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Microstructural control of boundary region between CVD diamond film and cemented carbide substrate

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Effects of the composition, texture and pretreatment of cemented carbide substrates on the microstructure of the boundary region between CVD diamond film and the substrate were investigated using a microwave plasma CVD in the $CO-H_2$ system. Optimum CVD conditions for a uniform coating on to the edge part of cutting insert were: microwave power, 550 W; total pressure, 30 Torr; total flow rate, 200 ml/min; CO concentration, 5–20 vol %; treatment time, 3–5 h. An adherent and tough diamond coating was prepared by initial coating at lower CO concentrations and by subsequent coating at higher CO concentrations. A cemented carbide substrate in the binary WC–Co system which comprised fine-grained tungsten carbide and low content of cobalt was suited for preparation of adherent diamond coating. De-cobaltization pretreatment of the substrate surface in acid solution followed by an ultrasonic microflawing treatment enhanced the nucleation density and adherence of diamond film to the substrate. The rotation of substrate was found to be effective for increasing the uniformity and decreasing the grain size of diamond film.

1. Introduction

CVD diamond coating has aroused intense interest in its application to precise cutting tools for non-ferrous work. However, the toughness and adherence of diamond film have been too weak to attain a long-lived cutting performance, which limits its extensive application to cutting tools for high Si–Al alloys. One of the major reasons for weak adherence is thermal stress due to the difference in the thermal expansion coefficients of diamond and the substrate material. Control of the microstructure of the diamond film–substrate interface is important [1–5] to decrease the thermal stress at the interface, which can be absorbed by the grain boundaries in both diamond film and substrate. Few reports have been published, however, concerning basic and detailed research on the relation between the microstructure of the boundary region and the adherence of diamond film for cemented carbide substrate [6–8], although many patents for improving the adherence of diamond films coated on tools have been applied for during the past decade.

We have previously reported the microflawing effects on the nucleation of diamond on cemented carbide substrate using CVD in the CH_4-H_2 system [9]. The nucleation density was increased remarkably by an ultrasonic microflawing pretreatment, with the resulting formation of a fine-grained microstructure of the grown diamond film. Further investigation is required, however, to enhance the adherence and toughness of the CVD diamond film. In this study, the effects of composition and texture of various cemented carbide substrates on the adherence and toughness of diamond film were investigated, as well as the effects of their surface pretreatments. In addition, CVD parameters in the $CO-H_2$ system were determined for the optimum diamond coating, especially on to the edge part of cutting tools.

2. Experimental procedure

The experimental apparatus used is described in a previous paper [9]. The $CO-H_2$ reactant system [10, 11] was employed to take account of a higher growth rate of diamond film, and for convenience in using a wide range of carbon source concentrations for diamond deposition. Optimum conditions of microwave power, total pressure and total flow rate in the CVD system were kept constant at 550 W, 30 Torr and 200 ml min^{-1}, respectively [10]. Various kinds of commercial cemented carbide substrates (typical size: triangular chip, 17 mm each side length, 4.6 mm thick) were used as a substrate and mounted on a quartz pedestal in the reactor. The substrate was pretreated in 1N-HNO_3 aqueous solution at 50 °C for 0–3 h in order to eliminate cobalt in the surface region of the substrate, after which the substrate surface was microflawed [9] for 30 min by dipping it in ethanol (50 ml) containing 1 g diamond powder (grain size; 0–0.25 μm) under an ultrasonic field (power, 200 W). Other etching pretreatments in the Murakami reagent (10% KOH + 10% $K_3Fe(CN)_6$ + 80% H_2O) or in O_2(10 vol %)–H_2 plasma stream were carried out. The effect of rotation of the substrate was examined by rotating the substrate pedestal by 0–20 r.p.m. The specimens before and after the CVD treatment were identified by X-ray diffraction and micro-Raman spectroscopy. The surface and polished cross section of the coated substrate were observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Effects of composition and texture of substrate

Figure 1 shows the influences of composition and texture of various cemented carbide substrates on the surface appearance of diamond film, where every

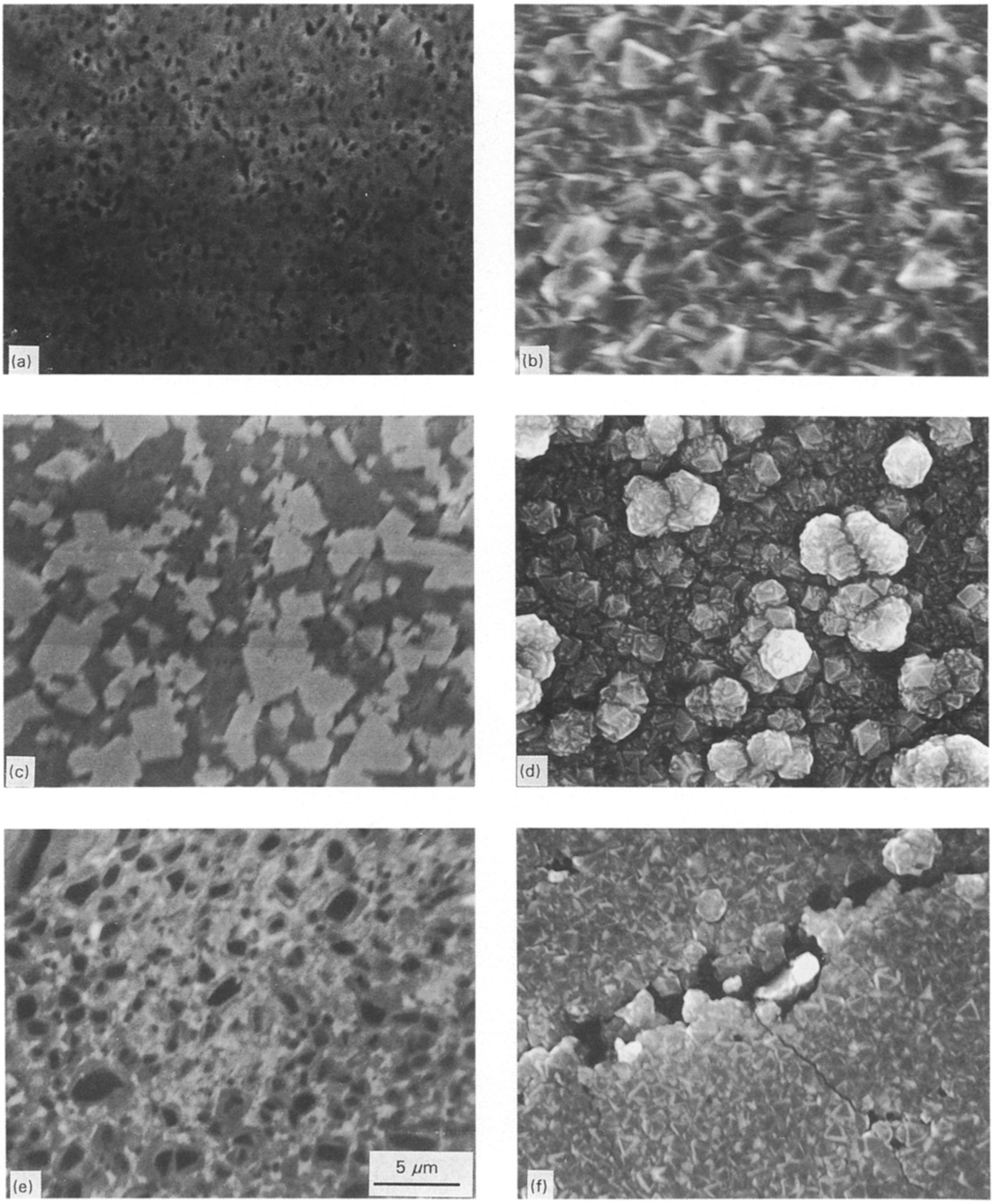


Figure 1 Scanning electron micrographs of the specimen surfaces before and after CVD treatment. CO concentration, 5 vol %. Substrate: (a, b) WC–Co; (c, d) WC–TiC–Co; (e, f) TiC–Ni. (a, c, e) Before CVD treatment; (b, d, f) after CVD treatment.

substrate surface was microflawed for 30 min in an ultrasonic field and CO concentration was kept constant at 5 vol %. A fine-grained and adherent diamond film was prepared using a binary WC–Co substrate which comprised fine WC grains and low Co content (nominal content, 4–7 wt %). On the other hand, coarse diamond grains were observed where a ternary WC–TiC–Co substrate was used, comprising coarse WC grains and a higher Co content (nominal content, 5–10 wt %) with additional content of 5–15% TiC, which led to an occasional peeling-off of the film from the substrate. An analogous tendency was confirmed using WC–TaC–Co or WC–TiC–TaC–Co substrate. When a typical cermet material in the TiC–Ni system was used as a substrate, the deposited film was easily peeled off and many cracks were found on the film surface (see Fig. 1f). It can be seen from these data that a WC–Co substrate with fine-grained WC grains and low Co content is desirable for adherent diamond coating on a cemented carbide substrate, as an increased nucleation density due to this binary substrate [9] helps the grain boundary to absorb the thermal stress at the film–substrate interface. It is also suggested that the coexistence of TiC or TaC, with thermal expansion coefficients higher than WC, disturbs the adherence of diamond film, because an average thermal stress at the interface increases in the presence of TiC or TaC. Considering the above results, only the binary WC–Co substrate was used in the following experiments.

3.2. Effects of CO concentration

Figure 2 shows the dependence of CO concentration on the average growth rate of deposited film near the edge part of the substrate. Other CVD parameters were kept constant as follows: microwave power, 550 W; total pressure, 30 Torr; total flow rate, 200 ml min^{-1}; treatment time, 5 h. The growth rate apparently increased with increasing CO concentration, attaining about 2 μm h^{-1} at a concentration of 25 vol % CO. The grain sizes of the deposits were found by SEM observation to increase with increasing CO concentration. At CO concentrations above 15 vol %, anhedral grains grew in the central portion of the substrate, whereas a dense film composed of fine-grained and euhedral grains was observed at the edge. Micro-Raman spectra of the peripheral portions of the substrates coated at CO concentrations of 5 and 25 vol % are shown in Fig. 3. The figure shows a diamond peak at 1333 cm^{-1} at 5 vol % CO, in addition to a broad peak (1450–1600 cm^{-1}) with low intensity of amorphous carbon observed at 25 vol % CO.

Figure 4 shows the fractured edge parts of the substrates which were coated at concentrations of 5 and 25 vol % CO. In the case of 5 vol % CO, the diamond film fractured through the grain boundary of the film, while at 25 vol % CO an intragranular fracture of the film occurred. This suggests that the intergranular bonding in diamond film obtained at 25 vol % CO is stronger than that obtained at 5 vol % CO, hence the toughness would be greater with increasing CO concentration. The scanning electron micrographs of the cross sections of these films are shown in Fig. 5. Although the growth rate is apparently lower for 5 vol % CO, the contact area of film to substrate is larger than for 25 vol % CO. Small voids can be seen between the film and substrate at 5 vol % CO, which would lead to a weak adherence of the

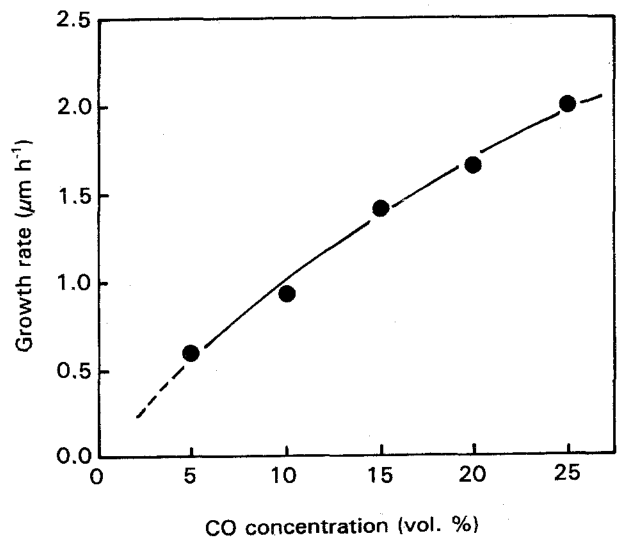


Figure 2 Growth rate plotted against CO concentration. Microwave power, 550 W; total pressure, 30 Torr; total flow rate, 200 ml min^{-1}; treatment time, 5 h.

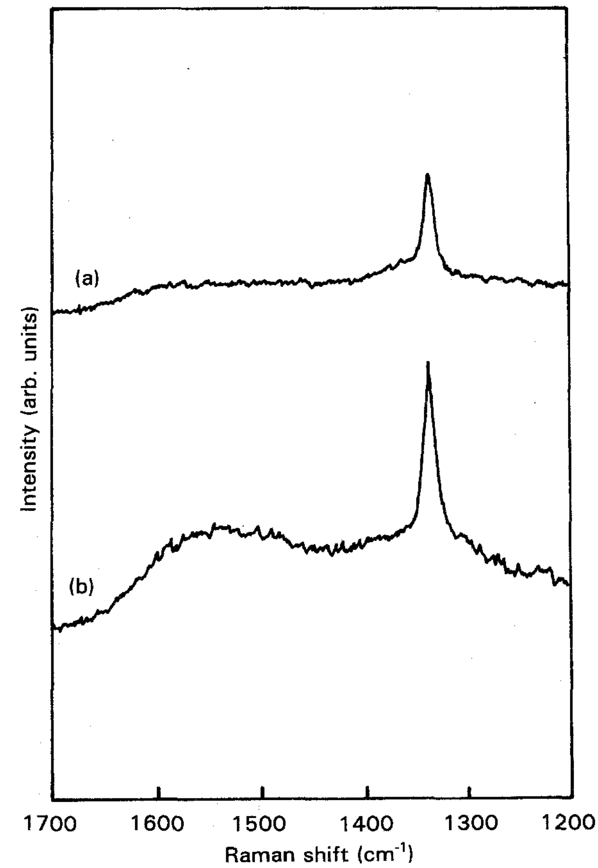


Figure 3 Micro-Raman spectra of peripheral portion of the substrate. CO concentration: (a) 5, (b) 25 vol %.

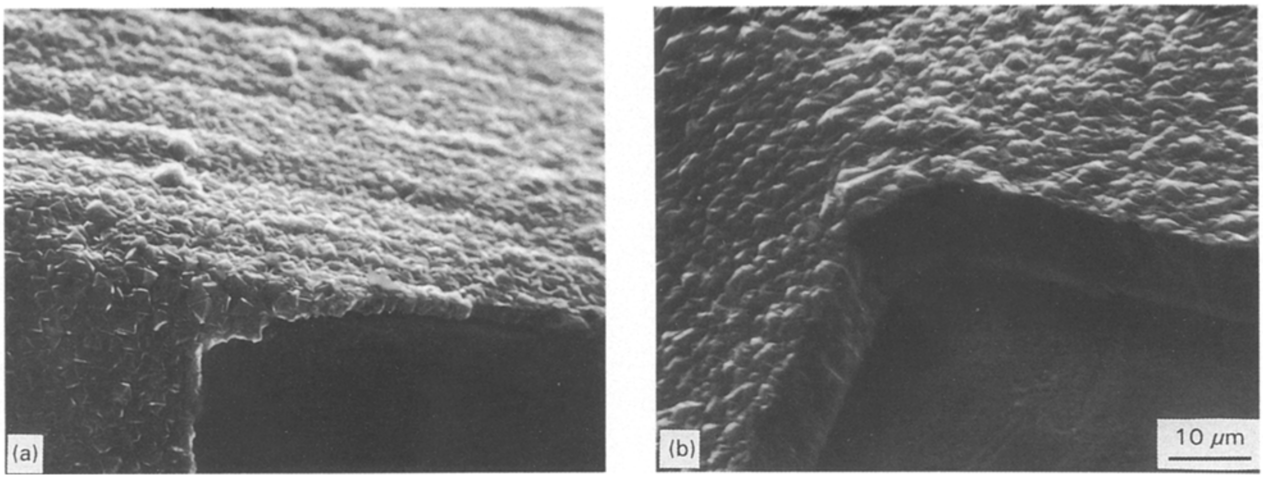


Figure 4 Scanning electron micrographs of the fractured edge parts. CO concentration: (a) 5, (b) 25 vol %.

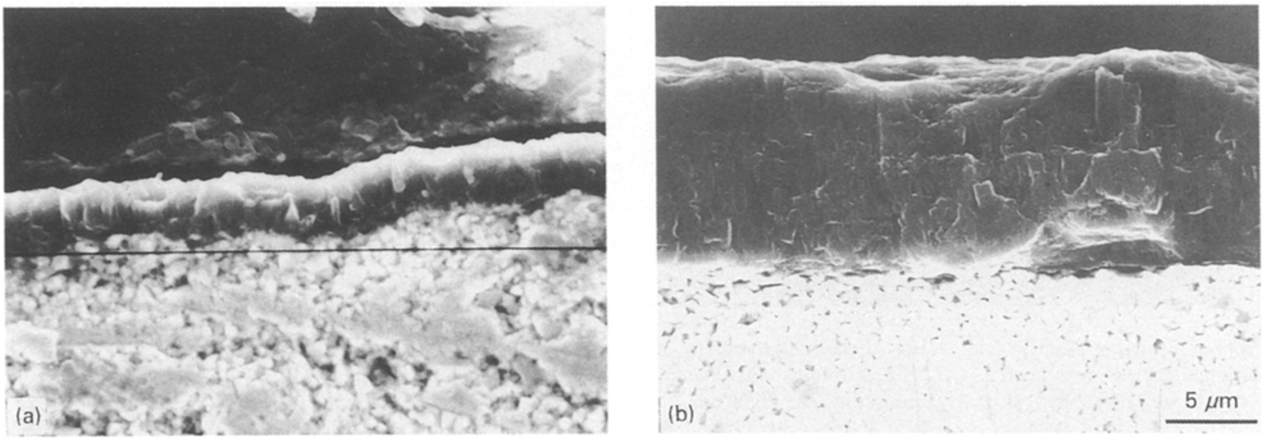


Figure 5 Scanning electron micrographs of the cross sections of films. CO concentration: (a) 5, (b) 25 vol %.

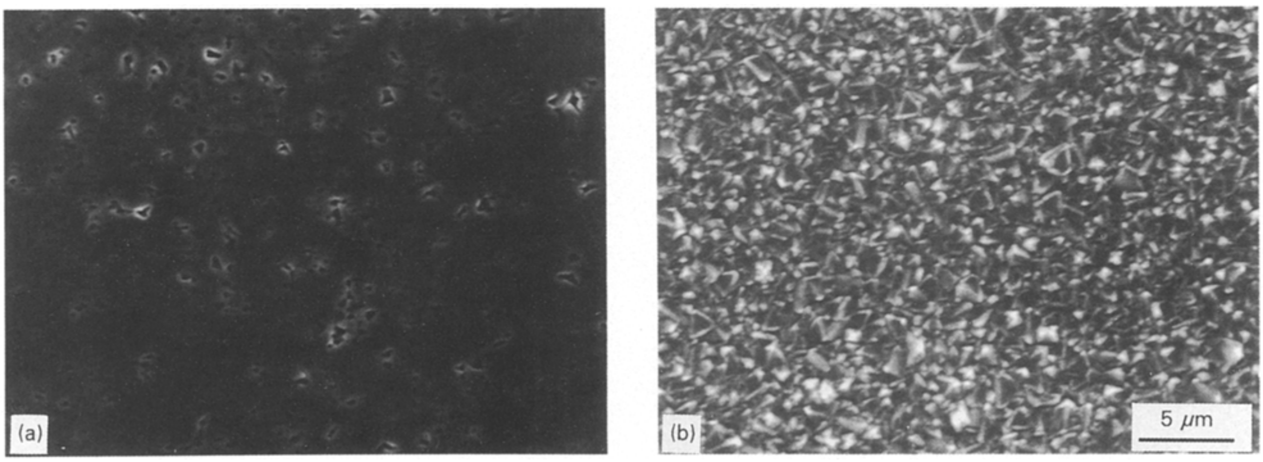


Figure 6 Scanning electron micrographs of the specimen surfaces before and after CVD treatment. CO concentration, 5 vol %. Substrate, acid-treated WC–Co. (a) Before CVD treatment; (b) after CVD treatment.

deposited film to the substrate. It is therefore likely that a schedule for introducing CO gas at a low concentration at the initial stage of CVD treatment, and subsequently at a high concentration at later stage, would be preferable for increasing the adherence and toughness of the film.

3.3. Effects of surface pretreatment of substrate

Figure 6 shows scanning electron micrographs of the specimen surfaces before and after CVD treatment, with the WC–Co substrate pretreated in 1N-HNO_3 aqueous solution at 50 °C for 3 h and then micro-

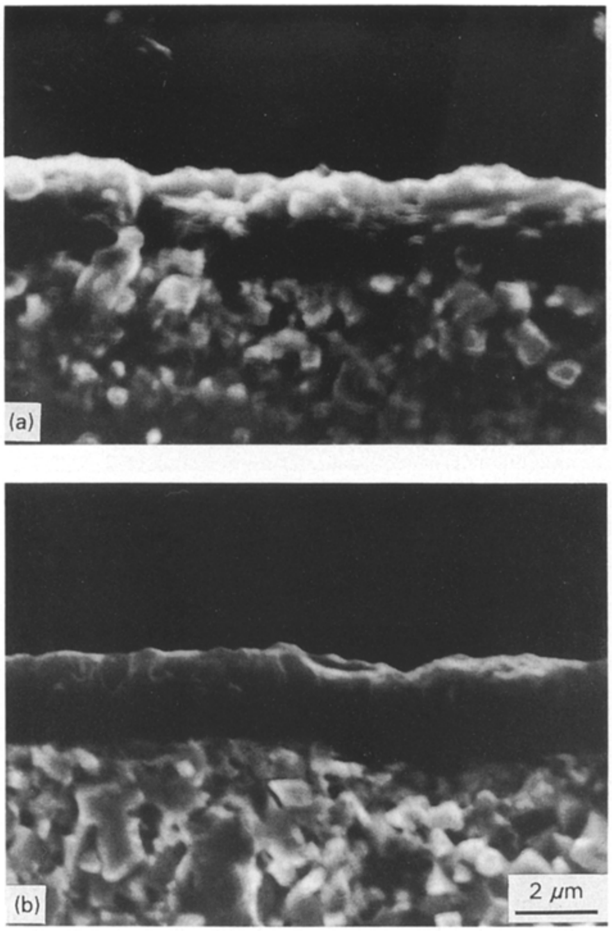


Figure 7 Scanning electron micrographs of the cross sections of diamond-coated edge parts. CO concentration, 5 vol % for 1 h → 20 vol % for 2 h. Acid pretreatment, (a) 0 min; (b) 30 min.

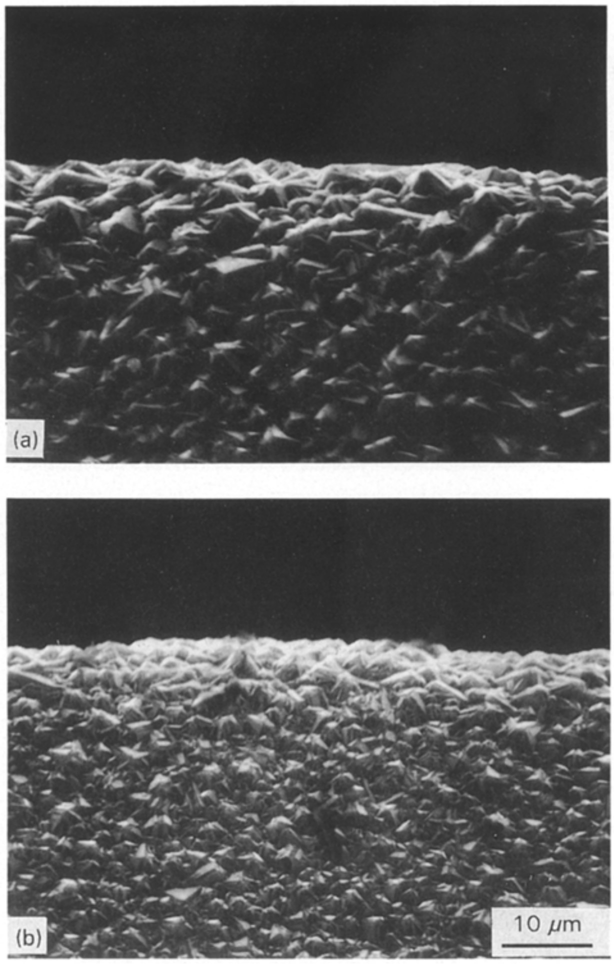


Figure 8 Scanning electron micrographs of the film surfaces. Rotation speed of substrate, (a) 0, (b) 15 r.p.m.

flawed for 30 min. The CVD conditions are the same as in Fig. 1. No peaks corresponding to cobalt or its related compounds were observed in the X-ray diffraction pattern of the specimen surface before the CVD treatment. Cobalt components in the surface region of the substrate would be corroded out, as can be observed from fine pits on the surface micrograph in Fig. 6a. Diamond grains grew more finely compared with the surface appearance of the same kind of substrate as that in Fig. 1b. The nucleation density increased due to the increase in the number of microflaws on WC grains [9], which have larger surface area than seen in WC grains where no acid treatment is applied.

Figure 7 shows scanning electron micrographs of cross sections of diamond-coated edge parts of the substrates, which are acid-pretreated for 0 and 30 min and then microflawed for 30 min. CO concentration was changed from 5 vol % for 1 h deposition to 25 vol % for 2 h deposition within the total treatment time of 3 h. Where there was no acid pretreatment, large diamond grains grew to form a coarse film microstructure and a rough surface, while a diamond film with a fine columnar microstructure was obtained by the acid pretreatment. The adherence between film and substrate was found to be enhanced with the increase in the contract area of WC grains (so-called

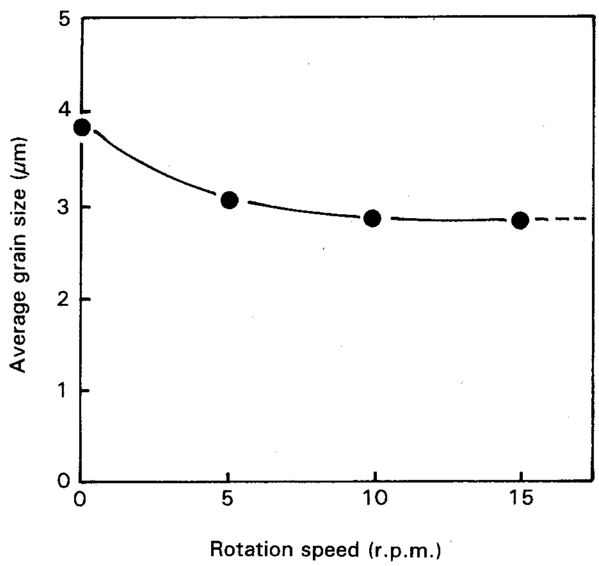
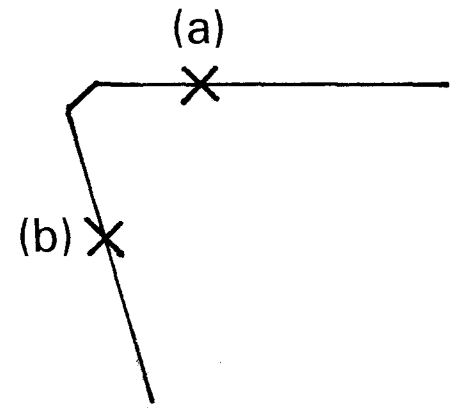
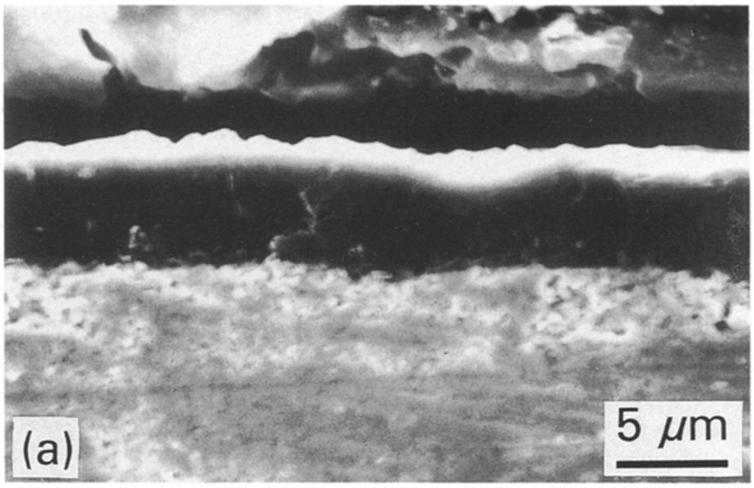


Figure 9 Average grain size plotted against rotation speed. CO concentration: 25 vol %.

"anchoring effect"). This effect appeared clearly even with acid treatment for 10 min, which would be enough to enhance the nucleation density and increase the adherence of the film.





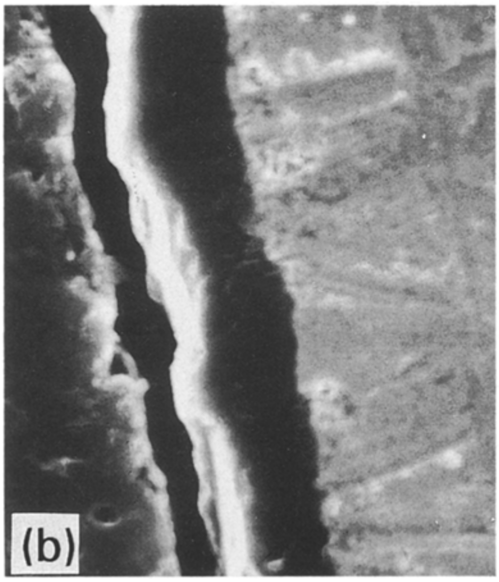


Figure 10 Scanning electron micrographs of the cross sections of the diamond-coated cutting insert. (a) Near cutting face, (b) near flank face.

The effects of other surface treatments, such as etching in Murakami reagent or vapour phase etching in O_2–H_2 plasma stream, were not necessarily effective for improving the adherence between diamond film and substrate.

3.4. Effects of substrate rotation

Figure 8 shows scanning electron micrographs of the film surfaces, where the specimen is rotated at 0 and 15 r.p.m. When rotation was applied, a fine-grained and uniform microstructure could be observed with no abnormal grain growth. A dense and fine columnar structure with good adherence was observed from the cross sectional view of the specimen. The influence of rotation speed on the average grain size of the film is shown in Fig. 9. The grain size became finer as the rotation speed increased. However, a marked effect on the decreasing grain size could not be observed with a rotation speed over 15 r.p.m. A rotation speed of 10–15 r.p.m. is sufficient to improve the film structure, due to the agitation effect of the surrounding gas atmosphere. Fig. 10 shows cross sections of the diamond-coated cutting insert, coated under the optimum conditions and pretreatments described above, i.e. acid treatment for 10 min followed by ultrasonic microflawing for 30 min and CVD treatment at CO concentrations of 5 vol % for 0.5 h and subsequently 20 vol % for 4 h, with substrate rotation applied at 10 r.p.m. Adherent and dense films were seen on both sides of the cutting face and flank face.

4. Conclusions

The effects of substrate composition, texture, pretreatment and CO concentration on the coating of adherent and tough diamond film on to the edge part of the substrate were elucidated in CVD in the CO–H_2 system on cemented carbide substrates.

1. WC–Co substrate which contained fine-grained WC, low cobalt content and no other carbide phase was suited for preparation of the adherent diamond coating.
2. Diamond films with good adherence and toughness were prepared by initial coating at lower CO concentrations and by subsequent coating at higher CO concentrations.
3. De-cobaltization pretreatment of the substrate was effective for the formation of adherent and fine-grained diamond film.
4. The rotation of the substrate was found to be effective for increasing the uniformity and decreasing the grain size of diamond film.

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