

Diamond deposition on cemented carbide by chemical vapour deposition using a tantalum filament

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Diamond deposition on WC-Co cemented carbide was examined by chemical vapour deposition using a tantalum filament. The filament was much superior to conventional tungsten filament for high-temperature use. Diamond film was deposited at a filament temperature up to about 2600°C for tantalum filament, which was much higher than the maximum filament temperature available for tungsten (2000°C). The critical methane concentration in H₂-CH₄ gas for diamond deposition became higher with increasing filament temperature. A deposition rate about 20 times higher was obtained when using a tantalum filament compared with a tungsten filament. The origin of the improved deposition rate of diamond on WC-Co substrate using a tantalum filament is discussed.

1. Introduction

It has been reported that diamond films can be synthesized by chemical vapour deposition (CVD) processes [1-9]. Diamond coating by CVD processes has become a useful technique for cutting tools, wear-resistant parts and corrosion-resistant materials. The method of activating reaction gases using a hot filament [2, 5-8] is an important CVD process, as are plasma methods using micro-wave or radio frequency [3, 4, 9]. However, the deposition rate of diamond film is low, i.e. below about 0.5 μm h⁻¹ in the conventional hot-filament method using a tungsten filament. The deposition rate is limited by the maximum filament temperature available, approximately 2000°C. The limitation results from the deformation of tungsten filament.

In the present study, the applicability of tantalum filament for high-temperature diamond deposition on WC-Co substrate by CVD process was examined.

2. Experimental procedure

Fig. 1 shows a schematic drawing of the diamond deposition apparatus used. The conditions for diamond deposition are listed in Table I. Commercial tantalum, wire, 0.5 mm diameter and 99.95% purity, was used as a filament. Tungsten wire, 0.5 mm diameter and 99.9% purity, was also used for comparison. At first, the deformation of tantalum and tungsten filaments were examined by heating in H₂-5% CH₄ gas at 2200 to 2400°C for 0.5 to 4 h. The filament temperature (T_f) was measured using an optical pyrometer. X-ray diffraction (XRD) analysis was made by SHIMAZU

VD-1 to follow the phase change of the filament material during carburization. For the analysis, the filament was crushed to powder form.

The diamond deposition experiments were carried out using carburized tantalum filaments. The WC-3 mass % Co with a WC grain size of about 1 μm was used as a substrate whose size was 4 × 8 × 2 mm³. The substrate surface was polished, scratched by diamond powder and then etched in HNO₃ solution to remove cobalt phase near the surface. Such treatments were effective to enhance the nucleation of diamond particles on the substrate [7, 8]. The substrate temperature (T_s) was measured using a thermocouple inserted into the substrate as shown in Fig. 1, which was kept at about 900°C by heating and/or cooling the substrate holder. Surface structures were examined by scanning electron microscopy. Raman spectra were measured to identify the type of surface deposits present.

3. Results

3.1. Filaments

Fig. 2 shows the appearance of tantalum and tungsten filaments heated in H₂-5% CH₄ at T_f of 2200°C for 1

TABLE I Conditions for chemical vapour deposition

Gas composition	H ₂ -(1 to 10)% CH ₄
Total gas pressure	4 kPa
Total gas flow rate	20 ml min ⁻¹
Filament temperature (T_f)	2000 to 2800°C
Substrate temperature (T_s)	900°C
Distance between filament and substrate	5 mm

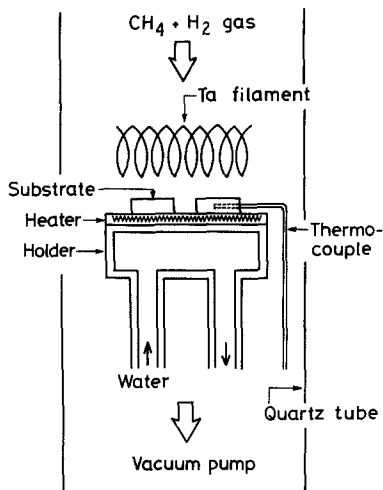


Figure 1 Schematic drawing of the diamond deposition apparatus.

and 4 h. The tantalum filament deforms very slightly at this temperature even after heating for 4 h, while the tungsten filament shows marked deformation particularly after 4 h. It was found that the tantalum filament kept its original shape with limited deformation below about 3000°C; i.e. the resistance to deformation of tantalum filament is superior to that of tungsten filament. This means that tantalum filament is available for diamond synthesis at much higher T_f than is tungsten filament. The filament deformation was marked only in a carburizing atmosphere; both filaments deformed little on heating in H_2 gas at 2200°C for 4 h.

Fig. 3 shows the X-ray diffraction patterns of tantalum filaments heated in $H_2-5\% CH_4$ at 2200°C at various heating times. The Ta_2C and TaC peaks appear for heating times of 0.5 and 1 h, but only TaC peaks appear after 2 h. Both W_2C and WC peaks were detected for tungsten filaments heated in $H_2-5\% CH_4$ at 2200°C up to 2 h, and only WC peaks were found for 4 h heating. In Fig. 3, the TaC peaks shift slightly towards lower diffraction angles with increasing heating time, which corresponds to an increase of lattice parameter of TaC. The lattice parameter of TaC is plotted as a function of heating time in Fig. 4. The TaC has a large composition range from $TaC_{0.6}$ to

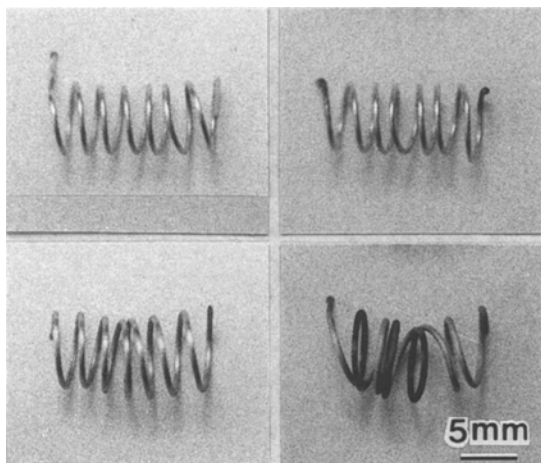


Figure 2 Appearance of tantalum and tungsten filaments heated in $H_2-5\% CH_4$ at 2200°C. Heating time: (a) 1 h, (b) 4 h.

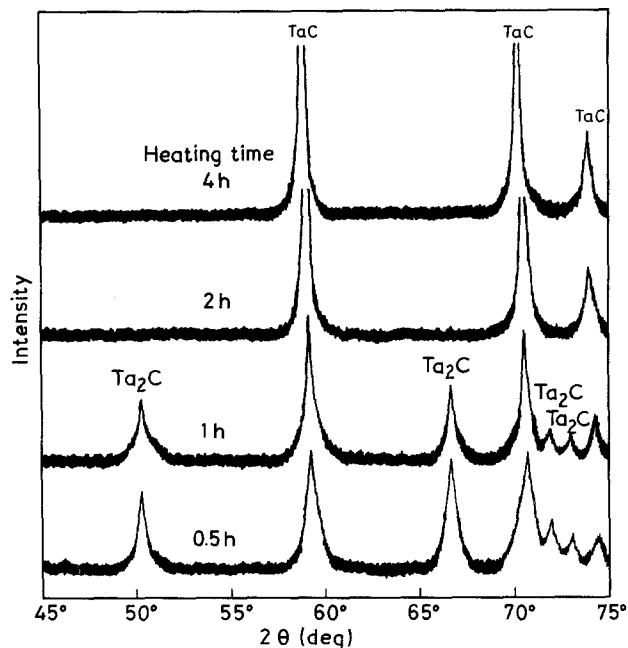


Figure 3 X-ray diffraction patterns of tantalum filaments heated in $H_2-5\% CH_4$ at 2200°C for 0.5 to 4 h. $CuK\alpha$ radiation was used.

$TaC_{1.0}$ and its lattice parameter increases with carbon content [10]. The lattice parameter increase with increasing heating time in Fig. 4 probably reflects the increments of carbon content in TaC up to stoichiometric composition, $TaC_{1.0}$.

Fig. 5 shows cross-sections of tantalum filaments heated at 2200°C in $H_2-5\% CH_4$ for 1 and 4 h. The microstructure of the filament heated for 1 h consists of three layers; tantalum core, Ta_2C and TaC phases. Among these phases, the peaks from tantalum were not detected in XRD patterns as in Fig. 3. This may be caused by the fact that tantalum phase could not be so finely crushed as to be detected by XRD analysis. The filament consists only of TaC phase after heating for 4 h, in agreement with XRD analysis.

3.2. Deposits

At $T_f = 2000^\circ C$, the conditions for obtaining diamond were almost the same as those in previous results for tungsten filament [7, 8]. That is, the deposits consisted of diamond in a CH_4 gas concentration below about 1% at $T_s \approx 900^\circ C$.

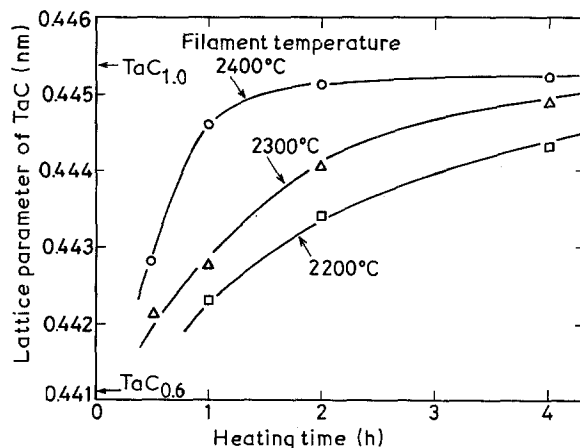


Figure 4 Effect of heating time and filament temperature on the lattice parameter of TaC. Atmosphere: $H_2-5\% CH_4$.

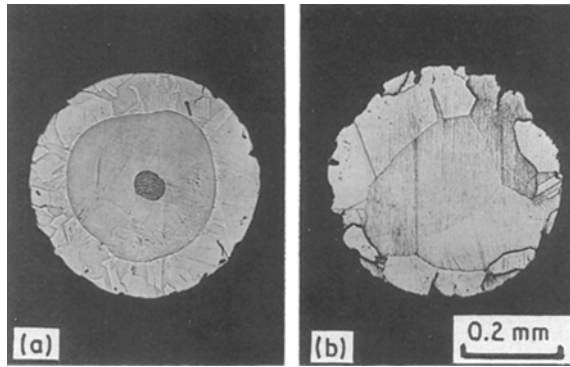


Figure 5 Cross-sections of tantalum filaments heated at 2200°C in H₂-5% CH₄ etched in Murakami's reagent. Heating time: (a) 1 h, (b) 4 h.

Fig. 6 shows the micrographs of deposits formed in H₂-1% CH₄ at various T_f . Up to $T_f = 2700^\circ\text{C}$, T_s could be kept at about 900°C, but it rose to about 1000°C for $T_f = 2800^\circ\text{C}$ due to the limitation of cooling efficiency of the present apparatus. Granular structures are formed below $T_f = 2700^\circ\text{C}$, in which the size of grains becomes larger at higher T_f . On the other hand, a very fine structure is developed at $T_f = 2800^\circ\text{C}$.

Fig. 7 is the Raman spectra of the deposits formed at various T_f . In the spectra at T_f from 2400 to 2700°C, a sharp peak at 133.4 mm⁻¹ is observed at each temperature, which is characteristic of diamond [2]. The spectrum at 2800°C has two broad peaks at 156.0 and 136.0 mm⁻¹ which are characteristic of graphitic carbon [2]. A broad peak around 156.0 mm⁻¹ in the spectrum at 2700°C may also arise from graphitic carbon.

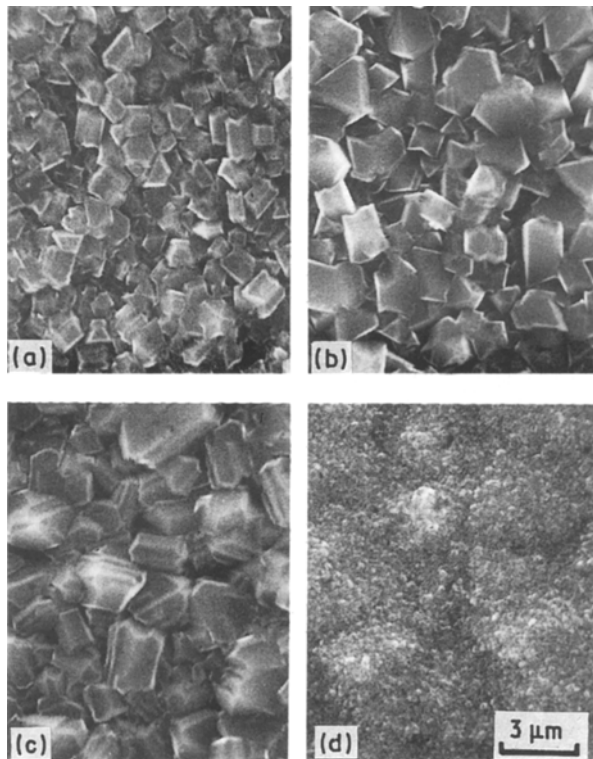


Figure 6 Scanning electron micrographs of surface layers deposited for 1 h in H₂-1% CH₄ at T_f of (a) 2400°C, (b) 2600°C, (c) 2700°C and (d) 2800°C, respectively.

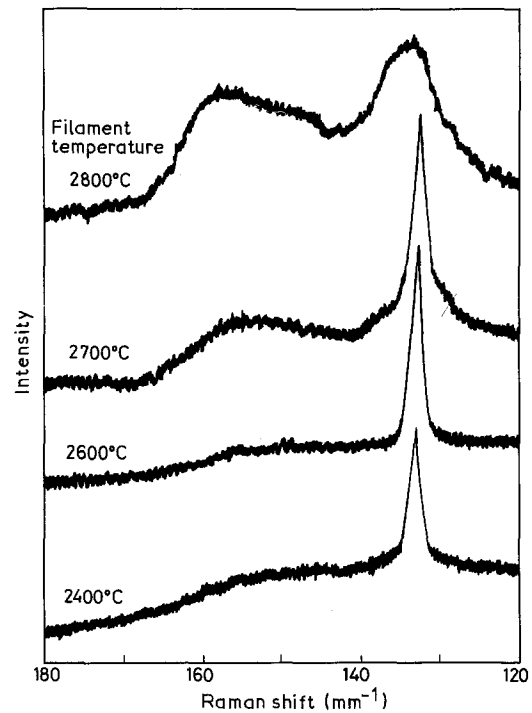


Figure 7 Raman spectra of surface deposits.

Fig. 8 shows the effect of T_f on the mean thickness of diamond film deposited for 1 h in H₂-1% CH₄. The thickness, i.e. the deposition rate, increases exponentially with increasing T_f . The deposition rate at 2700°C is about ten times as large as that at 2000°C.

The effect of CH₄ concentration in flowing gas on the microstructure and the Raman spectra of deposited films are shown in Figs 9 and 10, respectively. The experiments were performed at constant $T_f = 2600^\circ\text{C}$ and $T_s = 900^\circ\text{C}$. Polycrystalline diamond film was formed for CH₄ concentrations up to 5%. For 7% CH₄ gas, the polycrystalline structure deteriorated, and the peaks of graphitic carbon appeared in the Raman spectra together with the peak of diamond. The film formed in 10% CH₄ gas consisted mainly of graphitic carbon, which had finer microstructure than polycrystalline diamond. It has been reported that the polycrystalline diamond is deposited at CH₄ concentrations below about 1% at 2000°C [2, 7, 8]. The present results indicate that the diamond is deposited

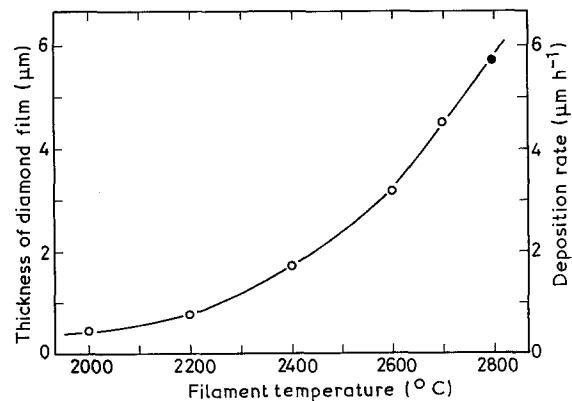


Figure 8 Effect of T_f on the mean thickness of diamond film deposited for 1 h in H₂-1% CH₄. The film contained a large amount of graphitic carbon at 2800°C.

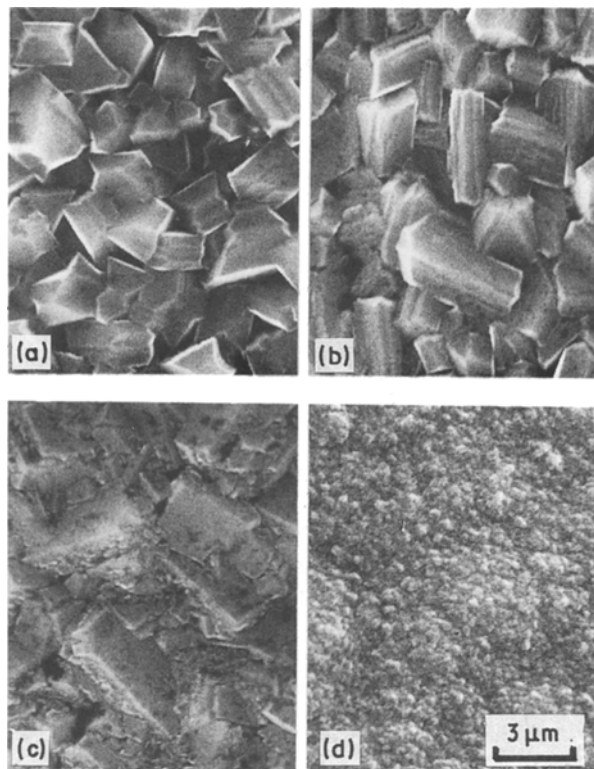


Figure 9 Effect of methane concentration on the surface microstructures of films deposited at $T_f = 2600^\circ\text{C}$ for 1 h. Methane concentration: (a) 3%, (b) 5%, (c) 7%, (d) 10%.

at higher CH_4 concentrations at 2600°C than at 2000°C .

Fig. 11 shows the effect of CH_4 concentration on the mean thickness of films deposited at $T_f = 2600^\circ\text{C}$ for 1 h. The thickness, i.e. the deposition rate, increases markedly with increasing CH_4 concentration. The maximum deposition rate of diamond at 2600°C was

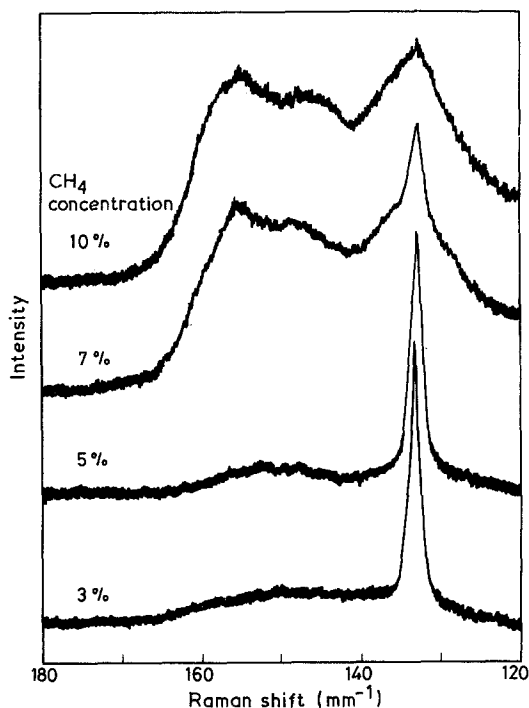


Figure 10 Raman spectra of deposited films formed in various methane concentrations. The deposition conditions are the same as those in Fig. 9.

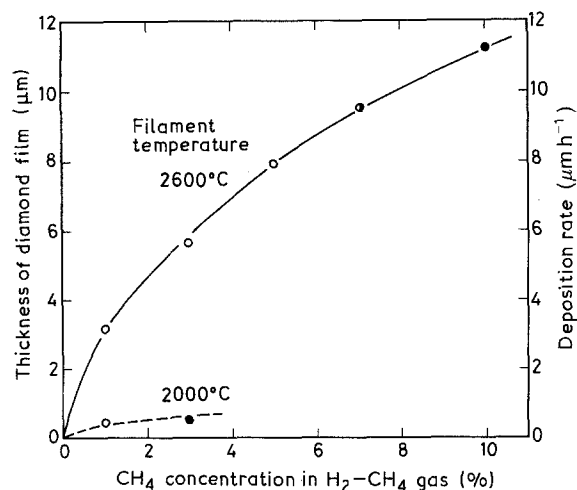


Figure 11 Effect of CH_4 concentration on the mean thickness of deposited films at $T_f = 2600^\circ\text{C}$ for 1 h. Substrate temperature was kept at 900°C .

about $8 \mu\text{m h}^{-1}$ for 5% CH_4 , which was about 20 times larger than that at 2000°C for 1% CH_4 .

Fig. 12 shows the cross-sections of diamond-coated samples. The diamond films have columnar grains whose diameter becomes larger from the interface between film and substrate to the surface.

4. Discussion

4.1. Tantalum filament for high-temperature use

Diamond synthesis by CVD has been made by using tungsten filament. The maximum temperature available for this process was about 2000°C due to the limitation of filament deformation. The present study revealed that tantalum filament is a useful material for diamond deposition up to about 2700°C in H_2 -1% CH_4 gas. The tantalum filament is much superior to tungsten filament for high-temperature CVD, despite the fact that tantalum has a lower melting temperature ($T_m = 2990^\circ\text{C}$) than tungsten (3380°C) [11]. This is because the filament is carburized during the process, i.e. tungsten and tantalum filament finally change into WC and TaC, whose T_m are 2785 and 3985°C , respectively. The high T_m of TaC is probably the origin of the high-temperature resistance of the original tantalum filament. The homologous temperature T/T_m of 2000°C is 0.74 for WC and 0.53 for TaC. It is possible to expect that WC will be deformable above about 2000°C due to the high T/T_m as experimentally found in this study. A material which forms a stable carbide with high T_m , may be suitable for the filament material for hot-filament CVD at high temperatures.

4.2. The deposition rate of diamond

It has been pointed out that the generation of activated species of hydrocarbon with sp^3 hybridized C-C bond, and also of atomic or ionic hydrogens around a hot filament, is important in diamond deposition on a substrate [1, 2, 12]. The diamond is not formed directly from CH_4 gas, but probably from the activated species. Various types of activated species may participate in the diamond deposition [12]. However, the

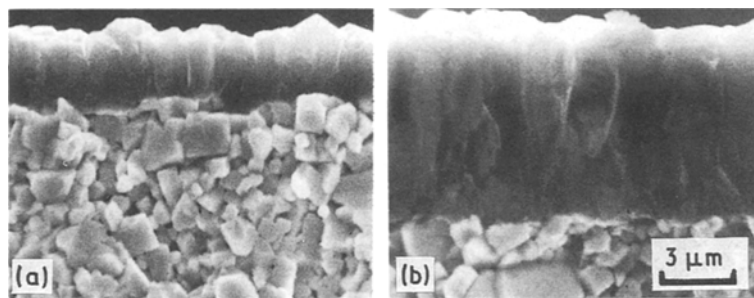


Figure 12 Cross-sections of diamond-coated WC-Co obtained at $T_f = 2600^\circ\text{C}$ for 1 h in methane concentration of (a) 1% and (b) 5%. F, diamond film; S, substrate.

critically important species for diamond deposition has not yet been identified. On the other hand, two roles of atomic or ionic hydrogens have been proposed [12]; (1) the attack and removal of graphitic carbon deposited on the surface, and (2) the prolonged lifetime of the activated species and/or the decomposition of the species into a higher-energy state, i.e. a hydrocarbon with lower hydrogen content. Although it has not been clarified which role is dominant, the importance of atomic or ionic hydrogens may be understood from the fact that the diamond is deposited only in $\text{H}_2\text{-CH}_4$ gas of low methane concentration. It is expected from the dissociation constant for the reaction [13], $\text{H}_2 \rightarrow 2\text{H}$, that the content of atomic hydrogens in the gas increases exponentially with temperature. Such an increase of atomic or ionic hydrogens may induce the increased deposition rate of diamond at higher temperatures, which is $0.4 \mu\text{m h}^{-1}$ at 2000°C , and $3 \mu\text{m h}^{-1}$ at 2600°C for a gas containing 1% CH_4 as in Fig. 8. The present data indicate that an additional effect arises at higher filament temperature. The critical CH_4 concentration to produce diamond increases at higher temperatures as in Figs 9 to 11. The critical concentration is about 1% CH_4 at 2000°C and 6% CH_4 at 2600°C , which results in the increment of maximum deposition rate of diamond at higher filament temperature. The present result shows that the use of tantalum filament is very effective for improving the deposition rate of diamond on cemented carbides.

5. Conclusion

The applicability of tantalum filament for diamond deposition on WC-Co substrate by thermal CVD was examined. The following results were obtained.

1. The tantalum filament was much superior for high-temperature use compared with tungsten filament. The maximum available temperature was about 2600°C for tantalum and about 2000°C for tungsten.

2. The filaments were carburized in $\text{H}_2\text{-CH}_4$ gas during the CVD process. The final products were stoichiometric TaC for tantalum filament and WC for tungsten filament. The much higher melting tempera-

ture of TaC than WC is the origin of the superiority of tantalum filament for high-temperature use.

3. The deposition rate of diamond film increases with increasing T_f at a constant CH_4 concentration. The deposition rate at 2600°C in $\text{H}_2\text{-1% CH}_4$ was about eight times that at 2000°C ; about $3 \mu\text{m h}^{-1}$ at 2600°C and about $0.4 \mu\text{m h}^{-1}$ at 2000°C .

4. The high T_f enabled the diamond formation to occur at higher CH_4 concentration. Thus, the maximum deposition rate of about $8 \mu\text{m h}^{-1}$ was obtained at 2600°C .

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