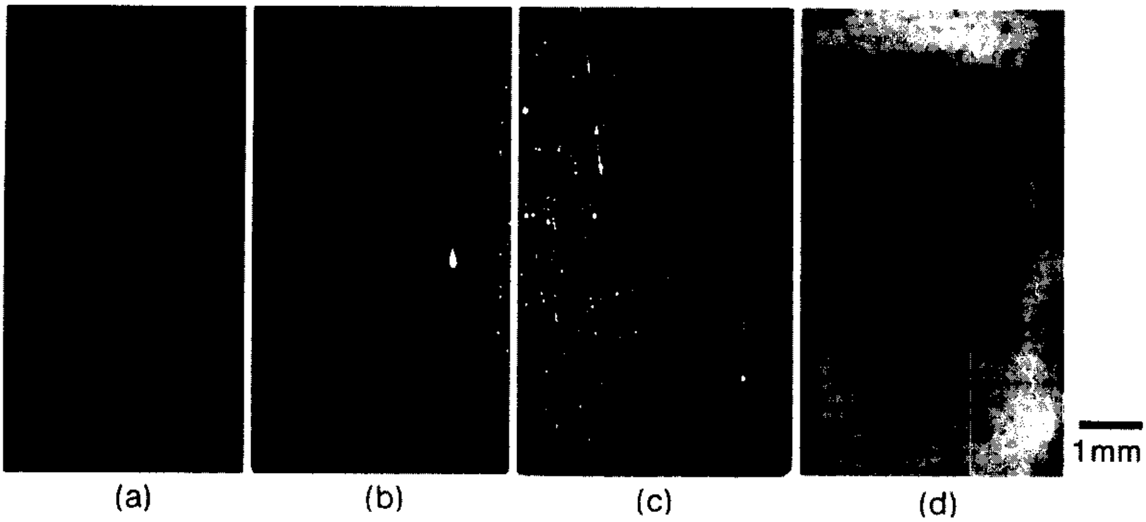

Fig. 6. Optical micrographs of diamond films about 5㎛ in thickness on ceramic substrate: (a) Si_3N_4, (b) WC, (c) TiC, (d) Al_2O_3.

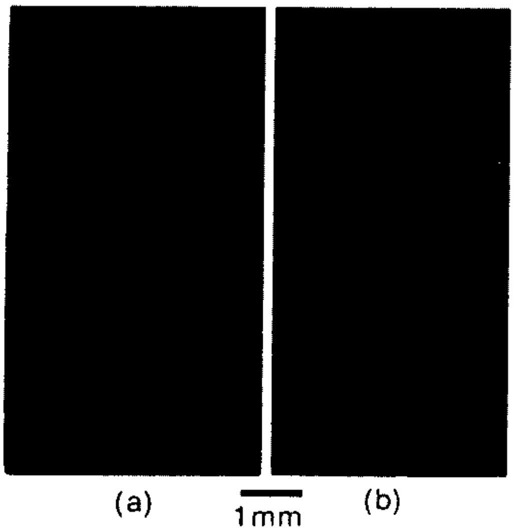

Fig. 7. Optical micrographs of diamond films about 12㎛ in thickness on (a) WC and (b) Si_3N_4 substrates.

value. The stress in the film on Si_3N_4 could not be measured exactly because it was too small.

Fig. 8 shows SEM images of the structure around indentation on diamond films of about 5 ㎛ thickness deposited on Si_3N_4, SiC and WC substrates. The surfaces of the substrates in Fig. 8(a-c) were polished and Fig. 8(d-f) were ground. For the polished surfaces, the film on Si_3N_4 substrate has faint cracks and good adhesion without separation around the indentation. The film on SiC substrate is similar to that on Si_3N_4, but a small degree of separation or bulging around the indentation is observed. The film on WC substrate with the polished surface shows a serious separation around the indentation. On the other hand, the films on the ground substrates all showed good adhesion and were free of separation and cracking around the indentations. It is, therefore, noted that the surface roughness introduced by

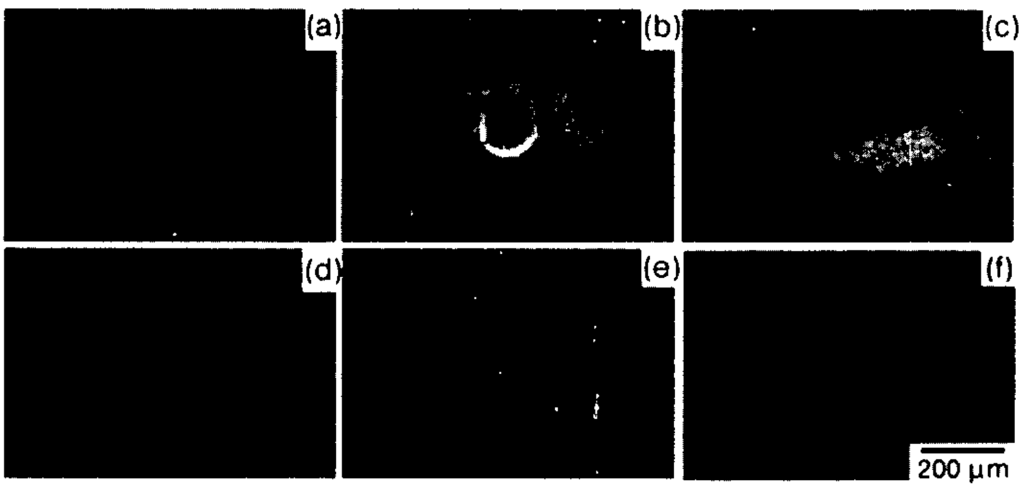

Fig. 8. SEM structures around an indentation on diamond film 5㎛ thickness. Load is 20kgf: (a, d) Si_3N_4, (b, e) SiC, (c, f) WC, (a, b, c) polished surface, (d, e, f) ground surface.

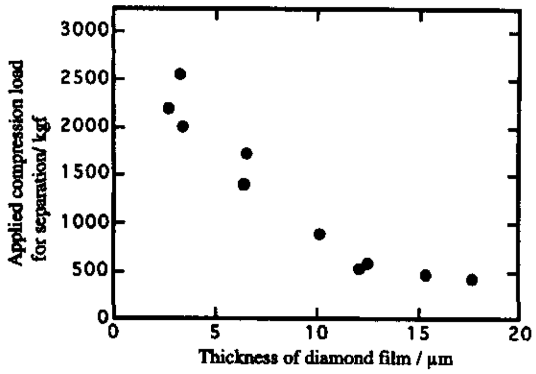

Fig. 9. Adhesion evaluation of diamond film deposited on WC-6 %Co substrate with a ground surface by the compression topple test.

Fig. 10. Interlocking between diamond film and substrate.

grinding improved adhesion.

Fig. 9 shows compression topple test results for diamond films deposited on a WC with a ground surface. The compression load for separation of the films is shown as a function of film thickness. It is seen that the applied load for separation decreases with increasing film thickness. Therefore, the thickness of the film is an important factor for adhesion of films to substrates.

From these results, it is found that there are several important factors for improving the adhesion of diamond film on ceramic substrates. Firstly, it is necessary to chose suitable substrate materials considering the thermal expansion coefficient. Ceramic substrates with a low thermal expansion coefficient such as Si_3N_4, SiC and WC are good candidates in this regard. Secondly, substrates with rough surfaces provide better adhesion owing to an interlocking effect between film and substrate (see Fig. 10). Thirdly, the film thickness needs to be controlled to optimize the adhesion strength of the diamond film. Films thicker than about 10㎛ might be unstable even when other factors are optimized.

4. Conclusions

Diamond films were deposited on various ceramic substrates by the CVD using Ta(TaC) filament, and followed by an evaluation of the adhesion of the films. Followings are the summary of the experimental results.

1) The morphology of the diamond thin films on Si_3N_4, SiC, WC, TiC and Al_2O_3 are slightly different, but they commonly show well facetted grains which present a characteristic of diamond synthesized by the CVD process.

2) The diamond thin film deposited on ceramic substrate tended to flake during cooling after deposition due to thermal stress. Films on TiC and Al_2O_3 substrates flaked much more easily than those on WC, and the film on Si_3N_4 did not flak at all, even up to 12㎛ thickness.

3) The indentation test showed surface roughness caused by grinding was very effective for good adhesion of diamond thin film to substrate.

4) The applied load for separation of films during the compression topple tests decreases with increasing film thickness.

5) Thermal stress, surface roughness of substrates and film thickness are of great importance to have good adhesion of the diamond film deposited on ceramic substrate.

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