

Application of diamond films from CO–H₂ plasma to tool blade coating

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Diamond films were coated on WC–Co alloy tool blades using a microwave plasma of CO–H₂ mixed gas. Diamond film prepared at a CO concentration of 10% had good properties: Vickers hardness $\approx 8500 \text{ kg mm}^{-2}$ and adhesion force $\approx 1.7 \text{ kg mm}^{-2}$. No peel-off of the diamond film was observed after a cutting test of an Al–Si alloy rod at a cutting speed of 450 m min^{-1} for 0.5 h. It is thought that the high quality of the film originated from the selective etching of cobalt from the tool blade surface by CO–H₂ plasma.

1. Introduction

Diamond film has many potential applications in electronics, optics and tools for its good thermal conductivity, optical transparency and high hardness. Regarding the application to tool coating, a hard work-load and a long lifetime are expected.

The formation of diamond films from a CH₄–H₂ mixed gas plasma has been reported [1, 2]. The formation rate of this process, is however, rather slow: $\approx 1 \mu\text{m h}^{-1}$. The authors have reported previously that diamond can be produced at a high deposition rate of 3 to $7 \mu\text{m h}^{-1}$ by a microwave discharge in a CO–H₂ mixed gas [3]. A similar result was reported lately by Ito *et al.* [4]. Another advantage of using a CO–H₂ mixed gas plasma is the possibility of selective etching of cobalt from WC–Co alloy tool blades by excited CO produced in the plasma.

The applicability of the diamond film prepared by a microwave plasma of CO–H₂ gas to tool blade coating is studied here.

2. Experimental procedure

The microwave plasma deposition apparatus used in the present study was similar to that previously reported [5]. A WC–Co alloy (cobalt content 6 wt %) tool blade 15 mm \times 15 mm \times 5 mm height was used as a substrate. The substrate was set up at the centre of a silica glass reaction tube with inner diameter 40 mm and length 1000 mm. After evacuating the tube, a CO–H₂ mixed gas was introduced into the tube and microwaves were supplied to generate plasma in the mixed gas. Experimental conditions are summarized in Table I. The substrate was heated up to the pre-determined temperature by incident microwave power and a heater. The temperature was measured by a pyrometer.

The composition of the tool blade surface before and after etching was analysed by secondary ion mass

spectroscopy (SIMS). Products on the WC–Co tool blade were observed by scanning electron microscopy (SEM) and identified by low-angle X-ray diffractometry and Raman spectroscopy. Vickers hardness and adhesion force measurements were carried out to evaluate the films. A cutting test on Al–Si alloy rod was performed to evaluate the lifetime of the tool blades coated with diamond films.

3. Results and discussion

3.1. Etching pre-treatment

It is known that diamond does not grow on a substrate containing iron-group elements (iron, cobalt, nickel). The presence of cobalt in the blade surface hinders diamond growth and reduces the adhesion force of the diamond films to the tool blade. Selective etching of cobalt from WC–Co tool blades by an HCl solution has been proposed [6]. We have investigated the possibility of selective etching of cobalt using a plasma, since a dry process is more convenient than a wet process. Since Co(CO)₄ and Co(OH)₂ are known to be volatile compounds, a gas mixture CO + H₂ or H₂O + H₂ can be a candidate for a plasma etching gas. The plasma etching is carried out under the following conditions: etching gas composition, 2.5% CO + 97.5% H₂ or 2.5% H₂O + 97.5% H₂; microwave power, 0.6 kW; temperature, 800 °C; pressure, 1300 Pa; etching time, 20 min.

TABLE I Experimental conditions

Feedstock gas	5 to 50% CO + H ₂
Total gas flow rate	100 SCCM
Microwave	2.45 GHz, 0.3 to 0.7 kW
Pressure	20 to 40 torr
Substrate temperature	800 °C
Substrate	WC–6 wt % Co alloy

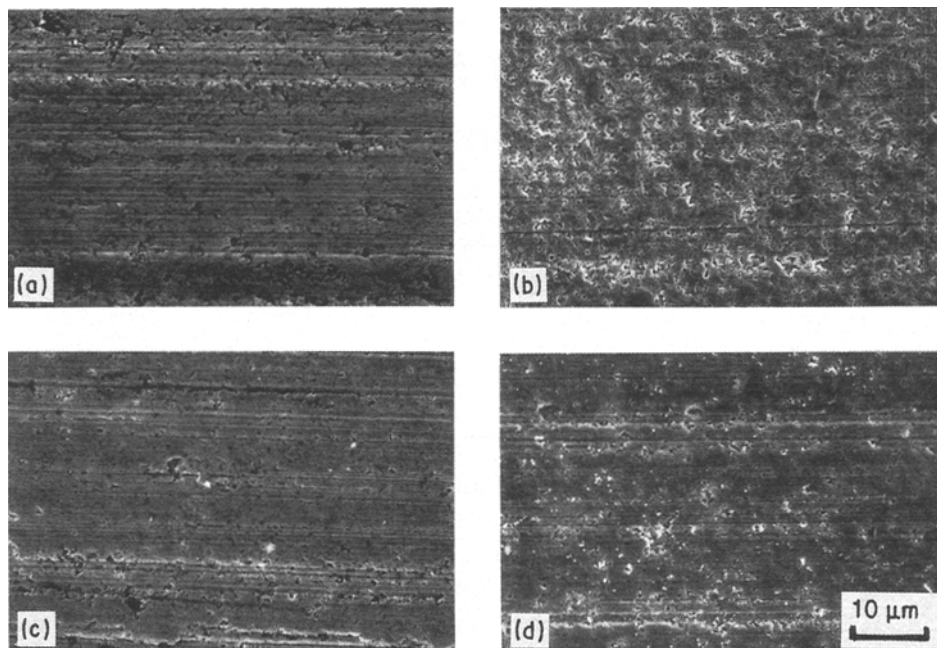


Figure 1 SEM photographs of etched tool blade surfaces: (a) non-etched, (b) etched with 2.5% H₂O + H₂ plasma, (c) etched with HCl, (d) etched with 2.5% CO + H₂ plasma.

Fig. 1 shows SEM photographs of blade surfaces before and after the etching. For the purpose of comparison, etching by an HCl solution was also carried out. Stripes seen on the blade surface without etching became obscure or disappeared in the tool blade etched by the CO-H₂, H₂O-H₂ plasma, and HCl solution. There is no doubt that the blade surface is etched by these gas plasmas or HCl solution. The etched surface was examined by SIMS analysis. Fig. 2 shows the relationship between the intensity of Co⁺ relative to Ar⁺ and the sputtering time. It is supposed that a sputtering time of 5 h corresponds to several tens of nanometres in depth. The relative intensity (Co⁺/Ar⁺) in the surface etched by H₂O-H₂ plasma is several times larger than that in the surface without

etching. On the other hand, the intensity in the surfaces etched by the CO-H₂ plasma or the HCl solution decreased to one-half to one-tenth compared with the surface without etching. These results indicate that cobalt is selectively removed from the tool blade in the CO-H₂ plasma or HCl solution etching.

Diamond deposition was carried out on non-etched and etched substrate. Diamond films obtained on the blades etched by HCl solution and H₂-CO plasma are shown in Fig. 3c and d, respectively. On the other hand, films composed of obscure ball-like particles and blocky particles were deposited on the blades without etching and etched by H₂O-H₂ plasma, respectively (Fig. 3a and b). The films and blocky particles contained graphite. It is concluded that the CO-H₂ plasma is a good method to remove cobalt selectively from WC-Co tool blade surfaces.

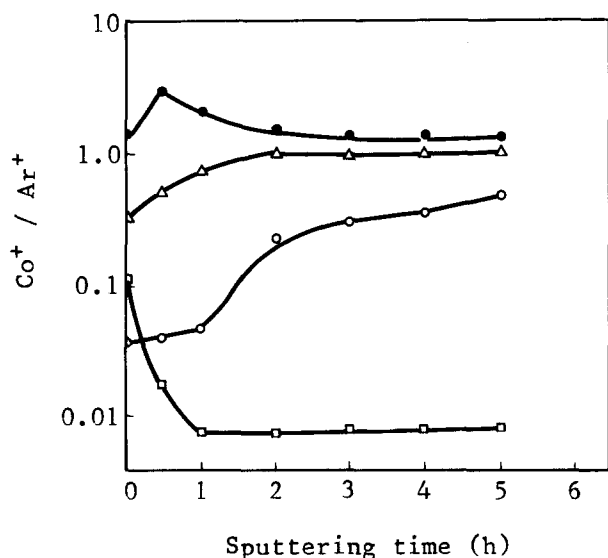


Figure 2 SIMS analysis of tool surfaces before and after etching (Ar⁺ ion gun, 2 kV, 10 mA). (Δ) Before etching; (●) 2.5% H₂O + H₂ plasma; (□) HCl; (○) 2.5% CO + H₂ plasma.

3.2. Properties of diamond films

Hardness and adhesion force are important factors determining the applicability of diamond films to tool blade coating. Fig. 4 shows the dependence of the Vickers hardness of diamond film on tool blades etched by CO-H₂ plasma on the CO concentration in the CO-H₂ mixture. The films prepared at CO-5% have a Vickers hardness of 10 000 kg mm⁻² which is almost equal to that of natural diamond. Increasing the CO concentration from 10 to 50%, the hardness is reduced to 4000 kg mm⁻², which is still twice as large as that of titanium nitride (2300 kg mm⁻²), the coating presently utilized. It is thought that the tendency may be ascribed to an increase of amorphous carbon content in the diamond film. It was found experimentally that the content of amorphous carbon in the film increased with the CO concentration in the feed gas. It is known that amorphous carbon has a smaller hardness than diamond.

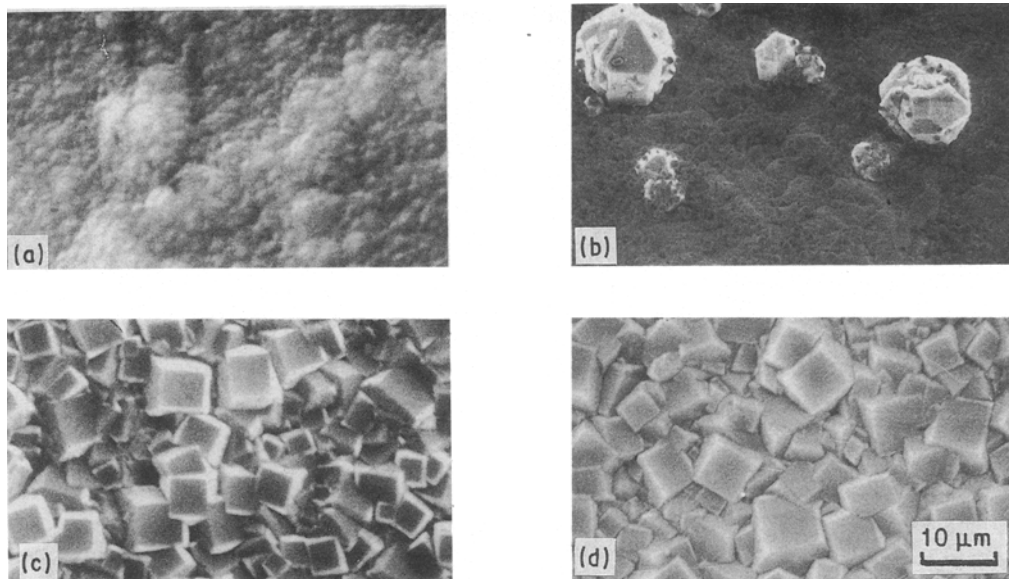


Figure 3 SEM photographs of deposits on non-etched and etched tool blades: (a) non-etched blade, (b) HCl-etched blade, (c) blade etched with 2.5% $\text{H}_2\text{O} + \text{H}_2$ plasma, (d) blade etched with 2.5% $\text{CO} + \text{H}_2$ plasma.

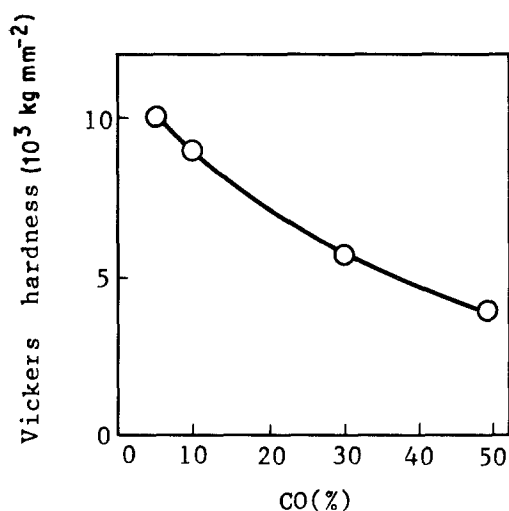


Figure 4 Dependence of adhesion force on CO concentration in diamond film deposition on tools.

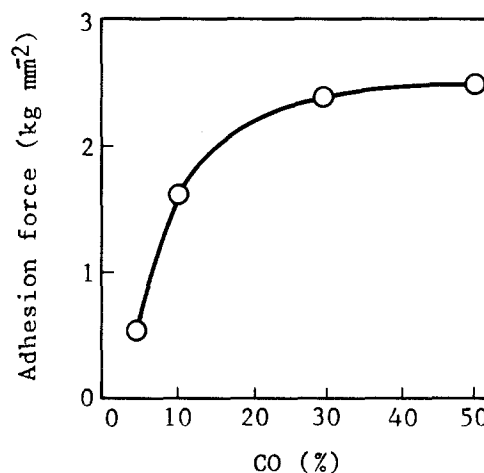


Figure 5 Dependence of Vickers hardness on CO concentration in diamond film deposition.

The adhesion force of the diamond films to tool blades measured by the drawing test is shown in Fig. 5. The force increases rapidly from 0.5 to 2.5 kg mm^{-2} with an increase of CO concentration from 5 to 50% in the feed gas.

Diamond film prepared at the CO concentration of 10% is considered to be suitable, judging from the results shown in Figs 4 and 5.

3.3. Cutting tests

Diamond films were coated in the CO-H_2 plasma at CO concentrations of 5 and 10% on a commercial WC-Co tool blade etched in the 2.5% CO-H_2 plasma. Fig. 6 shows SEM photographs of the blade surfaces coated with diamond films. The thickness of these films is estimated to be 3 to $4 \mu\text{m}$, based on the deposition rate and reaction time. Lifetimes of the diamond film coated on the tool blade were evaluated by cutting a 11.7% Al-Si alloy rod at a cutting speed of 450 m min^{-1} , depth of 0.5 mm and a rod feeding speed of 25 mm min^{-1} . These values are about 1.5 times as severe as the conventional cutting conditions

for TiN-coated tools. Fig. 7 shows optical micrographs of the blade after the cutting test of Al-Si alloy rod for 15 and 30 min. No peel-off is observed in any films after 15 min. After 30 min, the film coated in the 5% $\text{CO} + \text{H}_2$ gas is peeled off at the edge of the tool blade, but no peel-off is observed in the film coated in the 10% $\text{CO} + \text{H}_2$ gas. Fig. 8 shows optical micrographs of the rod surface after the cutting test. The brightness of the rod surface cut by the diamond film-coated tool is better than for that cut by the TiN-coated tool.

The film prepared in the 10% $\text{CO} + \text{H}_2$ gas has a good potential for practical application, since the standard lifetime of TiN-coated tools is about 20 min.

4. Conclusion

Diamond films were coated on WC-Co alloy tool blades using a CO-H_2 mixed gas plasma. A high quality of the diamond film was obtained at a CO concentration of 10% in the feed gas on the tool blade etched by 2.5% $\text{CO} + \text{H}_2$ plasma. The tool coated

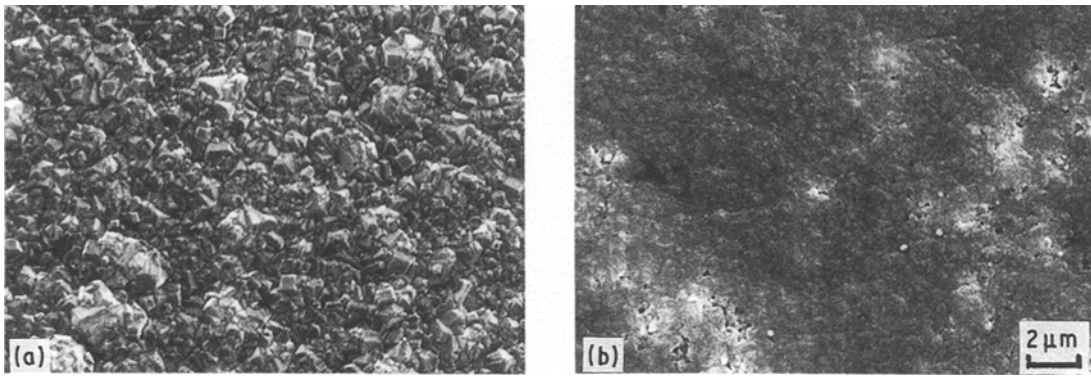


Figure 6 SEM photographs of diamond films coated on tools. Prepared at CO concentration (a) 5%, (b) 10%.

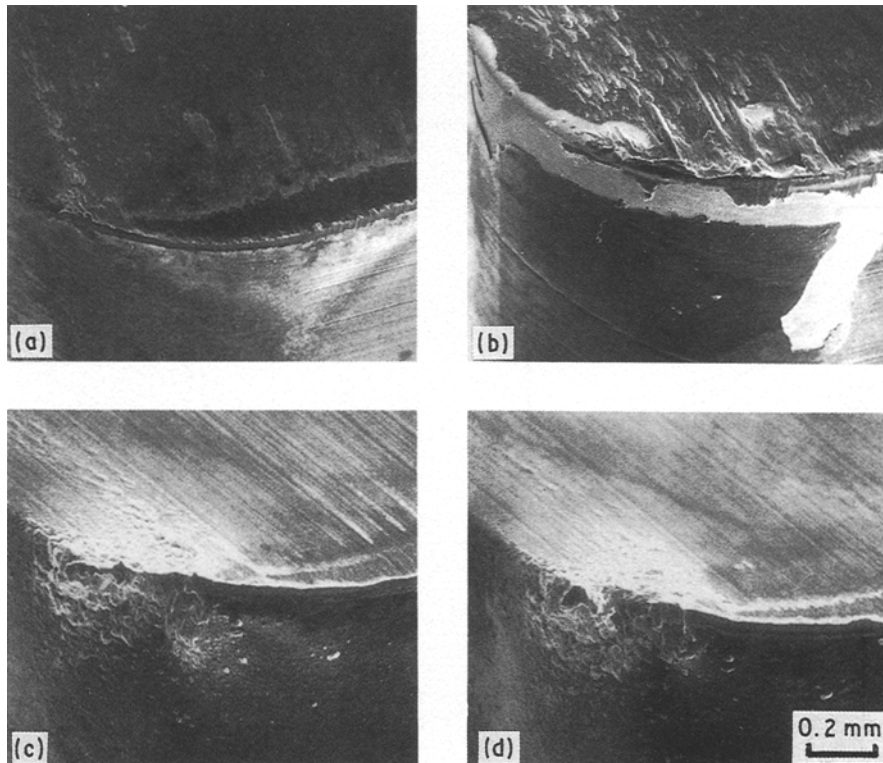


Figure 7 Optical micrographs of diamond film coated on tool after cutting tests. Prepared at 5% CO (Fig. 6a): (a) after 15 min, (b) after 30 min. Prepared at 10% CO (Fig. 6b): (c) after 15 min, (d) after 30 min.

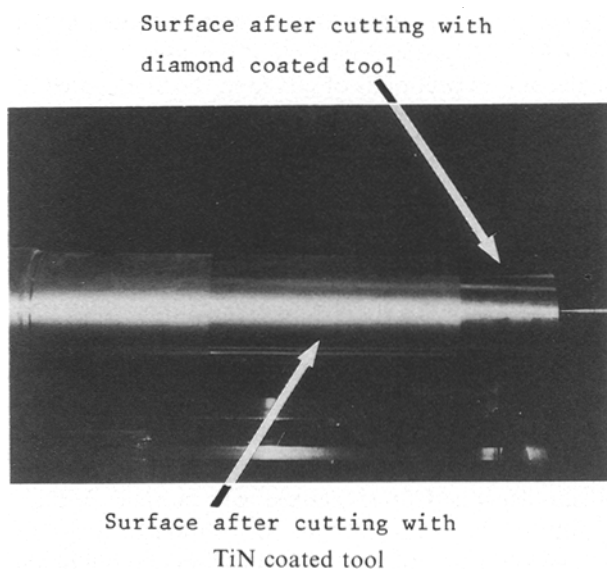


Figure 8 Optical micrograph of rod surface after cutting test.

with diamond films tolerated a hard work-load and had a longer lifetime than conventional TiN-coated tools.

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