Nucleation and Growth of Diamond Films on Ni-Cemented Tungsten Carbide: Effects of Substrate Pretreatments

Riccardo Polini,[†] Giancarlo Marcheselli,[‡] and Enrico Traversa*,[†]

Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata," 00133 Roma, Italy

Fabbrica Italiana Leghe Metalliche Sinterizzate (F.I.L.M.S.) S.p.A., 28020 Anzola d'Ossola (Novara), Italy

The nucleation and growth of diamond films on Ni-cemented carbide is investigated. Substrates made of WC with 6 wt% of Ni were submitted to grinding, and then to different pretreatments (scratching, etching, and/or decarburization) before diamond deposition. Diamond synthesis was carried out by hot-filament chemical vapor deposition (HFCVD) using a mixture of CH_4 (1% v/v) and H_2. Depositions were performed for different lengths of time with the substrates at various temperatures. The specimens were analyzed before and after deposition by scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and X-ray diffractometry (XRD). Raman spectra showed that the phase purity of the diamond films was not affected by the presence of nickel on the substrate surface. After wet etching pretreatments, the nucleation of diamond was enhanced, mainly at the WC grain boundaries. Continuous films were obtained on scratched and etched substrates. The decarburizing treatment led to the formation of metallic tungsten and of brittle nickel–tungsten carbide phases. These phases reacted in the early stages of diamond film formation with gaseous carbon species with a parallel process which competes with stable diamond nucleus formation. The diamond film formed after long-term deposition on these samples was not continuous.

I. Introduction

THE chemical vapor deposition (CVD) of diamond on cemented carbides allows the development of new cutting tools for machining nonferrous alloys. The lower cost of diamond-coated cutting tools with respect to polycrystalline diamond (PCD) tools has stimulated much work, and several papers presented in the scientific literature report successful diamond deposition on cobalt-cemented tungsten carbides.[1–4] Many difficulties must be overcome in the diamond deposition process when cobalt is used as a binder, because of the solubility of carbon in the metal and the formation of a graphitic layer between the substrate and the coating. Moreover, depending on the deposition conditions, cobalt-enriched particles segregate on the substrate surface, leading to poor adhesion and, in the early stages of diamond film formation, to degradation of diamond crystals due to their chemical reaction with Co-rich particles.[5] The chemical nature of the surface is also important in determining the purity of the diamond film deposited as well as its adhesion to the insert. Saijo et al.[6] have demonstrated that the formation of fine grains of metallic tungsten caused by the surface decarburization of pure WC improves the adhesion of the diamond film. The transformation of metallic tungsten into

fine-grained WC during the subsequent diamond deposition process increases the contact area between the diamond film and the substrate. Park et al.[7] reported that, on as-polished cemented carbides containing 5 wt% Co, the films grown at temperatures below 950°C by hot-filament CVD are composed mainly of graphite-like carbon. A preliminary etching with $H_2O_2:H_2SO_4 = 9:1$[7] or $HNO_3:H_2O = 1:1$[8] on as-polished inserts was effective to increase the purity of diamond films.

With a view to avoiding the problems observed for cobalt-cemented carbides, we have studied the nucleation and growth of diamond on WC cutting inserts in which nickel was used as a binder. The substrates were submitted to different pretreatments similar to those commonly used to prepare Co-based substrates before the diamond deposition. Little information is reported in the literature on the state of WC/Co substrates after these preliminary steps. Here we report the effects of the different pretreatments on surface morphology and phase composition, and on subsequent diamond nucleation and growth behavior on WC/Ni inserts.

II. Experimental Procedure

Samples 10 mm × 10 mm × 3 mm made of WC, sintered with 6 wt% Ni, were used as substrates. After the sintering process, all the samples were diamond-ground and then machined to bore a hole (3 mm in diameter and 2 mm in depth) in the center of the face which had not been subjected to diamond deposition. This hole accommodated the Pt/Pt–Rh10% thermocouple used to measure the substrate temperature (maintained at 650° or 750°C) during the deposition process. All the samples were washed with acetone in an ultrasonic vessel. These specimens will be named "as-ground" in the text. Different pretreatments were performed on the as-ground inserts. Specimens were labeled with capital letters indicating the pretreatment the inserts were submitted to. Label S indicates scratching with a 15-μm diamond powder suspension. Label E indicates a 10-min etching with $HNO_3:H_2O = 1:1$ in an ultrasonic vessel. After the etching treatment, the weight loss of the insert was 0.14%. Label H indicates a decarburizing treatment in hydrogen; i.e., the insert was mounted in the deposition chamber and exposed at 830°C for 40 min to pure hydrogen (99.9990%) flowing at 10^4 Pa on a tantalum filament heated to 2170°C, 0.65 cm from the substrate.

Diamond synthesis was performed in a conventional stainless steel hot-filament chemical vapor deposition (HFCVD) chamber of approximately 15-L capacity with an internal diameter of 25 cm.[9] The gas phase, a mixture of hydrogen (purity 99.9990%) and methane (purity 99.995%) with a CH_4/H_2 volume ratio fixed at 1.0%, was activated by a hot tantalum filament (0.03 cm in diameter) wound in a 0.14-cm internal diameter spiral and accurately positioned by means of a cathetometer at 0.80 cm from the substrate. A new filament was used in each deposition run. The filament temperature (2170° ± 20°C) was monitored by a two-color optical pyrometer (Land Infrared model RP 12). The total pressure of the flowing gas mixture in the reactor was $6.6 × 10^3$ Pa with a flow rate of 300

sccm and 4.8 × 10³ Pa when the flow rate was 200 sccm. Gas composition and flow rates were set up by digital mass flow controllers (MKS model 258/259). Table I summarizes the substrate pretreatments and deposition conditions. Decarburization in pure hydrogen was carried out *in situ* prior to diamond deposition without any intervening pretreatment. Diamond deposition carried out on different samples in the same conditions led to reproducible results.

All the specimens were analyzed before and after deposition by scanning electron microscopy (SEM, Leica Cambridge model Stereoscan 360), energy-dispersive spectroscopy (EDS, Link model eXL II), and X-ray diffractometry (XRD, Philips model PW 1729) techniques. In the latter case, Cu$K\alpha$ radiation, Ni filtered, was used (λ = 1.54178 Å). Raman spectra (Spex model Triple Mate) were obtained using the 4880-Å radiation from an Ar$^+$ laser in the standard backscattering configuration.

III. Results and Discussion

(1) Effect of the Pretreatments on the Substrate

Figure 1 shows the surface morphology of as-ground and scratched (S) substrates. On as-ground samples (Fig. 1(a)), the scrapes left by the grinding treatment are quite evident and characterize its surface morphology. The subsequent polishing treatment with the diamond powder suspension has the expected smoothing effect shown in (b).

Figure 2 shows the morphological development of the scratched samples when submitted to etching (E) and/or decarburization in a monohydrogen atmosphere (H). As shown in Fig. 2, the effect of the wet chemical etching on the surface morphology is much more evident than that of the decarburizing treatment.

The etched grain boundary network seen after the decarburizing treatment suggests that monohydrogen also reacts with the metallic binder to form gaseous nickel hydrides. This hypothesis is in line with the results of Mehlmann *et al.*[10] In fact, these authors have reported that, during diamond deposition at 940°C on WC–6 wt% Co, the $CH_4/H_2 1\%$ activated gas mixture has a strong etching effect on cobalt, attributed to the formation of cobalt hydrides.

Comparison between SE and SEH does not show significant differences, indicating that on wet-etched samples the subsequent treatment in hydrogen does not significantly modify the surface morphology. It may be assumed that the same morphology would be observed if the etching were performed after the decarburizing treatment.

Figure 3 shows the XRD spectra of the specimens. The diffraction pattern of the as-ground specimens is not reported, because it is the same as that observed on scratched samples. The decarburizing treatment leads to the formation of metallic tungsten,[6] but the amount of this phase depends on the pretreatments. In fact, on the preliminarily etched specimens (SEH), the amount of tungsten is higher than in the SH samples. This fact is attributable to the greater contact area between substrate and gas phase that etched specimens exhibit (see Fig. 2(a)). On decarburized specimens (SH and SEH), the occurrence of mixed nickel–tungsten carbides is clearly shown by X-ray diffractograms. It is a well-established fact that, during the sintering process of WC/Co inserts, carbon activity must be controlled to avoid the formation of brittle, undesirable η phases, mainly Co_3W_3C and Co_6W_6C.[11] In the SH specimens we observed the formation of $Ni_6W_6C(\eta_{66}$ phase), while in the SEH samples the Ni_2W_4C (η_{24}) phase was also detected. These compounds are formed according to the following decarburizing reaction:

Table I. Pretreatments and Deposition Conditions of WC/Ni Samples (LD Indicates Long Deposition Run)

Sample no.	Pretreatment	Deposition temperature (°C)	Deposition time (min)	Pressure (Pa·10³)	Flow rate (sccm)
0	None	750	20	6.6	300
1	None	650	180	4.8	200
2	E	650	190	4.8	200
3	S	750	20	6.6	300
4	SE	750	20	6.6	300
4 LD	Sample 4	750	+380	6.6	300
5	SH	750	20	6.6	300
5 LD	Sample 5	750	+380	6.6	300
6	SEH	750	20	6.6	300
6 LD	Sample 6	750	+380	6.6	300
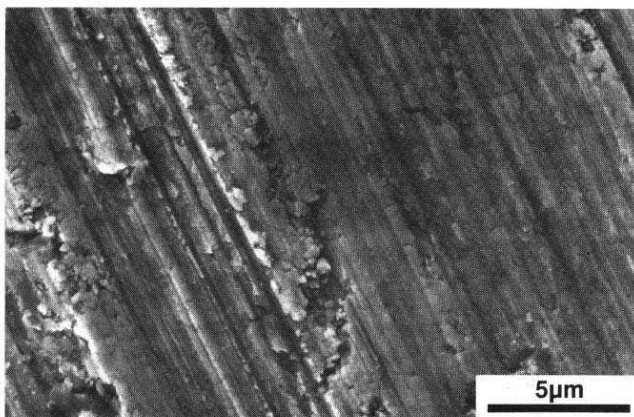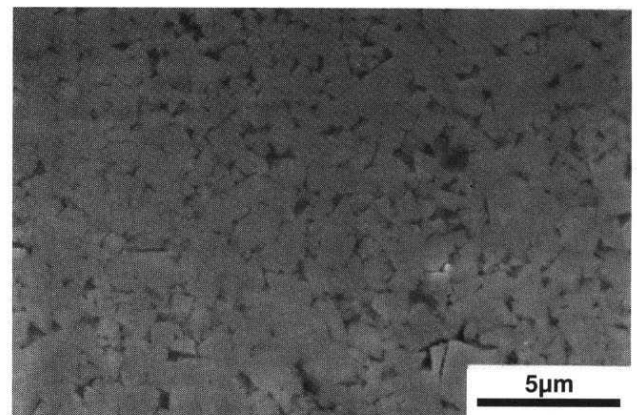
(a)　　　　　　　　(b)

Fig. 1. Surface topography of (a) as-ground and (b) scratched WC–6 wt% Ni substrates.

(a)

(b)

(c)

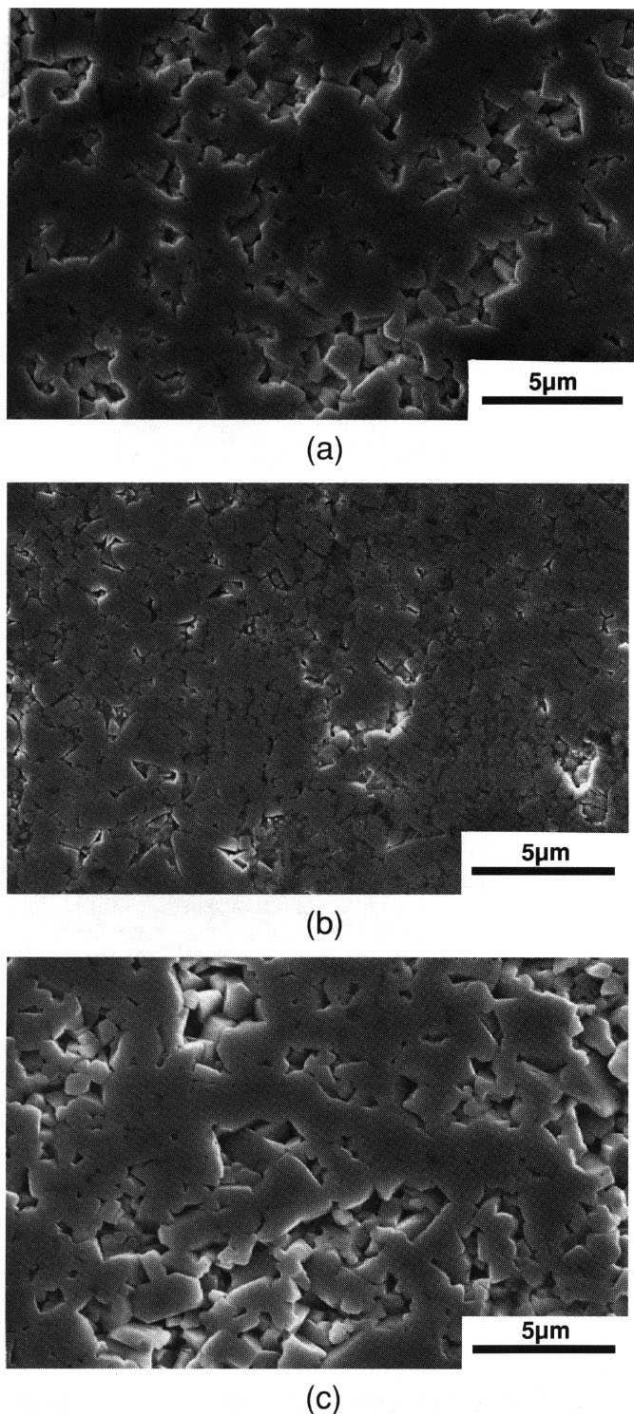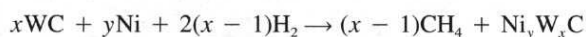**Fig. 2.** Surface topography of scratched WC/Ni samples (a) after wet etching with $HNO_3:H_2O = 1:1$, (b) after decarburization in a monohydrogen atmosphere, and (c) after both etching and decarburizing treatment.

$$xWC + yNi + 2(x - 1)H_2 \rightarrow (x - 1)CH_4 + Ni_yW_xC$$

and have the same crystal structure and lattice parameters which are very similar to those of η carbides containing cobalt (ASTM 6-611, 20-796, 23-939, 27-1125). In the SEH specimen, the formation of mixed nickel–tungsten carbides was more abundant, due to the greater degree of decarburization, discussed previously.

(2) Deposition on as-Ground Specimens

Figure 4 shows the SEM picture of sample 0 after 20 min of deposition at 750°C. The nucleation occurred almost entirely along the scrapes left on the substrate surface by the grinding wheel (see Fig. 1(a)). With the aim of checking if the presence
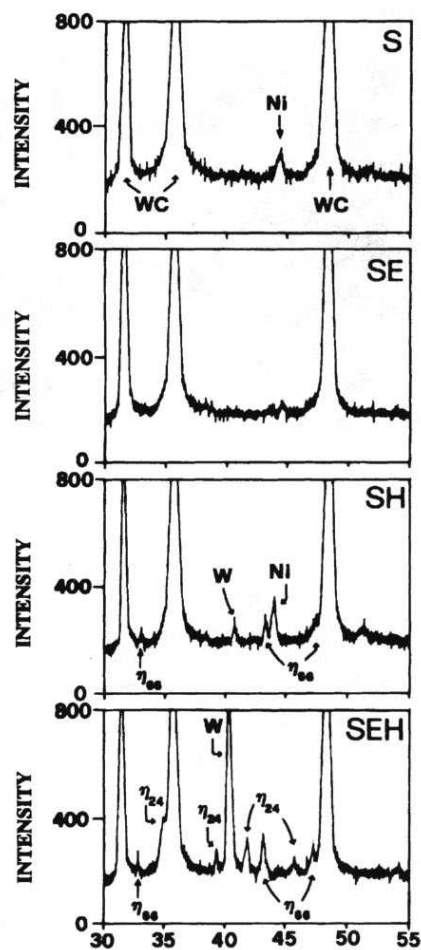

Fig. 3. X-ray diffraction spectra of WC/Ni specimens after different pretreatments (see Table I).

of the metallic binder on the as-ground substrates affected diamond growth, as in the case of WC/Co inserts, samples 1 and 2 were submitted to diamond deposition at 650°C without scratching with diamond paste, but only sample 2 was etched with nitric acid. After 3 h of processing, both the substrates were covered by a noncontinuous diamond layer. Figure 5 shows SEM micrographs which confirm the above-mentioned diamond nucleation pattern corresponding to the scrapes. The Raman spectra shown in Fig. 6 indicate that the film deposited is made of pure diamond (peak at 1334 cm^{-1}), and neither amorphous carbon nor well-ordered graphite are present (no bands centered at ~1550 cm^{-1} nor at ~1600 cm^{-1}). It is worth noting that the quality of the diamond film on the as-ground substrate is the same as that of film grown on the etched substrate. This fact suggests that the presence of nickel on the surface neither affects the phase purity of the deposit nor induces a preferential formation of non-diamond carbon. In contrast, on cobalt-cemented WC the removal of the binder by chemical etching is necessary to avoid the concomitant deposition of graphite-like carbon at substrate temperatures lower than 950°C.[7]

(3) 20-min Deposition Results on Pretreated Specimens

In Fig. 7, the SEM micrographs of specimens 3–6 after 20 min of diamond deposition at 750°C are reported. These samples were submitted to different pretreatments (see Table I). The results can be summarized as follows. The effect of the presence of metallic nickel is evident in Figs. 7(a) and (c). In fact, in the case of sample 3 (scratched but not etched), many round-shaped particles are formed over the gaps between WC grains. EDS microanalysis showed that these particles are enriched in nickel with respect to the average Ni concentration
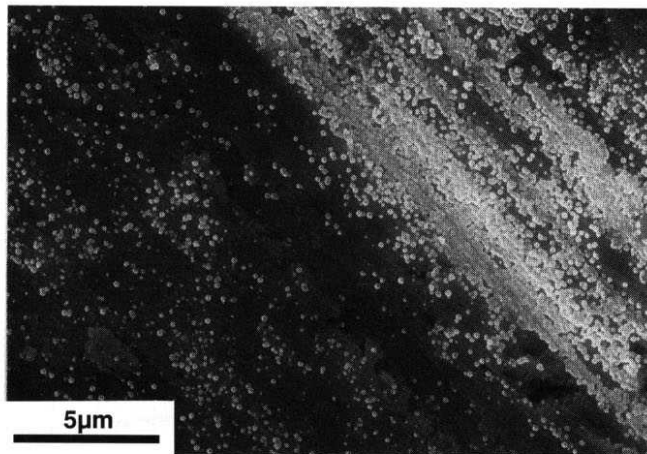
Fig. 4. SEM picture of as-ground specimen after 20-min diamond deposition at 750°C.

Fig. 6. Raman spectra of diamond deposits shown in Fig. 5.

of the substrates. This has also been observed for cobalt on Co-cemented tungsten carbide: Mehlmann *et al.*[5] observed, after 1 h of deposition at 870°C on unetched WC–5.8 wt% Co substrates, a large number of cobalt-containing particles with a morphology very similar to that exhibited by particles formed on our S sample (Fig. 7(a)). Therefore, the mechanism leading to the formation of these particles is probably the same in the case of WC–6 wt% Ni substrates. Their occurrence is not due merely to a thermal effect, because these particles did not form on our specimens decarburized at 830°C in a hydrogen atmosphere. Yang *et al.*[12] observed, after diamond deposition at 1200°C on polycrystalline nickel, the formation of Ni–C–H ternary compound with the same morphology. These authors suggest that such a material would be molten during diamond growth and that this liquid phase may act as an essential intermediate state to the formation of diamond. In our case, we performed the diamond deposition at a lower temperature (750°C) and so we cannot assume that this ternary compound was molten during the HFCVD process. It is more likely that this nickel-containing phase is formed by a reaction between the metallic nickel and the carbon and hydrogen in the gas phase and that its particular morphology is due only to surface tension effects. The absence of nickel on the surface of the etched specimen (Fig. 7(b)) leads to a higher nucleation density, mainly at the grain boundaries, over the gaps left after binder removal. This nucleation pattern was also observed on porous sintered tungsten[13] and resembles the surface topography effects reported by Dennig and Stevenson[14] and confirmed in our laboratory.[15] So,
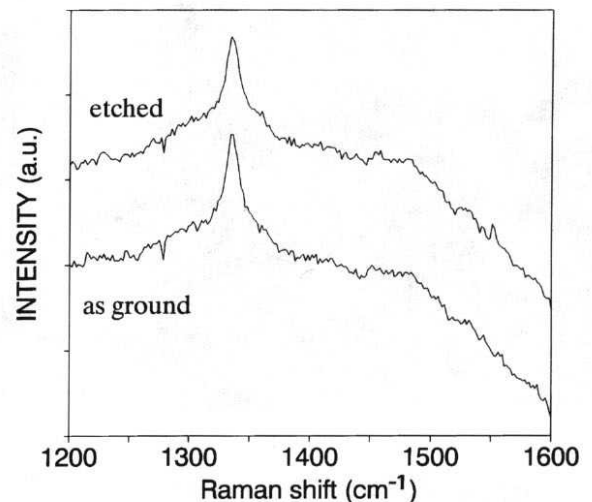
at least in the temperature range we investigated, we cannot conclude that the Ni–C–H phase is essential to the formation of diamond. On the contrary, on unetched substrates there is competition between diamond nucleation at grain boundaries and the occurrence of Ni-rich particles. We observed the same trend in the decarburized specimens (Fig. 7(c) and (d)). Without etching prior to the treatment in a hydrogen atmosphere, many nickel-containing particles nucleate and grow on the surface. The removal of nickel by wet etching allows more abundant diamond nucleation at grain boundaries.

The XRD analysis of specimens 3–6 showed WC and Ni phases. A small amount of metallic tungsten was still present only in sample 6 (SEH). These results indicate that undesirable η_{66} and η_{24} phases disappear under the carburizing conditions of the diamond synthesis. Therefore, the decarburizing pretreatment of the substrates does not compromise the mechanical properties of the insert, because brittle η_{66} and η_{24} phases reconvert to tungsten carbide and metallic nickel during the early stages of the diamond deposition process.

It is interesting to note that the nucleation density of sample 6, pretreated according to the SEH sequence, was lower $(1.0 \times 10^9 \text{ cm}^{-2})$ than in the case of sample 4 $(1.4 \times 10^9 \text{ cm}^{-2})$ which was not submitted to the decarburizing treatment in a hydrogen atmosphere. This may be attributable to a reaction between carbon species chemisorbed on the substrate surface and the decarburization products (metallic tungsten and η phases). It is a well-established fact that the amount of diamond nucleation depends on the steady-state surface concentration of
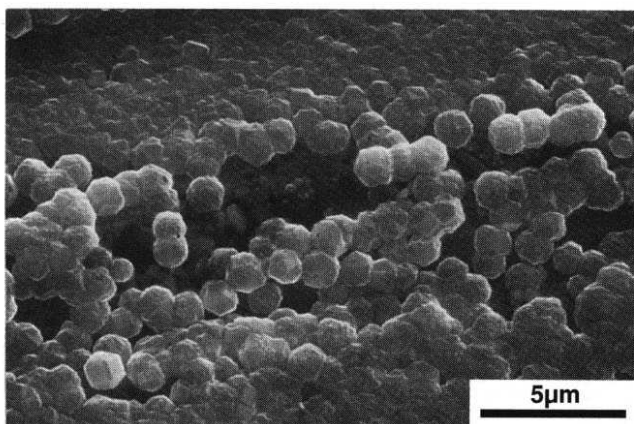
(a)
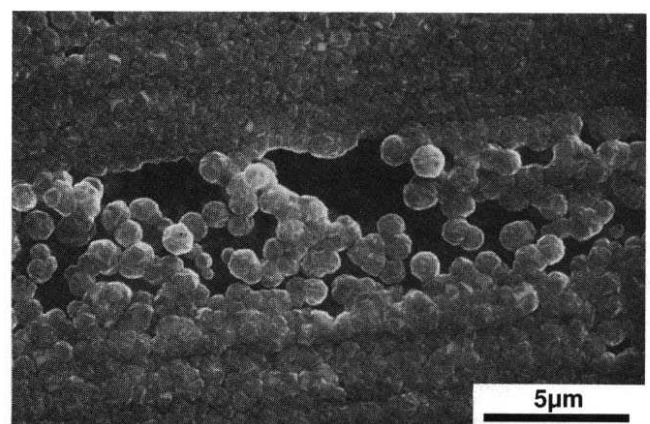
(b)

Fig. 5. Diamond noncontinuous films on (a) as-ground and (b) etched substrates after 3-h deposition at 650°C.
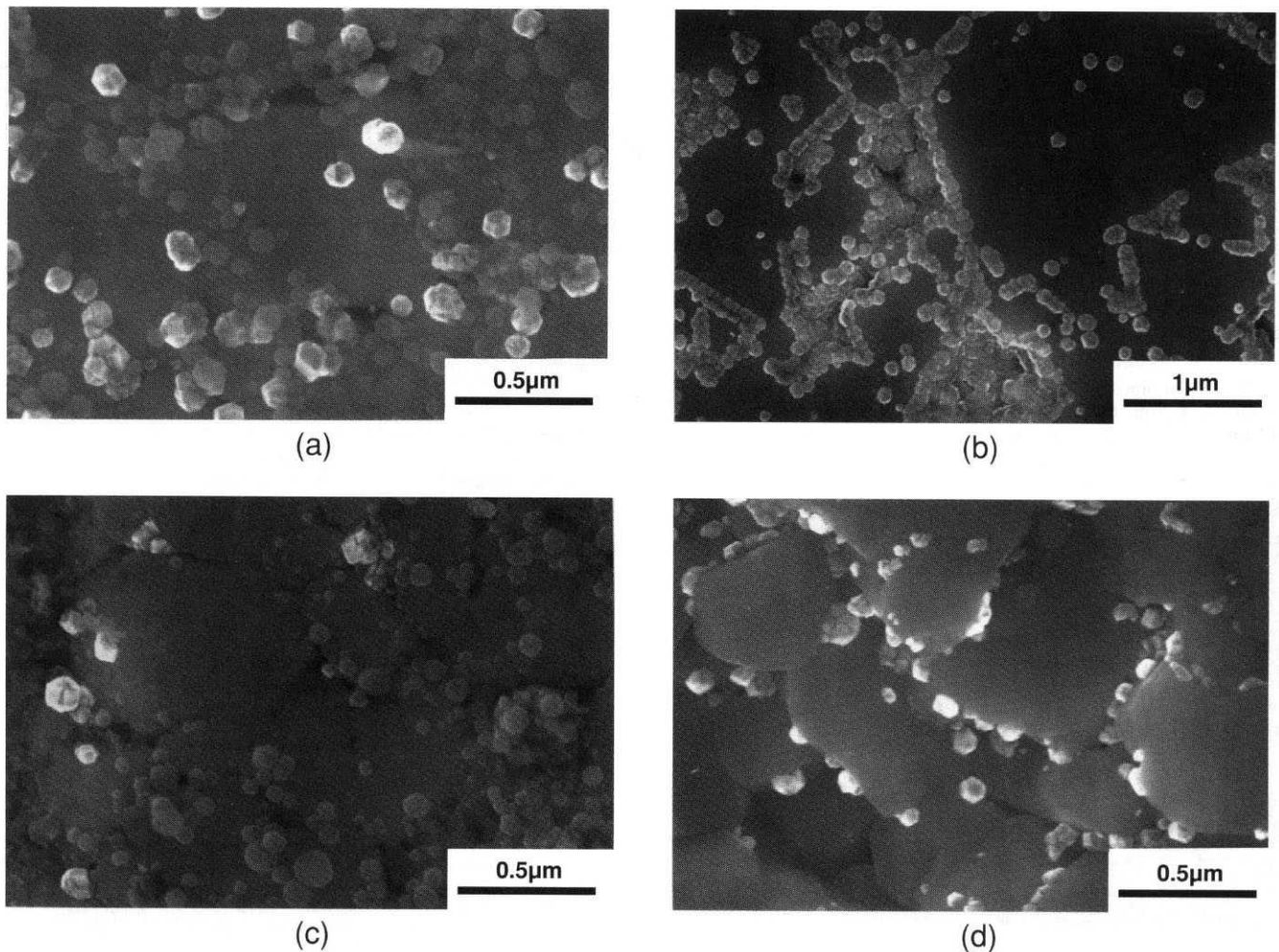
(a)

(b)

(c)

(d)

Fig. 7. SEM pictures showing the diamond nucleation pattern of (a) sample 3 (S), (b) sample 4 (SE), (c) sample 5 (SH), and (d) sample 6 (SEH). Substrate temperature = 750°C; deposition duration = 20 min.

carbon,[16] and carburization reactions may compete with stable diamond nucleus formation.[13,16,17] Therefore, on decarburized samples one has to expect lower nucleation densities.

(4) Long-Term Deposition Results

Specimens 4, 5, and 6 were submitted to a further 380 min of deposition at 750°C. Figure 8 shows the appearance of the continuous film obtained on specimen 4, which, as discussed in the previous section, exhibited a higher nucleation density. The surface morphology of the film reveals the good crystallinity of the deposit. Figure 9 is a SEM image of a cross section of the substrate–diamond film interface. The thickness of the film (2 μm) indicates that the growth rate at 750°C was 0.30 μm/h. This deposition rate may be increased by heating the substrate at higher temperatures, but in this case greater stress at the film–substrate interface should be expected. In fact, the amount of thermal stress (σ) in the film is proportional to the deposition temperature according to the following relationship:[18]

$$\sigma = (\rho_{dia} - \rho_{sub}) \cdot \Delta T \cdot E_{dia}$$

where ρ_{dia} ($= 3.0 \times 10^{-6}\,K^{-1}$) and ρ_{sub} ($= 6.5 \times 10^{-6}\,K^{-1}$) are the thermal expansion coefficients of diamond and WC/Ni, respectively; ΔT is the difference between substrate temperature during the deposition process and room temperature; E_{dia} is Young's modulus of diamond (1 TPa).[19] The calculated value of σ in the diamond film is -2.5 GPa (compression).

The micrograph of the transverse section also shows the existence of small voids at the film/substrate interface, which should have deleterious effects on film adhesion.
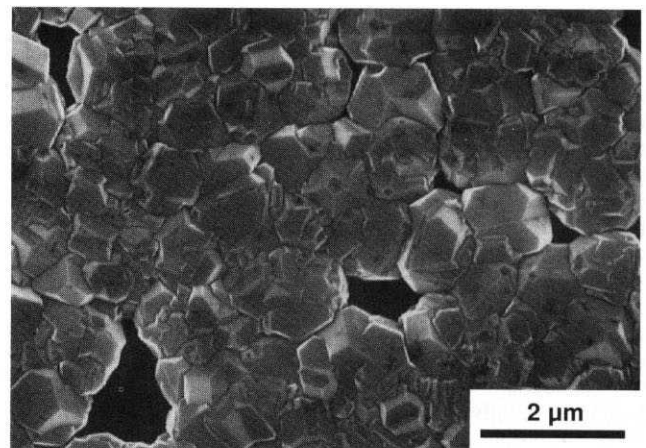

Fig. 8. SEM picture of the continuous films grown on sample 4 (SE). Substrate temperature = 750°C; deposition duration = 400 min.

Figure 10 shows the SEM micrograph of the deposit obtained on sample 6 after a further 380 min of processing with the greater average grain size and the presence of discontinuities in the film. Both these phenomena are a consequence of the lower nucleation density.

On sample 5, where the grain boundary nucleation was inhibited by the presence of nickel, the deposit obtained after a further 380 min was not continuous.
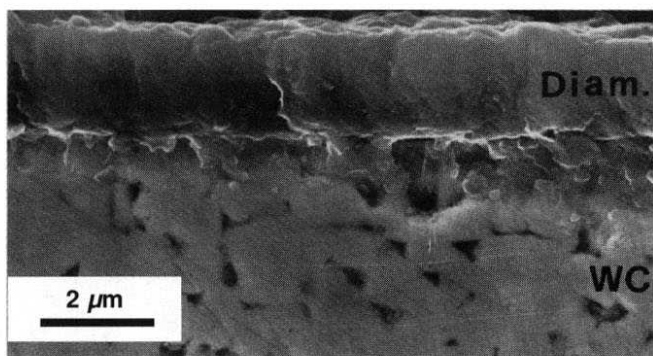
Fig. 9. SEM picture of the cross section of the diamond film grown on sample 4. Substrate temperature = 750°C; deposition duration = 400 min.
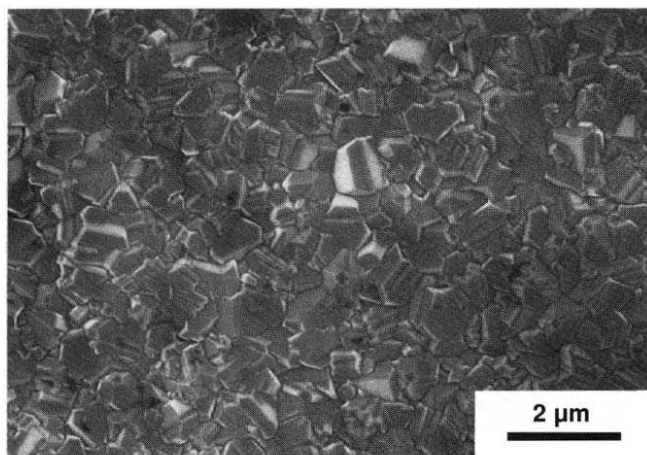

Fig. 10. SEM picture of the noncontinuous diamond film grown on sample 6 (SEH). Substrate temperature = 750°C; deposition duration = 400 min.

IV. Conclusions

Diamond deposition was successfully carried out on as-ground cemented carbides containing 6 wt% Ni. The quality of diamond films grown at temperatures as low as 650°C is not affected by the presence of nickel on the substrate surface, as confirmed by comparing Raman results on as-ground and etched samples. If the binder is not chemically removed, round particles form over the gaps between WC grain boundaries. The occurrence of this phase, presumably a ternary Ni–C–H compound, strongly reduces the amount of diamond nucleation and does not allow the formation of continuous diamond film even after 400 min of deposition. Moreover, the presence of this phase may have deleterious effects on film adhesion. Following the wet etching of Ni, diamond nucleation is more abundant and localized mainly at WC grain boundaries. The preliminary decarburization of the samples in a monohydrogen atmosphere does not significantly modify the topology of the substrate and leads to the formation of metallic tungsten and of brittle η phases, which readily react in the early stages of diamond film formation with gaseous carbon species, restoring WC and Ni. On decarburized specimens (SEH), the nucleation density is

40% less than that obtained on specimens submitted to scratching and wet etching pretreatments only (SE). This suggests that the reaction of carbon with metallic tungsten and η phases is a parallel process which competes with stable diamond nucleus formation. The long-term deposition results indicate that contact between the substrate and the deposit and, therefore, adhesion, must be improved, but the absence of any deleterious effects of nickel on the quality of the diamond film supports the use of this metal instead of cobalt as a binder and should stimulate further work on the diamond coating of WC–Ni cutting tools.

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