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ANALYSIS OF HOT FILAMENT CVD DIAMOND FILMS ON ETCHED AND UNETCHED WC-Co SURFACES

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Abstract

Hot filament CVD diamond films have been grown on 6%Co and 10%Co tungsten carbide substrates. We have shown that the presence of Co is a problem for diamond deposition, but it does not follow that substrates containing the larger amount of Co produced the most Co rich films. Films with Co particles on the surface and at the film/substrate interface showed poor adhesion, some spontaneously delaminating. However adherent films were produced on a 10%Co coarse grain substrate which had been acid etched and pre-abraded with diamond powder.

1. INTRODUCTION

The potential market for diamond coated cemented carbide tools is very large, with a possible value up to as much as $75m by the year 2000 in the USA alone[1)]. At present however, poor adhesion strength of the films to the cemented carbide is a critical obstacle[2)]. A major culprit is thought to be the Co present as the binder phase in the carbides. This paper addresses the effect of etching substrates of two different Co contents before diamond deposition.

2. MATERIALS AND METHODS

The substrates used were 10 mm by 10 mm and 1 mm thick specimens of tungsten carbide with either 6% Co or 10% Co, which had been polished using 1 µm diamond paste. When etching was carried out, concentrated nitric acid was used. Samples were usually abraded with 1-3 µm diamond powder just before diamond deposition.

Table 1 Sample preparation and etching times

Cobalt content (%)	Nitric acid etch (min)	Pre-treatments
6%	0, 10 and 15	Abraded and non-abraded
10%	0 and 10	Abraded and non-abraded

A hot filament CVD reactor (Ta filament at 2000°C) was used to deposit diamond film on the tungsten carbide substrates.. The gas mixture used was 1% methane in hydrogen, and the chamber pressure was kept constant at 30 Torr. Substrate temperature was in the range 800-900°C. Diamond growth rates at typically 0.5 μm/hour.

The diamond coatings were characterised by scanning electron microscopy and energy dispersive X-ray spectroscopy (EDS). Adhesion was investigated using a purpose built scratch tester[3].

3. RESULTS AND DISCUSSION

3.1 Effect of surface pretreatment

With untreated substrates, the diamond nucleation was very slow. A few very large crystals formed but four hours deposition did not give a continuous film (Fig. 1a). If the substrates were abraded, a continuous film (grain size 1-2 μm) was formed (Fig. 1b), indicating a higher diamond nucleation density. In both cases many spherical particles could be seen, and EDS showed these particles to be Co rich (Fig. 2a).

Etching the substrates in concentrated nitric acid removes Co from the surface layer. For both 6% and 10% Co samples, growth on an etched but not abraded sample could be accomplished. However, the grain size was very large (larger than the abraded but not etched sample) and the film was not wholly continuous after four hours deposition (Fig. 1c). The 6% samples still showed some Co, see comments in the next section. Acid etch followed by abrasion produced the conditions to grow continuous films (Fig. 1d). For both types of substrates, the films are of mixed morphology and have a grain size 0.5 - 1.5 μm.

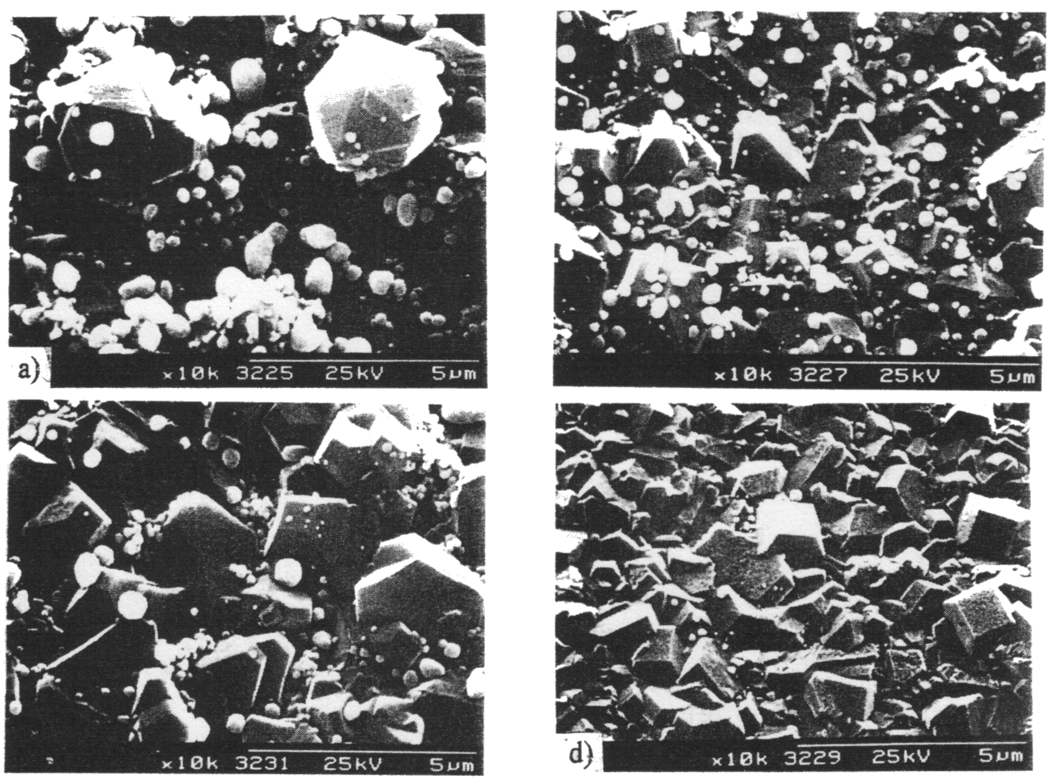

Fig. 1. Diamond films on WC 6%Co after 4 hours deposition: a) As received sample, b) Abraded before growth, c) 10 min. etch before growth, d) Etch and pre-abrasion.

Surprisingly, the etched substrate WC-6%Co samples showed Co containing particles (Fig. 2a) on their surface whilst films deposited on the 10%Co substrates did not (Fig. 2b). This trend continued even when the 6% samples were etched for a longer time (15 min). We conclude that the smaller grain size of the 6% Co samples makes it more difficult to extract the Co and thus Co is extracted to a much shallower depth during the etch. As seen in Figs. 1c and 1d, Co is thus able to travel to the substrate surface during the growth cycle. In the larger grain size specimens (10%Co), the Co is concentrated at multiple grain boundaries and these larger deposits are more easily removed.

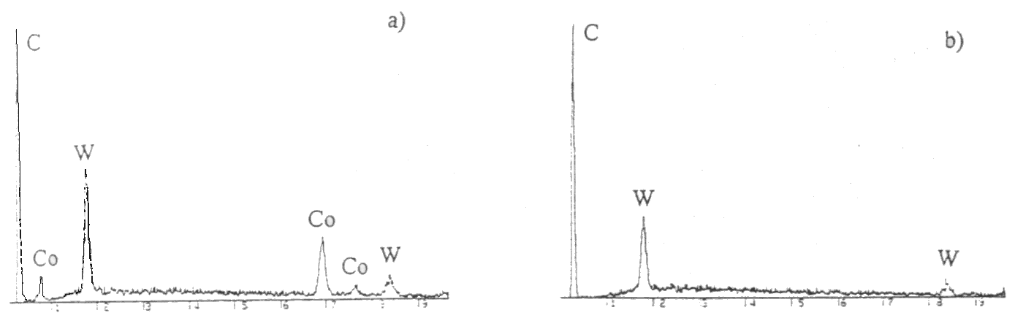

Fig. 2. EDS analysis: a) Co particle on diamond film on 15 min etch WC 6%Co substrate, b) General acquisition of diamond film on 10 min etch WC 10%Co substrate.

3.3 Film delamination

The continuous films produced by 4 hours deposition on acid etched and abraded samples adhered to the substrate. Some of the thicker films on 6% Co samples showed a tendency to spontaneously delaminate, indicating high levels of internal stress and a weak interface. However it seems likely that failure was a mixture of interfacial failure and cohesive failure in the etched substrate layer, since EDS of the underside of the delaminated film (Fig 3b) showed tungsten carbide grains to be present, (white regions in Fig. 3a). Small Co particles could also be seen in both sides of the film and it seems likely that poor film quality is linked to the presence of these particles. On the topside of this film we saw diamond "agglomerations" similar to those observed by Mehlmann et al.[4)], which they link with the nucleation of diamond on disordered graphite obtained during the diamond-Co interaction.

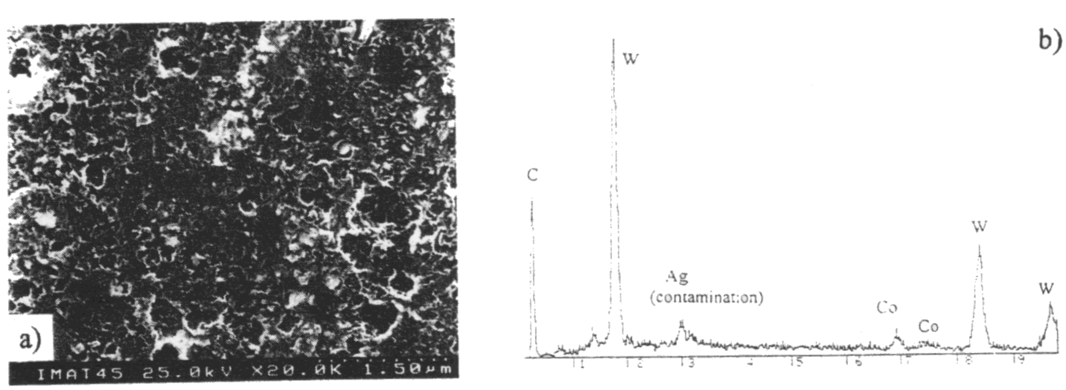

Fig. 3. Underside of delaminated diamond film from 6 hours growth on WC 6%Co: a) SEM view, b) EDS analysis of WC area.

Adherence of the films on 10%Co substrates was better. Fig. 4 shows a cross-section of such a film. Scratch testing of the films with a diamond stylus at 25g and 100g did not produce delamination. At the higher loads the scratches were visible by a damage path in which the tips of diamond grains broke off (Fig. 5) but the diamond grains did not pull out. As the micrographs show, the film surfaces are quite rough leading to a coefficient of friction of about 0.4.

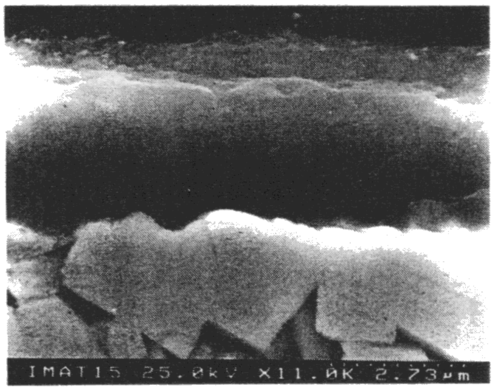

Fig. 4. Cross section of 3 µm thick diamond film on WC 10%Co substrate

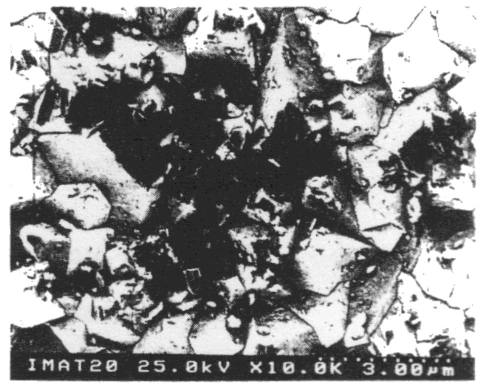

Fig. 5. 4 µm diamond film on WC 10%Co substrate, region of 100g scratch.

4. CONCLUSIONS

We have confirmed the findings of other investigators (e.g. Lux and Haubner[5)] or Peng and Gan[6)]), that Co on the cemented carbide surface has a detrimental effect on diamond deposition. Under otherwise similar growth conditions, more mobile Co on the substrate surface will result in films of bigger grain size and more non-diamond phase. The surprising result is that the substrates with which the Co content is most easily controlled are those with the larger Co content (10%). We suggest that this is due to differences in the size and shape of Co regions in the 6%Co and 10%Co substrates.

We have demonstrated that it was necessary to pre-abrade our substrates with diamond powder to give sufficient nucleation density for formation of a continuous diamond film.

5. ACKNOWLEDGEMENTS

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