

INVESTIGATIONS OF DIAMOND LAYERS GROWTH ON STEEL

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A hot-filament-assisted chemical vapour deposition system has been used in an attempt to grow diamond layers on steel substrates. Deposition of diamond layers was performed in hydrogen-methane gas mixture. To overcome the common problems associated with the nucleation and growth of diamond on steel, the substrates were first coated with thin chromium nitride buffer layers. The results obtained in this study show that chromium nitride layer can provide a viable solution for deposition of continuous and adherent diamond layers on steel. The study indicates that thicker CrN layers can accommodate more easily the residual stresses which develop upon cooling. It was also found that diamond layers containing small amounts of non-diamond phase, grown at lower substrate temperature are less prone to cracking and delamination.

Keywords: Diamond layers, Chemical vapour deposition (CVD)

1. Introduction

Due to its exceptional properties – highest hardness, highest room temperature thermal conductivity, extreme electrical insulation, high sound propagation velocity, wide range optical transparency, superior chemical stability and low coefficient of friction - diamond is a fascinating high technology material [1]. Its potential applications range from optics, electronics and surgical blades to cutting and grinding tools [2,3]. The first synthetic diamond particles were obtained in 1955 at General Electric Research Laboratory [4] by using high temperature and high pressure conditions to convert graphite into diamond. Produced by this method, diamond is in the form of powder and small particles (usually less than 1-3 mm in size) which have been used almost exclusively for fabrication of cutting and grinding tools. An impressive development of diamond applications has started in 1982 when Matsumoto and co. [5] published a detailed procedure for producing diamond layers by chemical vapour deposition (CVD) method. The new technique offered the possibility to coat three-dimensional objects with diamond films extending in this way the application spectrum for diamond. Being very simple and not protected by a patent, the hot-filament-assisted chemical vapour deposition (HF-CVD) apparatus presented by Matsumoto and co. has been extensively used by scientists engaged in the study of diamond coatings. Other CVD systems for growth of diamond layers have also been developed after 1982. Such systems use microwaves [6], acetylene torches [7] or plasma jets [8] as activation means for CVD of diamond.

Polycrystalline diamond films have been grown on various kinds of substrates for engineering applications. Steels are one of the most popular material in today's technology. If diamond could be deposited on them, there would be a large field for applications. However, there are three major obstacles for growing diamond layers on ferrous substrates by CVD techniques [9,10]: (i) diffusion of carbon into these materials at high rates due to high deposition temperature; (ii) catalytic effect of iron on growth of graphite; (iii) high differences between thermal expansion coefficients of diamond and iron which can cause detachment of diamond films upon cooling. To overcome these problems a possible solution is to deposit a buffer layer between steel substrate and diamond layer. Chen and co. [9] reported successful deposition of adherent diamond films on stainless steel using an intermediate layer but its nature is not mentioned in the paper. Ahn and co. [10] indicated in their study that a silicon buffer layer can block diffusion of carbon and iron catalytic effect. Aluminium nitride [11] and

titanium nitride [12] intermediate layers have also been proposed as possible solutions, but the results were only partially satisfactory.

In this paper, an attempt to deposit diamond layers on tool steel substrates is presented. In a search for a suitable buffer layer, special attention was paid not only to minimise carbon diffusion and catalytic effect of iron on graphite formation but also to limit the residual stress in the diamond film upon cooling from deposition temperature. The results obtained by using chromium nitride as intermediate layer are encouraging and could represent a viable solution for growing diamond films on steel.

2. Experimental details

Substrates were cut from A2 tool steel bars at dimensions $14 \times 8 \times 2 \text{ mm}^3$. One side of the substrates was mirror polished and then coated with a CrN layer by reactive magnetron sputtering [13,14]. The thickness of the CrN layer varied from $0.6 \text{ }\mu\text{m}$ to $6.5 \text{ }\mu\text{m}$. For comparison, a steel substrate was also exposed to conditions for diamond growth without being coated with CrN layer.

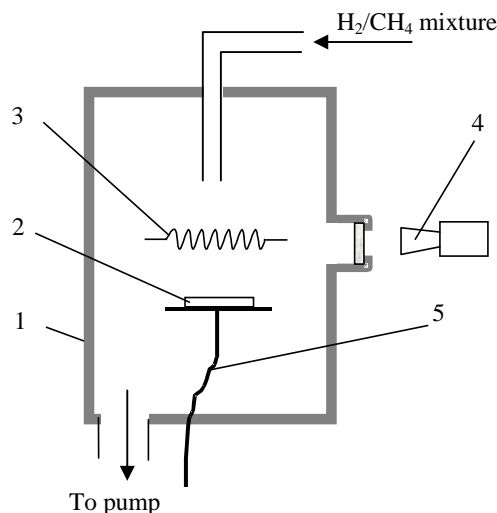


Fig. 1. Schematic illustration of the HF-CVD system used for deposition of diamond films:
1 - vacuum chamber; 2 - substrate; 3-tungsten filament; 4-infrared pyrometer; 5-thermocouple.

Prior diamond deposition, samples were slightly polished with $0.25 \text{ }\mu\text{m}$ diamond particles to promote higher nucleation density and then ultrasonically cleaned in acetone and methanol. Deposition of diamond was carried out in a HF-CVD system similar to that described by Matsumoto and co. [5]. A schematic presentation of the deposition reactor used in this study is shown in Fig. 1. A hydrogen-methane mixture was used as a reaction environment. The substrates were placed just below a heated tungsten filament which here plays a double role: to thermally activate the chemical reactions needed for diamond growth (mainly formation of atomic hydrogen and decomposition of methane into more reactive fragments) and to heat the substrate to desired temperature. Since no additional heater for the substrate was used in this study, its temperature was adjusted by modifying the distance between filament and substrate. The tungsten filament was resistively heated using a low voltage a.c. power supply and its temperature was measured by an infrared pyrometer. To avoid the phase transition of steel substrates which occurs around $780 \text{ }^\circ\text{C}$, its temperature was kept well below this value. However, because substrate temperature was measured by a chromel-alumel thermocouple placed in contact with the back side of the substrate, the true temperature of the substrate surface may have been somewhat higher than measured values. The main deposition conditions are presented in Table 1.

After deposition, samples were examined mainly by scanning electron microscopy (SEM). Raman spectroscopy was also used to characterise diamond films deposited on several samples.

Table 1. Deposition conditions used for diamond growth.

Parameter	Value
Filament temperature, T_f , [°C]	2000
Substrate temperature, T_s , [°C]	450 – 600
Distance filament-substrate, d_{fs} [mm]	5 – 10
Pressure, p , [kPa, (Torr)]	2,6 (20)
Gas composition (H_2/CH_4 ratio), [vol. %]	99/1
Total gas flow, Φ_g , [sccm]	200
Deposition time, t , [h]	2 – 4

3. Results and discussions

The carbon film deposited on uncoated steel substrate had a black colour and was easily removed from the sample by scratching it with a piece of wood. An SEM picture of such a film obtained after a deposition time of 4 h is shown in Fig. 1. The carbon particles display a ball-like shape, very different than normal morphology of diamond particles. Based on the data published in the literature we considered this carbon film to be formed from mainly from graphite and amorphous carbon.

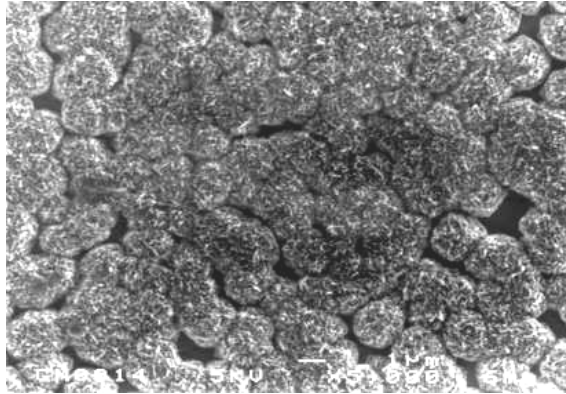


Fig. 2. SEM picture of the carbon film deposited on uncoated steel substrate (deposition time 4 h, substrate temperature 600 °C).

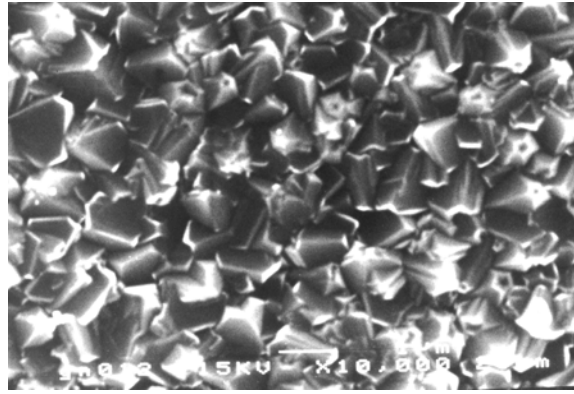


Fig. 3. SEM picture of the diamond film deposited on the steel substrate coated with a 1.5 μm CrN intermediate layer (deposition time 4 h, substrate temperature 600 °C).

The films deposited on the steel samples coated with a 4.0 μm CrN intermediate layer have shown highly faceted, polycrystalline diamond grains as presented in Fig. 2. However, due to residual stresses, the diamond film cracked and delaminated itself upon cooling from more than 80% of the substrate surface. It appears that 1.5 μm CrN intermediate layer can prevent rapid diffusion of carbon towards substrate and that of iron towards surface and therefore allow diamond nucleation and growth. Though, the thermally induced residual stress in the diamond layer must have been still very high and led to cracking and delamination of the diamond film. Since diamond film detached from the substrate at the interface with the CrN layer it was concluded that CrN follows the expansion and contraction of the steel substrate during heating and cooling even though the coefficient of thermal expansion of CrN is much closer to that of diamond than to that of steel (thermal expansion coefficients, α [$\times 10^6 \text{ K}^{-1}$], are: 10.5 – 13 for steel, 2.3 for CrN and 0.9-1.2 for diamond [14,15]. The magnitude of the thermally induced stresses, σ_{th} , in the diamond coating and CrN layer are proportional to the differences between the thermal expansion coefficients of the materials in contact, $\Delta\alpha$, and with temperature change measured from stress-free state (considered to be at deposition temperature) to room temperature, ΔT , according to the following relationship:

$$\sigma_{th} \approx E \cdot \Delta\alpha \cdot \Delta T$$

where E is the Young's modulus of the layer. The very high value of the residual stress develops in the diamond film due to its high Young's modulus and because the thin ($1.5 \mu\text{m}$) CrN layers actually follows the expansion and contraction of the substrate. An improvement in the adhesion of the diamond film was achieved by applying thicker CrN layer ($6.5 \mu\text{m}$). In contrast to this result, when thinner ($0.6 \mu\text{m}$) CrN films were used as buffer layers, the diamond films detached from the substrate even when the nucleation density was low and the diamond film was not continuous. In Fig. 3 it is shown such a piece of diamond film detached from the substrate during cooling from deposition temperature. However, the morphology of the film indicates that even such a thin CrN layer can minimise the diffusion of carbon and iron atoms through the CrN layer allowing diamond nucleation and growth to take place. These observations lead to the conclusion that the thicker the CrN layer the smaller the residual stress in the diamond film. The residual stresses between the diamond film and the steel substrate appears to be distributed mostly across the CrN layer and its interfaces with the steel substrate and the diamond layer.

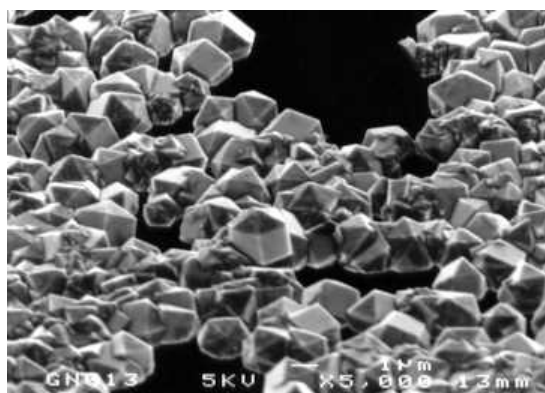


Fig. 4. SEM picture of the diamond film deposited on the sample coated with $0.6 \mu\text{m}$ CrN layer (deposition time 2 h, substrate temperature 600°C).

In order to further reduce the residual stress in the diamond film, the substrate temperature was reduced to 400°C . The morphology of the films deposited at this temperature displayed less faceted and much smaller diamond grains as shown in Fig. 3. Analysis of the film by Raman spectroscopy showed that the film consists mainly of diamond phase as indicated by the peak situated around 1335 cm^{-1} in the Raman spectrum as presented in Fig. 4. The broad peak located around 1580 cm^{-1} in the Raman spectrum is due to the presence of an amorphous carbon phase in the film formed because of the lower substrate temperature.

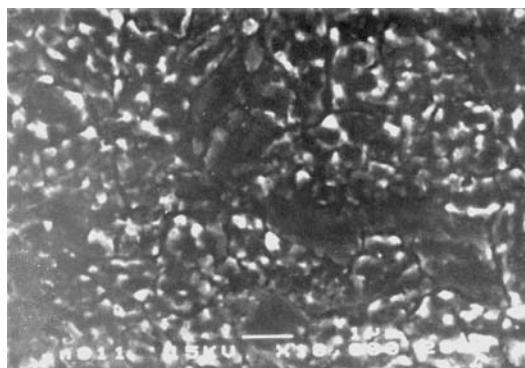


Fig. 5. SEM picture of the diamond film deposited at 400°C substrate temperature for 4 h on a steel substrate coated with $4 \mu\text{m}$ CrN intermediate layer.

The adhesion of the diamond films was performed by applying a pressure sensitive adhesive tape onto the surface of the diamond film and pooling it off to reveal the degree of the coating detachment. Though, this method is considered rather crude, it is still accepted in the industry. The tests performed with the adhesive tape showed that diamond films deposited at lower substrate temperature (400 °C) and using thicker ($>4\text{ }\mu\text{m}$) CrN buffer layers pose very good adhesion. These diamond films were not detached from the substrate during the tests.

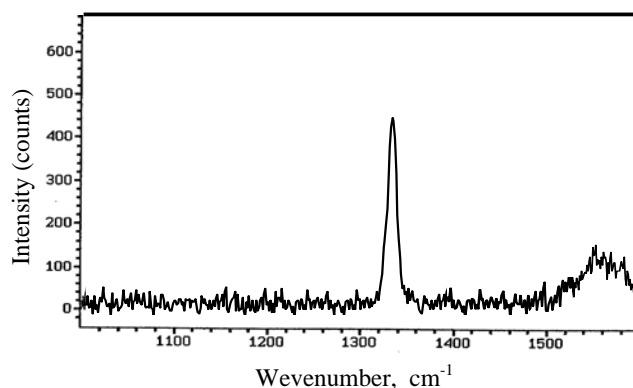


Fig. 6. Raman spectrum of the diamond film shown in Fig. 3.

4. Conclusions

A study on diamond growth on steel substrate was carried out. The results achieved in this study led to the following conclusions:

- No diamond could have been grown directly on steel; graphite and amorphous carbon formed instead.
- By applying a CrN intermediate layer the diffusion of carbon toward the substrate was prevented and polycrystalline diamond films were obtained.
- The adhesion of the diamond film to the substrate was improved by reducing the substrate temperature during deposition and by increasing the thickness of the CrN layer.
- When a thicker CrN intermediate layer was used, the residual stress in the diamond film appeared to diminish due to closer values in the thermal expansion between the two materials. The residual stress between steel substrate and diamond is distributed across the CrN layer (if thick enough) and its interfaces with steel and diamond.

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