

## Nucleation and Growth of Diamond Films on Ni-Cemented Tungsten Carbide: II, Effects of Deposition Conditions

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Diamond films were deposited by hot-filament chemical vapor deposition (HFCVD) on substrates made of WC sintered with 6 wt% of Ni. The as-ground substrates were scratched with diamond powder (S samples) or scratched and wet-etched (SE samples). Diamond synthesis was carried out at substrate temperatures ranging between 600° and 1050°C, and using 1.0% or 2.0% CH<sub>4</sub> in H<sub>2</sub>. The diamond nucleation density, as measured by scanning electron microscopy (SEM) and automatic image analysis (AIA), did not significantly change in the 600°–900°C temperature range, while at substrate temperatures higher than 900°C a steep decrease of the density of nuclei was observed and attributed to the thermal annealing of nucleation sites. The activation energy of the growth process was measured and found to be  $21 \pm 2$  kcal/mol. Neither nucleation density nor growth rate were affected by an increase of CH<sub>4</sub> concentration in the feed gas, while a lack of crystallinity was observed at the higher methane concentration. Raman analysis showed that phase purity of the films was affected mainly by the substrate temperature: the lower the temperature, the better the film quality. The presence of Ni on the substrate surface did not induce the preferential formation of non-diamond carbon phases, as confirmed by comparing the Raman spectra obtained from both S and SE substrates. As a comparison, continuous films were deposited on scratched WC–5 wt% Co substrates under the same experimental conditions. The results indicated that the use of Ni as a binder is preferable to Co.

### I. Introduction

THE chemical vapor deposition (CVD) of diamond on cemented carbides has received considerable attention in recent years.<sup>1</sup> Due to the importance of coated tools, many deposition experiments have been run on Co-cemented tungsten carbide using both hot-filament CVD (HFCVD)<sup>2–7</sup> and plasma-assisted CVD (PACVD).<sup>8–11</sup> The use of cobalt as a binder causes a number of problems, due to the solubility of carbon in the metal and the formation of a graphitic layer between the substrate and the diamond coating.<sup>7</sup> Moreover, depending on deposition conditions, Co-enriched particles segregate on the substrate surface and react with growing diamond crystallites.<sup>6</sup> Park *et al.*<sup>4</sup> reported that on as-polished cemented carbides containing 5 wt% Co the films grown by HFCVD at temperatures below 950°C are composed mainly of graphite-like carbon, and the performance of a preliminary etching with

H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub> = 9:1 was necessary to suppress the codeposition of sp<sup>2</sup>-carbon.

In a previous paper published in this journal,<sup>12</sup> we reported the effects of substrate pretreatments on the nucleation and growth behavior of diamond films grown by HFCVD on cemented tungsten carbide, sintered with 6 wt% Ni as a binder instead of cobalt. The results of this work indicated that high-purity diamond films could be obtained, at deposition temperatures below 750°C, on as-ground substrates and that the presence of Ni on the substrate surface did not induce the preferential formation of non-diamond carbon phases. If the binder was not removed by chemical etching of WC–Ni substrates, round Ni-rich particles formed over the gaps between WC grains during the early stages of the deposition process. On substrates abraded with 15-μm diamond powder suspension and etched with HNO<sub>3</sub>:H<sub>2</sub>O = 1:1, continuous diamond films were grown over 400 min of deposition at 750°C. An *in situ* decarburization treatment performed prior to deposition in a hydrogen atmosphere led to the formation of η phases, namely Ni<sub>2</sub>W<sub>4</sub>C and Ni<sub>6</sub>W<sub>6</sub>C, which reacted with carbon species in the early stages of the CVD process, giving rise to slightly lower nucleation densities.<sup>12</sup>

On the basis of these promising results, we have investigated the effects of substrate temperature and gas phase composition on the nucleation density, growth rate, and phase purity of diamond grown on WC–6 wt% Ni substrates. We also present here a comparison of the results of this investigation with those obtained using Co-cemented WC substrates under identical deposition conditions.

### II. Experimental Procedure

The experimental details are similar to those previously reported.<sup>12</sup> Briefly, 10 mm × 10 mm × 3 mm samples of WC, sintered using 6 wt% Ni, were used as substrates. A number of tests were also performed with 5 wt% Co–WC substrates of the same size. All the specimens were scratched for 30 min with a 15-μm diamond powder suspension and for 1 min with 1-μm diamond paste, and then washed with acetone in an ultrasonic vessel. These specimens are referred to in the text as S samples. The WC–Co samples underwent only this pretreatment. In order to remove the binder from the substrate surface, several specimens (labeled SE samples) were also etched with HNO<sub>3</sub>:H<sub>2</sub>O = 2:1. The weight loss of the inserts after etching was in the range of 0.10 to 0.20 wt%. Diamond depositions were performed in a stainless steel hot filament CVD reactor using a mixture of methane (purity 99.995%) and hydrogen (purity 99.9990%) with volume ratios fixed at 1.0% or 2.0%. The gas phase was activated by a dc-heated tantalum filament maintained at a constant temperature (2175° ± 15°C) during the whole deposition process and positioned at 0.80 cm from the substrate. A new filament was used in each deposition run. The total pressure of the flowing gas mixture was 6.6 kPa and the flow rate was 300 sccm. Substrate temperatures were

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**Table I. Deposition Conditions, Nucleation Densities and Growth Rates of Scratched and Wet-Etched Wc/Ni Substrates Submitted to Short Process Runs**

Sample No.	Deposition temp (°C)	Deposition time (min)	CH <sub>4</sub> content (%)	Nuclei/μm <sup>2</sup>	Growth rate (μm/h)
1	600	150	1.0	3.7	0.09
2	700	20	1.0	5.7	0.45
3	750	20	1.0	5.0	1.0
4	800	20	1.0	3.2	0.9
5	800	20	1.0	4.9	0.9
6	800	25	1.0	1.1	1.2
7	900	20	1.0	1.8	2.5
8	1000	15	1.0	0.11	3.6
9	600	150	2.0	4.6	0.08
10	700	20	2.0	5.9	0.4
11	800	20	2.0	3.1	1.3
12	900	20	2.0	1.8	2.2
13	950	20	2.0	0.22	5.1
14	1050	15	2.0	0.052	5.6

between 600° and 1050°C, as measured by Pt/Pt–Rh10% thermocouple.<sup>12</sup> Deposition times were varied between 15 and 150 min for the preparation of noncontinuous films (see Table I) and between 260 and 400 min for the deposition of continuous films.

All the samples were analyzed before and after deposition by scanning electron microscopy (SEM, Leica Cambridge model Stereoscan 360), and energy dispersive spectroscopy (EDS, Link model eXL II). On those samples submitted to deposition runs short enough to ensure the formation of noncontinuous films, we used automatic image analysis (AIA, Leica Cambridge model Quantimet 970) to measure the nucleation density and the size distribution of diamond crystallites. The maximum diameter,  $d_m$ , to deposition time,  $t_D$ , ratio was used as a growth parameter, assuming a linear growth rate function ( $G = d_m/t_D$ ).<sup>13,14</sup>

Diamond continuous films were analyzed by SEM and by Raman spectroscopy (Spectrograph: Spex model Triple Mate) using the 5145-Å radiation from an Ar<sup>+</sup> laser in the standard backscattering configuration. Laser power was 100 mW on the sample.

### III. Results and Discussion

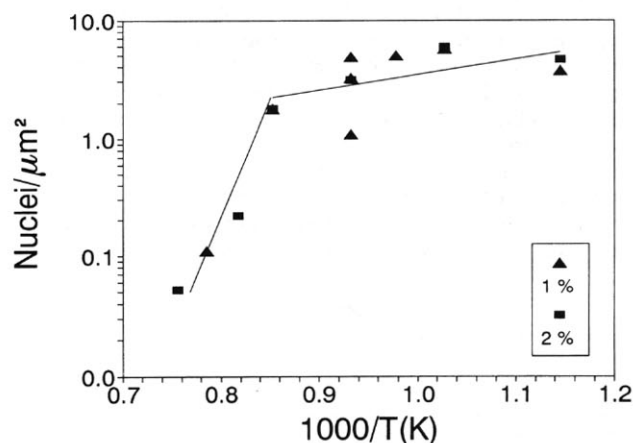
#### (1) Nucleation

Table I shows the deposition conditions and the AIA results obtained from SEM pictures of scratched and etched (SE) samples submitted to short deposition runs. All substrates were pretreated according to the SE sequence in order to avoid, during the early stages of the deposition process, the formation of Ni-containing particles, which may influence the nucleation density.<sup>12</sup>

The data point out that nucleation density does not vary significantly on increasing the methane concentration in the gas phase from 1.0% to 2.0%.

The Arrhenius plot of the nucleation density is shown in Fig. 1. The statistical analysis of the data indicates that, in the 600°–900°C temperature range, there is no significant dependence of the nucleation density on the substrate temperature. The steep decrease in nucleation density at temperatures higher than 900°C might be attributable to thermal annealing of the nucleation sites. In order to check this hypothesis, we performed a 20 min heat treatment at 1000°C in a hydrogen atmosphere on an SE sample. Following this treatment we submitted the substrate to a 20 min diamond deposition at 750°C (CH<sub>4</sub>/H<sub>2</sub> = 1.0% v/v). Figure 2 shows the SEM micrograph of this specimen (a) and of specimen 3 (b), submitted to deposition treatment under identical conditions. While the latter showed a clear formation of diamond crystallites, the former had mainly round-shaped particles with only a few diamond crystallites. EDS microanalysis showed that these particles were highly Ni-enriched with respect to the average. This means that the heat

treatment in hydrogen atmosphere led to the surface segregation of Ni-rich particles. Only few diamond crystallites nucleated and grew, and a statistically significant evaluation of their density was not possible. Therefore, the observed nucleation density was much lower, as shown in Fig. 2(a), than the one measured, under identical deposition conditions, on a non-previously annealed sample. One could argue that the decrease in the nucleation density at higher temperatures might be due to the competitive effect of Ni diffusion. A similar effect has also been observed by Mehlmann *et al.*<sup>7</sup> on WC-Co substrates, where nucleation density decreased by two orders of magnitude after a 1 h heat treatment in hydrogen atmosphere at 920°C, prior to diamond deposition. These authors also found that the binder, on etched substrates, segregates to the substrate surface during annealing, and they suppose that Co enrichment could inhibit the nucleation of diamond. However, on our samples deposited at temperatures higher than 900°C, we observed that the reduction of the density of diamond nuclei was not accompanied by the segregation of Ni-rich particles, as shown in Fig. 3 for specimen 8. This suggests that the decrease of nucleation density is attributable to the reduction of site density due to stress relaxation or removal of nonequilibrium defects at the substrate surface rather than to the surface diffusion of the binder. The comparison of all these results indicates that the diffusion velocity of the binder strongly depends on the presence of carbon in the gas phase. The findings by Park *et al.*<sup>4</sup> also confirm this conclusion. These authors reported that, on WC–5 wt% Co etched substrates, a 60 min annealing in H<sub>2</sub>–0.3% CH<sub>4</sub> atmosphere at 950°C did not give rise to the formation of Co-containing phases on the substrate surface and



**Fig. 1.** Arrhenius plot of the diamond nucleation density as measured on SE WC-Ni substrates submitted to short deposition runs (CH<sub>4</sub> = 1.0% (▲) or 2.0% (■)).

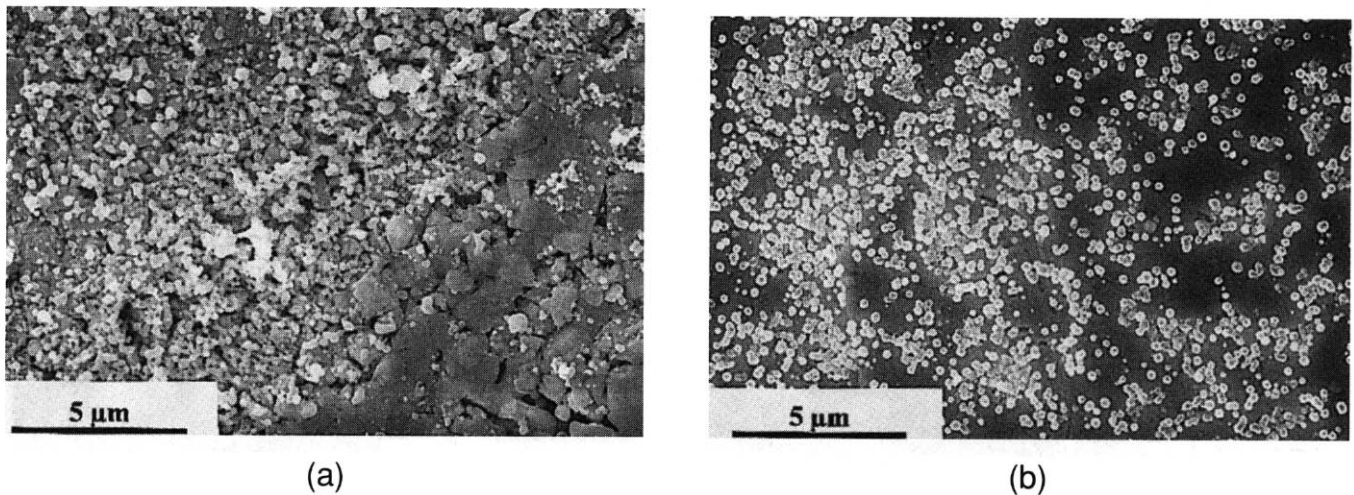


Fig. 2. Comparison of the nucleation behavior at 750°C of SE samples (a) submitted or (b) not (sample 3) to a 20 min heat treatment at 1000°C in a hydrogen atmosphere.

concluded that chemical etching is very helpful in reducing the Co effects during deposition at the same temperature.

Figure 4 shows the SEM micrographs of (a) specimen 7 and (b) specimen 12 after a 20 min deposition at 900°C with 1.0% and 2.0% CH<sub>4</sub>, respectively. It can be seen that the spread of the size of diamond crystallites is greater than 0.5 μm. The size distribution functions, measured on the other samples at the end of the short deposition runs, also show a spread in crystallite diameter ranging from 0.2 to 1 μm, depending on the deposition conditions. This indicates that the hypothesis of seeding (i.e., tiny diamond particles planted on the substrate surface during the scratching pretreatment) can be discarded. In fact, it has been reported that, if seeds are not detectable by SEM prior to deposition (as in our samples<sup>12</sup>), the spread of their dimensions does not exceed a few tenths of a nanometer.<sup>15</sup> Therefore, the origin of the spread derives from a time-dependent heterogeneous nucleation process, i.e.; greater crystallites nucleated and started to grow earlier during the CVD process.<sup>16,17</sup> In contrast, on seeded substrates, all seeds should start growing at the beginning of the CVD process. It may be said that the origin of such a wide spread of crystallite diameters depends on a spread of microscopic growth law; i.e., during the deposition process, growing crystallites "see" different gas environments with different concentrations of growth species, namely monohydrogen and methyl radicals. But this argument cannot explain the random distribution of crystallite diameters over substrate areas as small as few squared micrometers which was observed. A concentration gradient of growth species may

develop along the substrate surface, especially in single-filament CVD reactors, where the growth rate is higher below the hot filament and lower at the edges of the substrate.<sup>18</sup> Nevertheless, both in the center and at the edges of the sample, random distribution of crystal diameters may be seen, with any changes regarding only the mean diameter. Therefore, because seeds are not detectable by SEM, our conclusion is that the spread in crystallite diameter, greater than a few tenths of a nanometer, points to diamond formation occurring via a heterogeneous nucleation process.

The fact that nucleation density does not depend on the substrate temperature in the 600°–900°C range and on the methane concentration suggests that all the nucleation sites created by the scratching are transformed into stable nuclei. According to a kinetic model previously developed,<sup>16</sup> the diamond heterogeneous nucleation proceeds via a two-step mechanism: active sites on the substrate surface are in equilibrium with unstable germs which can irreversibly transform into nuclei. Germs are created by the chemisorption of carbon species and correspond to carbon clusters smaller than  $3/2n^*$ ,  $n^*$  being the number of atoms in the critical cluster.<sup>19</sup> Therefore, in the absence of the thermal destruction of nucleation sites, the irreversible transformation of germs into nuclei continuously shifts the equilibrium active sites  $\leftrightarrow$  germs to the right and gives rise to the conversion of all active sites into nuclei, irrespective of gas phase composition and substrate temperature.

## (2) Growth

Figure 5 shows the growth data, in the form of an Arrhenius plot, as determined by SEM observation of the samples described in Table I. The apparent activation energy for the growth process is  $21 \pm 2$  kcal/mol, a value in good agreement with the ones reported by Ohta *et al.*<sup>20</sup> (23 kcal/mol) for continuous film growth on Si wafers, and by Chen *et al.*<sup>21</sup> (24 kcal/mol) for the growth of well-separated crystallites on polycrystalline copper. The fact that growth rates have the same temperature dependence confirms that the role of the substrate is negligible, and that diamond growth is controlled by surface reactions occurring at the diamond surface in contact with the gas phase.<sup>13</sup>

Data reported in Table I and Fig. 5 indicate that growth rate is not significantly affected by increasing the CH<sub>4</sub> concentration in the gas phase from 1.0% to 2.0%. The SEM micrographs of samples 7 and 12, reported in Fig. 4, show the morphology of the deposits obtained after a 20 min deposition at 900°C using (a) 1.0% CH<sub>4</sub> and (b) 2.0% CH<sub>4</sub>. These micrographs indicate that, for samples deposited at the higher methane concentration, a lack of crystallinity occurs, i.e., the codeposition of non-diamond carbon. Similar findings have been also observed for samples deposited at different temperatures. Matsubara and

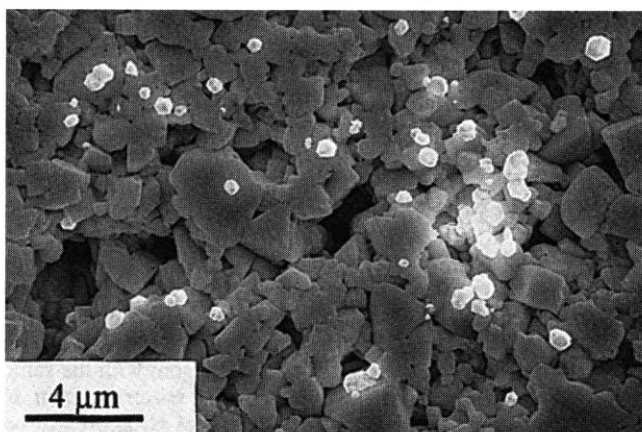


Fig. 3. Diamond crystallites nucleated on sample 8 (SE, substrate T = 1000°C, deposition duration = 15 min, CH<sub>4</sub> = 1.0%).

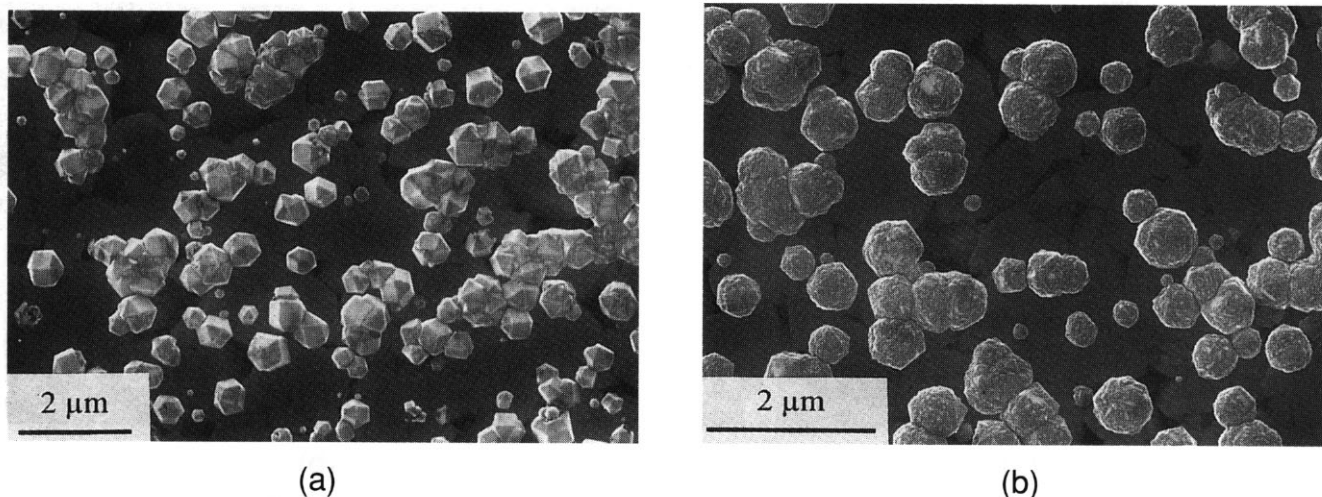


Fig. 4. Morphology of diamond crystallites after a 20 min deposition at 900°C grown with (a) 1.0% CH<sub>4</sub> (sample 7) and (b) 2.0% CH<sub>4</sub> (sample 12).

Sakuma<sup>3</sup> found that the growth rate of films deposited on WC-Co cemented carbides, using a tantalum filament at 2000°C, does not change on increasing the CH<sub>4</sub> content in the gas phase from 1.0% to 3.0%, when graphitic carbon became the main component of the film. Therefore, whenever the increase of methane concentration leads to the codeposition of non-diamond carbon phases, a proportionate increase in the growth rate should not be expected.

Both S and SE substrates were submitted to long deposition runs, at different temperatures, using 1.0% CH<sub>4</sub> in the gas feed. SEM pictures of the films grown at different temperatures on S samples are reported in Fig. 6. The morphology of the deposits indicates that the film quality decreases on increasing the substrate temperature, independently of the performance of a preliminary etching of the specimens. In fact, the same SEM results have been obtained for SE samples. In Fig. 7, the Raman spectra of the films shown in Fig. 6 are reported. The background level for samples deposited at 660°, 750°, and 850°C was similar. The intensity of the spectrum of sample deposited at 1000°C has been multiplied by 2. Similar spectra have been obtained on continuous films grown on SE samples under identical deposition conditions. In all the spectra the fingerprint of diamond is present at 1337 cm<sup>-1</sup>, but the film quality, as revealed by SEM, is affected by the deposition temperature. In the temperature range from 660° to 850°C, the amount of non-diamond carbon increases with temperature, and it is mostly present in the form of highly disordered sp<sup>2</sup>-carbon, as confirmed by the presence of the broad band at ≈1490 cm<sup>-1</sup>. For

samples deposited at 1000°C, the Raman spectra of both S and SE samples show the typical bands centered at ≈1360 cm<sup>-1</sup> (D band, attributable to scattering from a phonon in microcrystalline graphite) and at ≈1590 cm<sup>-1</sup> (G band, assigned to the first-order phonon mode in large single-crystal graphite<sup>22</sup>).

These results suggest that high substrate temperatures should be avoided during diamond deposition. In fact, a lack of purity of the deposit and an increase in defect concentration corresponds to an increase of the growth rate. The SEM picture shown in Fig. 6 indicates that deposits obtained at 750°C have a higher concentration of twins than films grown at lower temperature. Moreover, the deposits obtained at higher substrate temperatures reveal a grain size smaller than that of samples grown at lower temperatures. This is apparently in contrast with the reduction of the nucleation density observed at the higher temperatures. The finer microstructure of the deposits grown at 850°C and 1000°C is, however, explained by considering that a higher concentration of defects induces secondary nucleation, i.e. the heteroepitaxial nucleation of diamond crystallites in correspondence with grain boundaries and defects present on previously grown crystal faces.<sup>23</sup> Codeposited sp<sup>2</sup>-carbon phases are also preferential sites for secondary nucleation.<sup>22,24,25</sup>

It is worth noting that film quality is only slightly affected by a preliminary wet etching of the substrate, confirming the findings of our previous paper,<sup>12</sup> and that the relative amounts of diamond and sp<sup>2</sup>-carbon phases are determined mainly by the substrate temperature.

### (3) Comparison with WC-Co Substrates

In Fig. 8 the Raman spectra from continuous films grown on WC-5 wt% Co substrates are shown. The intensity of the spectrum (d) of the sample deposited at 1000°C has been multiplied by 4. These substrates were scratched, but not etched, prior to diamond deposition, which was performed under the same conditions as WC-Ni S samples. We made these tests in order to compare the effect of the presence of Co or Ni on the substrate surface on the quality of the diamond films grown under identical deposition conditions. A comparison with the data reported in the relevant literature<sup>4,6,7,9</sup> showed the unfavorable conditions produced by the presence of cobalt. In particular, good films were obtained by PACVD at temperatures higher than 950°C,<sup>4</sup> while other authors have reported that good films may be obtained by HFCVD at lower temperatures.<sup>26</sup>

Therefore, we decided to deposit some diamond films on WC-Co in order to have an internal comparison, with the same experimental setup. Comparison with the spectra shown in Fig. 7 demonstrates that, when Co instead of Ni is present on the substrate surface, a slightly higher codeposition of non-diamond carbon occurred. Besides, in our experimental conditions, the lower the deposition temperature, the better the

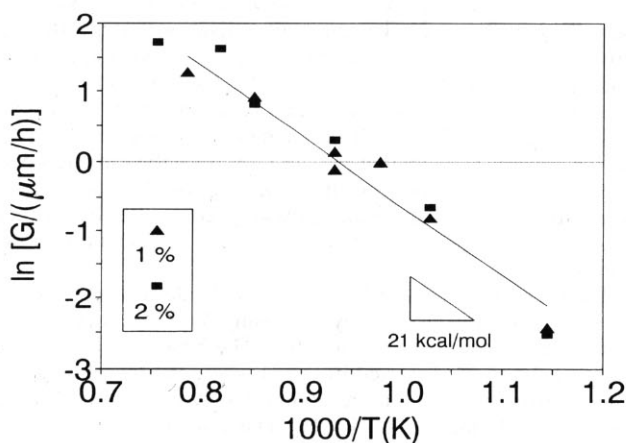


Fig. 5. Arrhenius plot of the diamond crystallites growth rate as measured on SE WC-Ni substrates submitted to short deposition runs (CH<sub>4</sub> = 1.0% (▲) or 2.0% (■)).

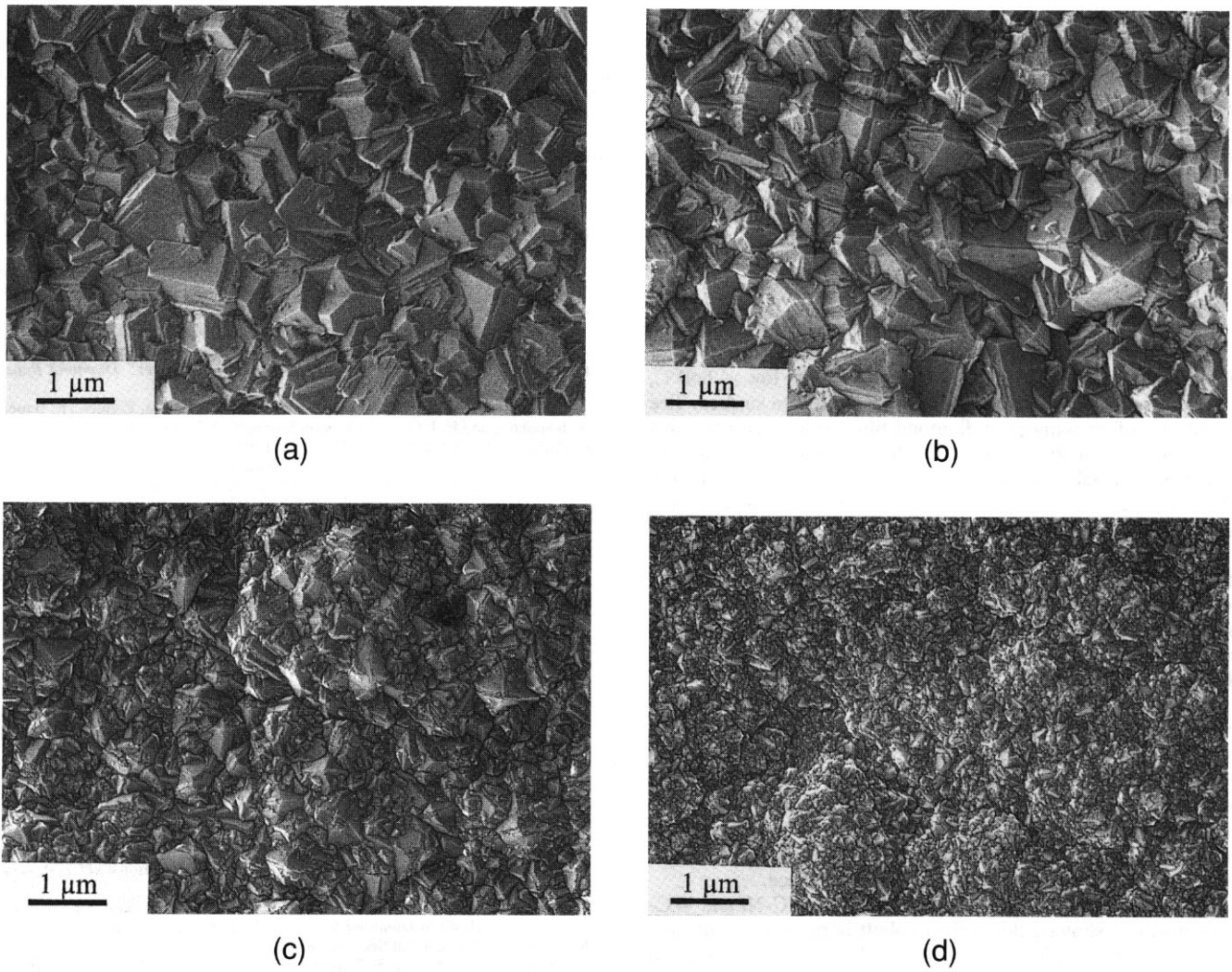


Fig. 6. Morphology of the continuous diamond films grown on W-6 wt% Ni scratched (S) substrates: (a) 660°C, 420 min; (b) 750°C, 400 min; (c) 850°C, 300 min; (d) 1000°C, 260 min. ( $CH_4 = 1.0\%$ ).

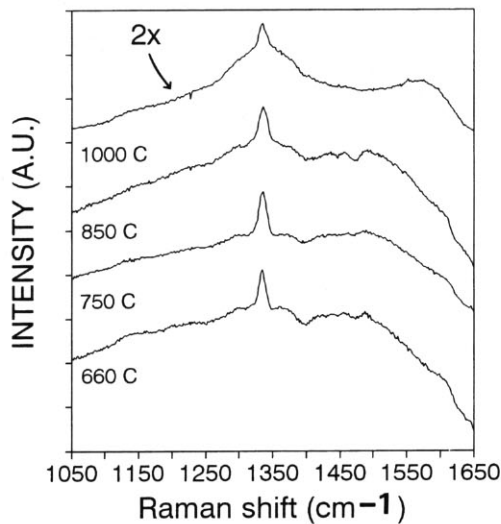


Fig. 7. Raman spectra of the diamond films grown on WC-6 wt% Ni scratched (S) substrates and shown in Fig. 6.

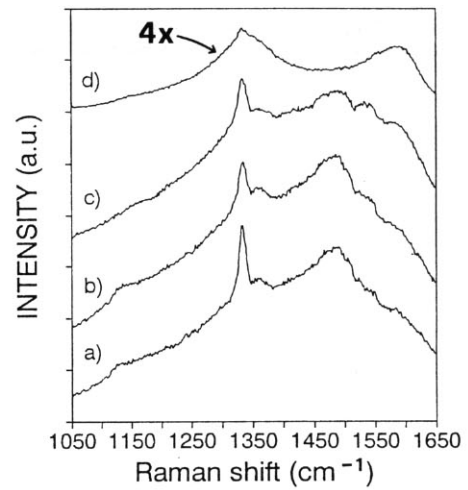


Fig. 8. Raman spectra of diamond films grown on WC-5 wt% Co scratched (S) substrates at (a) 700°C, (b) 750°C, (c) 850°C, and (d) 1000°C ( $CH_4 = 1.0\%$ ).

quality of diamond films grown on Co-cemented WC. At 1000°C, on WC-Co substrates, the diamond peak was almost not detectable. Only D- and G-bands attributable to graphitic carbon were found.

These data indicate that, in the same experimental conditions, good-quality continuous diamond films can be grown on unetched cemented carbides at deposition temperatures lower than 850°C and that the use of Ni as a binder is preferable to Co.

#### IV. Conclusions

Diamond deposits were grown by HFCVD on Ni-cemented tungsten carbide in the 600°–1050°C temperature range. Pure diamond films were obtained, at temperatures as low as 660°C, irrespective of the presence of Ni on the substrate surface. The possibility of growing pure diamond films at low temperatures is very important to improve the adhesion to the substrate. In fact, the residual compressive stress in the film, due to the thermal expansion mismatch with the substrate, reduces as the deposition temperature decreases.

The deposition temperature affects the purity of diamond films. The lower the substrate temperature, the better the quality of the films. The methane concentration does not influence the nucleation density or the growth rate, but the higher the CH<sub>4</sub> concentration, the less the crystallinity of the diamond and thus the purity.

Diamond nucleation on scratched Ni-cemented WC occurs via a heterogeneous nucleation process. The nucleation density is slightly affected by the substrate temperature in the 600°–900°C range, showing that all nucleation sites are transformed into stable nuclei. At higher temperatures there is a great reduction in nucleation density, attributable to the thermal annealing of nucleation sites. The growth rate is controlled by surface reactions taking place at the diamond/gas interface.

An internal comparison between unetched WC-Ni and WC-Co substrates showed that, when cobalt is present on the surface, a slightly higher codeposition of non-diamond carbon phases occurs under identical experimental conditions. This finding confirms that nickel is preferable as a binder to cobalt, insofar as the purity of deposited diamond films is concerned.

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