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Effect of Laser Surface Modification of Cemented Carbide Substrates on the Adhesion of Diamond Films

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Cemented Carbide기판의 레이저 표면 개질이 다이아몬드 박막의 접합력에 미치는 영향

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Abstract A novel method for improving the adhesion of diamond films on cemented carbide tool inserts has been investigated. This method is based on the formation of a compositionally graded interface by developing a microrough surface structure using a pulsed laser process. Residual stresses of diamond films deposited on laser modified cemented carbides were measured as a function of substrate roughness using micro-Raman spectroscopy. The surface morphology and roughness of diamond films and cemented carbides were also investigated at different laser modification conditions. It was found that the increasing interface roughness reduced the average residual stress of diamond films, resulting in improved adhesion of diamond films on cemented carbides.

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***Key words**: Diamond Films, Cemented Carbide, Adhesion, Surface Modification, Excimer Laser, CVD, Residual Stress, Microrough Surface, Raman Spectroscopy*

1. Introduction

Diamond-coated (DC) tools are expected to be one of the most important applications of CVD diamond because of its outstanding properties for tooling such as highest hardness, compressive strength, thermal conductivity, and chemical inertness combined with a low coefficient of friction[1,2]. DC tools are very useful for machining nonferrous alloys, composites, wood, rocks, etc.[3]. However the chemical reaction of diamond with ferrous materials makes it an unsuitable coating for ferrous based machining operations.

The development of DC tools has become very attractive for machining highly abrasive aluminum-silicon alloys in the automobile industry. However, there is a serious problem in adhesion of diamond films to cemented carbide substrate inserts. The reasons for the poor adhesion are i) large thermal stress at the interface of diamond and cemented carbide resulting from large thermal expansion mismatch, and ii) the interaction between carbon from incoming hydrocarbon gas and cobalt binder at the diamond deposition temperature[4-7]. Cobalt causes carbon dissolution and diffusion into the cemented carbide and catalyzes the diamond growth species into graphite. This graphite film weakens the bonding between diamond films and cemented carbide substrates.

Several approaches have been reported to improve the adhesion of diamond films. One approach is the use of etching agents such as HNO_3, HCl, $FeCl_3$, and H_2SO_4[8-11] to remove cobalt on the carbide surface. Another is the deposition of interlayers such as α-C, W, Ti, Mo, TiC, TiN, Si_3N_4, etc.[12,13] to form a diffusion barrier and to reduce residual stresses at the diamond-carbide interface. Others are plasma treatment for recrystallization, leading to WC grain size refinement[14] or heat treatment for WC grain coarsening[15].

In our study, a novel method to improve the adhesion of diamond films on cemented carbides has been investigated. This method involves the creation of micro-rough structures on cemented carbide surfaces using a KrF pulsed laser process prior to diamond coating as reported earlier[16-18]. This surface modification treatment resulted in excellent adherence by the formation of a compositionally graded mechanical interface. Residual stress was measured across the cross-section of diamond films as a function of interface roughness. The relationship between residual stress and roughness is discussed in this paper.

2. Experimental

Cemented carbide (WC-6%Co) tool materials were used as substrates for diamond coating. The surfaces of the cutting tool inserts were modified using a repetitive pulsed laser irradiation process ($\lambda = 248$ nm, $J = 25$ ns). The number of laser pulses was varied from 40 to 120 at 2 J/cm^2 to control the surface roughness. The line beam (30 mm × 0.2 mm) of a laser scanned the samples which were mounted on a x-y translation stage. The error in energy density measurement was within ±10%. The controlled laser irradiation resul-ted in the formation of a smooth undulating hill-valley structure on the substrate surface. Following surface modification, the tool inserts were etched by Mura-kami's reagent ($K_3Fe(CN)_6$:NaOH:H_2O=1:1:10 by weight) for two minutes to remove non-stoichiometric WC and provide further microroughness. This was followed by nitric acid treatment for one hour to re-move cobalt binder and thus to prevent graphite formation at the diamond-carbide interface.

After surface pretreatments, the carbide inserts were ultrasonically scratched and seeded in a diamond suspension for an hour to enhance diamond nucleation. Diamond was deposited by the hot filament chemical

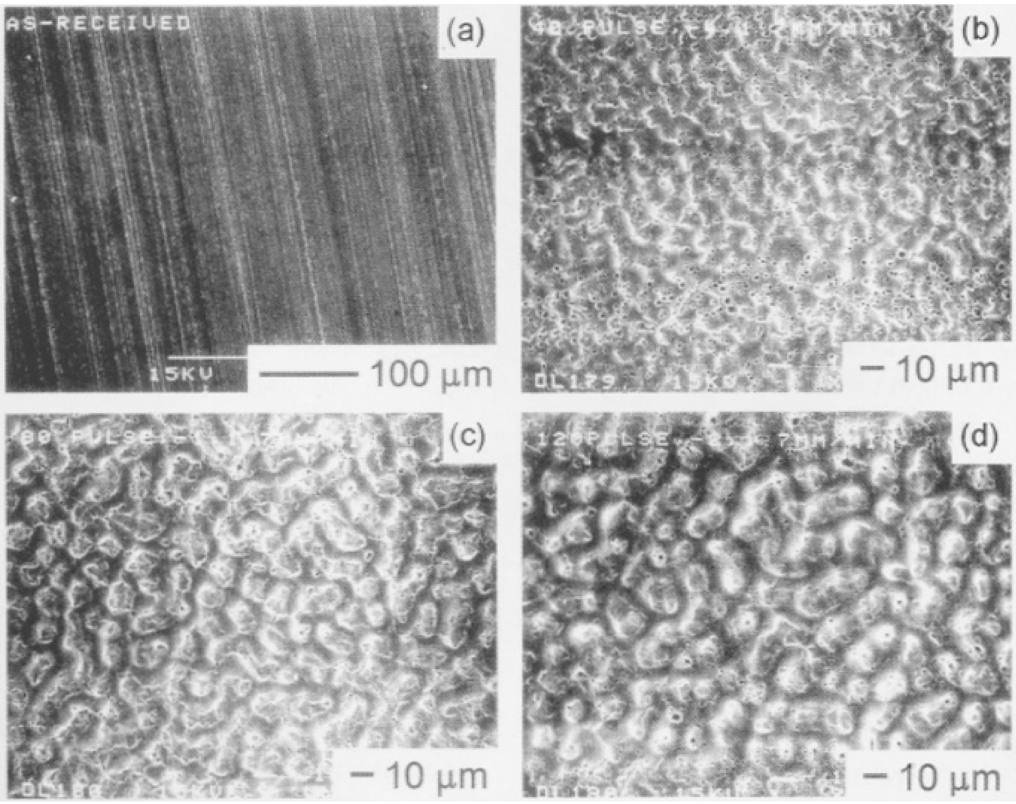

Fig. 1. Surface morphology of cemented carbide surfaces modified with (a) 0 (as-received), (b) 40, (c) 80, and (d) 120 pulses at 2 J/cm^2 using laser.

vapor deposition system (HFCVD) process using 1% methane in hydrogen at a total pressure of 20 torr with a flow rate of 200 sccm for 20 hrs. Substrate and filament temperatures were maintained at 960°C and 2100°C, respectively. The surface roughness of the tool inserts was measured with a Dektak surface profilometer having a mechanical stylus. Indentation was carried out to qualitatively analyze diamond adhesion to the substrate. Residual stresses of diamond films deposited on laser modified cemented carbide substrates were measured using micro-Raman spectroscopy (Jobin Yvon U1000 double spectrometer). Samples were excited by a coherent Ar ion laser (λ =514.5 nm) operated at 200 mW. The Raman spectrometer has a spectral resolution of 1 cm^{-1} and collected data through a CCD (charge coupled device) detector. For the measurement of stress distribution around the interface between diamond films and cemented carbide substrates, the laser spot size was set at ~4 μm using a 100X objective lens.

3. Results and Discussion

Fig. 1 shows the surface morphology of cemented carbides modified with a pulsed laser as a function of number of laser pulses irradiated at an energy density of 2 J/cm^2 which corresponds to values slightly above the ablation threshold energy. Fig. 1(a) shows the surface of an as-received cemented carbide. It has grinding streaks caused by final finishing. Upon irradiation with 40 laser pulses (Fig. 1(b)), a periodic micro-rough structure begins to form with a number of small pits due to preferential ablation of cobalt at WC particle boundaries. Computer simulation using SLIM (Simulation of Laser Interaction with Materials)[18] previously showed that surface temperatures when irradiated with 2 J/cm^2 reached approximately the boiling temperature (3143 K) of cobalt and the melting temperature (2993 K) of WC[19]. With more laser pulses (Fig. 1(d)), the micro-rough surface features developed periodicity increasing to ~20 μm. Once micro-rough structures are formed, the roughness increased rapidly with increasing number of laser pulses. The rapid increase in roughness is due to the difference in laser energy density between peak and valley regions of micro-rough features. Whereas incident laser beams are mostly scattered at peak regions due to geometrical effects, the reflected beams are collected at valley regions, resulting in higher energy density at the valley regions.

In order to investigate residual stress of diamond films deposited on laser modified cemented carbide substrates as a function of surface roughness, cemented carbides were modified at 2 J/cm^2 with different numbers of pulses (40, 80, and 120), etched with nitric acid for 30 minutes to remove cobalt on the surface, heat-treated for 5 hrs, then sonicated in diamond colloid, and coated with diamond for 20 hrs as shown in Fig. 2. The diamond film thickness was 15 μm. As the roughness of laser modified cemented carbide substrates was increased, the roughness of diamond films also increased. With 120 pulses (Fig. 2(g)), the diamond film possessed a cauliflower shape.

The residual stresses were measured using micro-Raman spectroscopy. Residual stress was evaluated from the shift of the Raman diamond peak with respect to the natural diamond value at 1332 cm^{-1}. Ager *et al.*[20] derived the relationship of Raman peak shift to the amount of residual stress. Rats *et al.*[21] also showed that the use of the average stress gage factor (-0.384 GPa/cm^{-1}) for the principal peak (doublet phonon) matched quite well with experimental results in order to calculate the residual stress in diamond. In this study, the same residual stress gauge factor for the doublet phonon was used to calculate the total residual stress as a function of diamond peak shift.

$$\sigma\,[GPa] = -0.384\Delta\nu = -0.384(\nu - \nu_0)[cm^{-1}]$$

where ν_0 and ν are the Raman peak position of the unstressed and stressed diamond, respectively.

Fig. 3 shows the surface residual stress converted from the shift of diamond Raman peak and full width at half maximum (FWHM) of the diamond Raman peak. As the surface roughness increases, the protrusions of the diamond film are larger along with the substrate

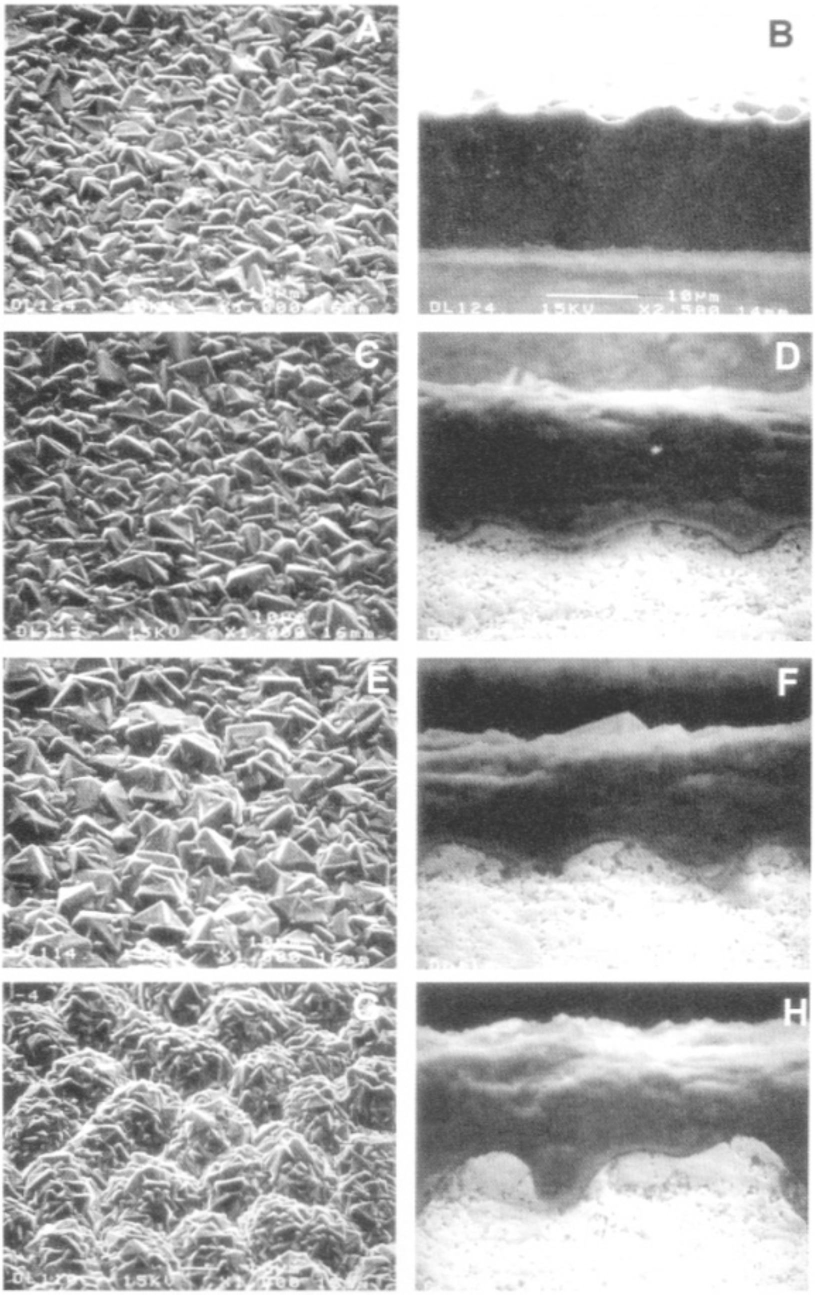

Fig. 2. SEM images of diamond films deposited on cemented carbides which were modified with (a) 0, (c) 40, (e) 80 and (g) 120 pulses at 2 J/cm^2.(b), (d), (f) and (h) are the cross-sections of (a), (c), (e) and (g) respectively.

roughness as shown in Fig. 2. Because of the large protrusions of the diamond film, residual stresses at peak regions (protrusions) on the diamond surface are strongly relaxed compared to those at valley regions. Ralchenko *et al.*[22] observed the same relaxation of stress. Although changes in residual stresses at valley regions on the diamond surface were not large, residual surface stress at valley regions decreased slightly with

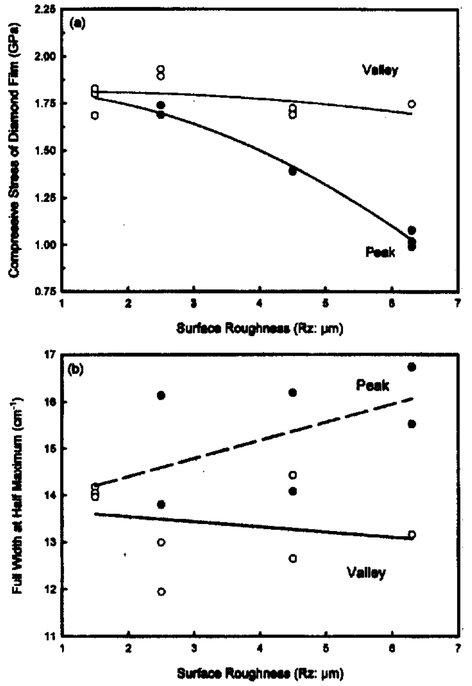

Fig. 3. (a) Surface residual stress changes on diamond films deposited on laser-modified substrates and (b) full width at half maximum (FWHM) of diamond Raman peak on the diamond film surface as a function of roughness using micro-Raman spectroscopy.

increasing roughness. In Fig. 3(b), FWHM of the diamond Raman peak at peak regions of a diamond film is large compared to that of an unstressed natural diamond Raman peak. It increases with increasing surface roughness due to the superposition of different stress states in the films. On the other hand, changes in FWHM of the Raman diamond peak at valley regions of a diamond film were small.

Fig. 4 shows the cross-sectional stress distribution from the diamond-substrate interface to the diamond free surface inside diamond films. An argon ion laser beam possessing ~4 μm spot size was used for the Raman measurement. Measurements were performed across the contiguous peak and valley regions. For an unmodified sample (Fig. 4(a)), the compressive residual stress was the highest at the interface (~1.2 GPa), and decreased slightly towards the free surface. In case of diamond films deposited on laser modified samples having 2.5 μm roughness (Fig. 4(b)), the difference in residual stress between peak and valley regions at the diamond-cemented carbide interface was surprisingly large. Residual stress at peak regions of the interface

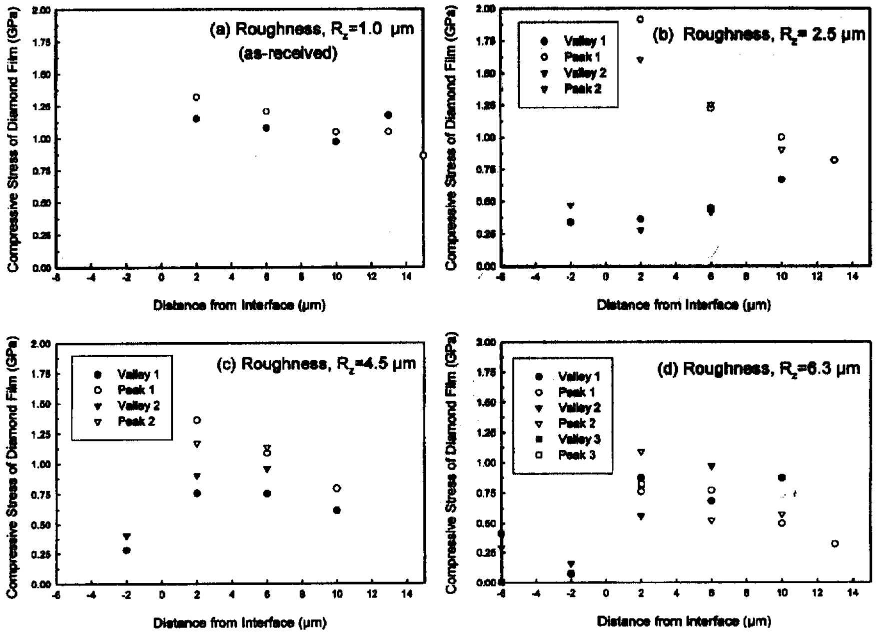

Fig. 4. Stress changes from the diamond-cemented carbide interface to the diamond films surface using micro spectroscopy: (a) interface roughness, Rz=1.0 μm (as-received), (b) Rz=2.5 μm, (c) Rz=4.5 μm, and (d) Rz=6.3 μm.

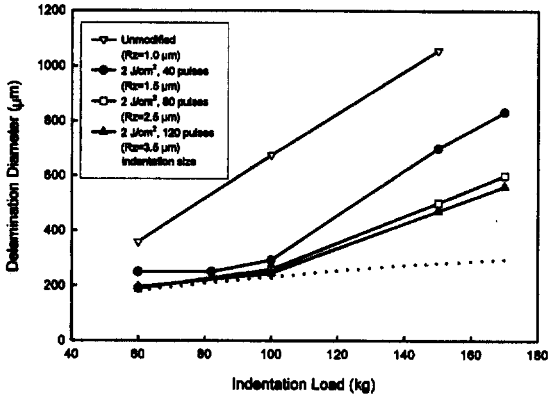

Fig. 5. Rockwell indentation adhesion test for diamond coated cemented carbides having different roughness.

was even larger than the compressive stress observed in an unmodified sample (~1.2 GP_a). It was found that residual stress in the films was concentrated at the peak interface. Raman measurements showed lower residual stress near the valley region compared to the residual stress near the peak region. The decrease in residual stress near peak regions and increase in residual stress near valley regions were shown as the measurements were conducted toward the free surface of diamond films, and the two stresses became almost the same at the free surface. With an increase in interface roughness to 4.5 μm, the residual stress at a valley interface was very small. The compressive residual stresses did not affect the valley regions due to geometrical blocking by peak features at the diamond-substrate interface. The difference in residual stress between peak and valley regions at a distance of 2 μm from the interface was small compared to the stresses measured in Fig. 4(b). In case of diamond films (Fig. 4(d)) with high interfacial roughness (~6.3 μm), the residual stress at the valley was found to be negligible. Reduced compressive stresses at the interface are expected to improve adhesion of diamond films. From the observation of whole stress distribution, the average residual stress decreases with increasing interface roughness of the diamond-substrate.

Fig. 5 shows the curves of delamination diameter of diamond films as a function of indentation load using a Rockwell indentation adhesion test[23]. The diamond film deposited on a cemented carbide unmodified with laser having a low interface roughness showed considerable delamination even at a low indentation load of 60 kg. However, the laser modified cemented carbides still did not exhibit delamination below 100 kg load. This figure shows that with increasing interface roughness, the indentation load to initiate and propagate a crack was found to decrease. These results clearly show that higher interface roughness resulted in better adhesion of diamond films on cemented carbide.

4. Conclusion

A novel method for improving the adhesion of diamond films on cemented carbide tool inserts has been investigated. Residual stresses of diamond films were reduced with increasing substrate roughness of the laser-modified interface. The reduced residual stresses enhanced the adhesion of diamond films deposited on cemented carbide substrates.

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