DIAMOND COATINGS ON CUTTING TOOLS BY HOT FILAMENT CVD

By

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DIAMOND COATINGS ON CUTTING TOOLS
BY HOT-FILAMENT CVD

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"Guru Bramha Gurur Vishnu Guru Devo Maheshvaraha
Guru Sakshath Parabramha Thasmi Shree Gurave Namaha"

The above Sanskrit verse equates the teacher to the trinities of Hinduism and ends with the student worshipping the teacher. With this I would like thank my advisor Dr. Komanduri for his guidance, support, and advice. I also would like to express my appreciation to Dr. Lucca and Dr. Ghajar and thank them for serving on my thesis committee.

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1. INTRODUCTION

Machining of abrasive work materials such as aluminum-silicon alloys, glass- epoxy composites using conventional tools such as high speed steels and cemented tungsten carbide results in rapid wear of cutting tools. Diamond being the hardest material, is perhaps the best and ultimate tool material. Therefore, polycrystalline diamond (PCD) tools made by the high pressure-high temperature (HP-HT) technique are being used for some of these applications. In PCD the thickness of the diamond layer on top of a cemented tungsten carbide tool is typically in the range of 0.5 to 1.5 mm. After this synthesis, the tools have to be shaped and finished using diamond grinding which is rather expensive. Because of this, the cost of the tool is very high.

Synthesis of diamond at low pressure was initiated about the same time as the HP-HT technique (Eversole, 1962). The important aspect of this method is that it does not require a HP-HT press. Hence, the capital cost involved in this method is low. Since, a thin layer of diamond coating (about 5 μm) is deposited on the finished tool, the need to finish diamond layer by grinding is eliminated, thus reducing the cost of manufacturing of the tool significantly. But, the initial growth rates by this method were very low only of the order of a few Å/hour. Hence, this method was not considered as a viable alternative at that time. Also, diamond is metastable under low pressure. Therefore, graphite formation was predominant and it was necessary to remove graphite periodically before further diamond deposition. Scientists from the former U.S.S.R found that introducing hydrogen over at 2000°C results in the formation of atomic hydrogen, which preferentially etches graphite leaving the diamond intact. As a result, the growth rates of diamond improved from few a Å/hour to about 1 μm/hour (Matsumoto,1982). Since, only about 5 μm coating is required for cutting tools, the low pressure chemical vapor deposition (CVD) becomes a viable alternative.

Table 1 gives some of the properties of diamond and other tool materials. It can be seen that there are significant differences in the properties between diamond and other tool materials which are considered as substrates for diamond coating. Because of this difference in properties, the greatest challenge is to produce adherent diamond coating on the tool substrates. The most widely used tools are cemented tungsten carbide, coated cemented tungsten carbide (titanium nitride or titanium carbide), and, silicon nitride. Hence, in the present investigation these tools are used as substrate materials.

Table 1 Properties of Diamond and Different Tool Materials (Lide Frederikse, 1994)

Material	Structure	Thermal Expansion Coefficient, $10^{-6}/^{o}C$	Lattice Constant, Å	Melting point, ^{o}C	Hardness, kg/mm^2
Diamond	Cubic	3.1	3.56	1500*	8000
Silicon Nitride	Hexagonal	3.5 (β–phase)	a = 7.6 c = 2.8	1900	1800
Tungsten Carbide	Hexagonal	5.0	a = 2.9 c = 2.831	2630	1500-1800
Titanium carbide	Cubic	7.4	4.315	3160	3200
Titanium nitride	Cubic	9.3	4.225	2930	1800 - 2000

* Graphitization temperature of diamond in vacuum

In Chapter 2 various methods of chemical vapor deposition techniques are described. Chapter 3 presents a review of the literature on low pressure diamond coatings on cutting tools by various techniques in general and HF-CVD in particular. The problem statement of the present investigation is given in Chapter 4. The description of the experimental set up used in the present investigation is described in Chapter 5. The experimental procedure, test results and discussion are covered in Chapters 6, 7, and 8, respectively. Chapter 9 presents the conclusions of present work.

2.0 CVD TECHNIQUES FOR DIAMOND DEPOSITION

Metastable growth of diamond occurs at low pressures when hydrocarbon gases are energized in the presence of hydrogen (Anthony, 1991). This process is shown by the following reaction:

$$CH_4 \xrightarrow{\text{Heat}} \text{Deposit (Diamond + Graphite)} + 2H_2$$

$$H_2 + \text{Deposit} \xrightarrow{\text{Heat}} \text{Diamond} + CH_4$$

A large number of CVD techniques, based on these and similar reactions have been developed. Table 2 summarizes various methods presently used to grow diamond using this principle (Lux and Haubner, 1989). The basic difference in these processes is the method used to supply energy to the reaction. The reaction can be activated either by high temperatures, electrical discharge, electromagnetic discharge, plasma jets or by a combination of these. The most widely employed techniques are the hot filament, microwave, and combustion synthesis. A brief description of these methods will be given in the following.

2.1 Hot Filament CVD (HF-CVD)

Developed in 1912, hot filament CVD (HF-CVD) was the initial method used for diamond growth. Figure 1 is a schematic of a typical setup of a HF-CVD reactor. Important process parameters and their typical values employed in this method are given in Table 3. In this method, a filament is heated to a temperature of 1,950°C - 2,300°C. Generally, the filament is made of tungsten, tantalum, or rhenium. A heated (700°C -1,000°C) substrate is placed at a

Table 2 Classification of Various Activated CVD Techniques for Diamond Synthesis (Lux and Haubner, 1989)

1	Activation by High Temperature • Hot Filament • Thermal Decomposition • Chemical Transport Reaction • Combustion Flame
2	DC Plasma CVD • Low Pressure DC Plasma • Medium Pressure DC Plasma • Hollow Cathode Discharge • DC Arc Plasma • DC Plasma Jet
3	RF Plasma CVD • Low Pressure RF Glow Discharge • Thermal RF plasma
4	Microwave Plasma CVD • 915 MHz Plasma • Low Pressure, 2.45 GHz Plasma • Atm. Pressure, 2.45 GHz Plasma
5	Combined Activation • Hot - Filament - Microwave • Hot - Filament - DC Discharge • Hot- Filament - Bias

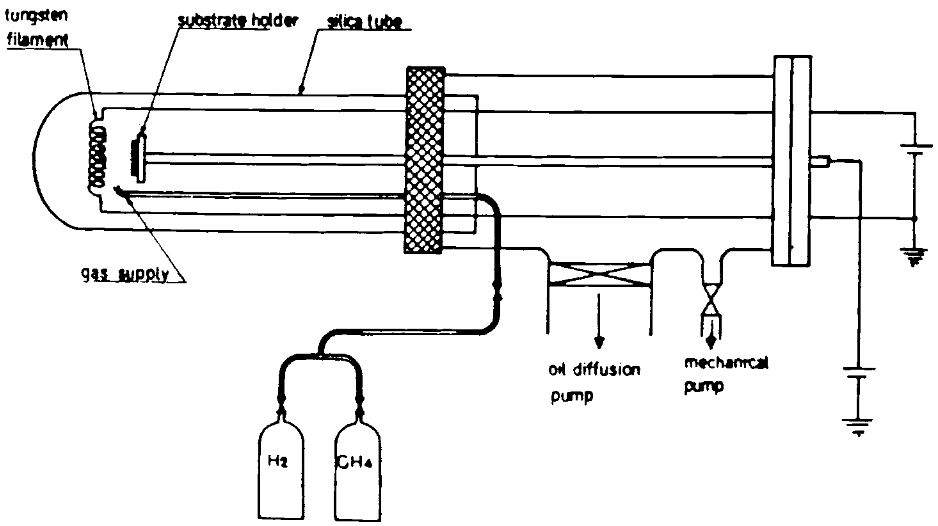


Figure 1 Schematic of a typical setup of HF-CVD reactor (after Bonnot, 1990)

Table 3 Typical Conditions for Diamond Deposition In HF-CVD (after Klages, 1993)

Filament Temperature,^{o}C	1950 -2300
Substrate Temperature,^{o}C	700 - 1000
Pressure, torr	20-50
Flow of rate CH_4/H_2 , sccm	0.5/99.5
Substrate - Filament Distance, mm	1- 20

distance of 1 to 20 mm from the filament. A mixture of molecular hydrogen and gaseous hydrocarbon (e.g methane) is passed over the heated filament. The molecular hydrogen, present in the mixture, is converted to atomic hydrogen at high filament temperatures. The atomic hydrogen thus formed facilitates the formation of diamond and etch any graphite that is formed during the reaction.

The reaction chamber is generally made of quartz or steel. The growth rates in this method are in the range of 0.3-2 μm/hr (Bachmann and Lydtin, 1991). The growth rates can be further increased by providing a bias to the substrate. The area of deposition is dependent on the filament structure and is typically in the range of 2-100 cm^2. In the present investigation it is about 3 cm^2. The main advantages of this method are the following (Haubner and Lux, 1993):

- the equipment (i.e. reactor and gas activation source) is inexpensive
- large areas of homogeneous deposition are possible by the use of multiple filaments
- deposition conditions can be easily controlled

The main disadvantages are the following

- diamond deposits may contain traces of filament material
- reproducibility is some what lower than microwave deposition systems

2.2 Microwave CVD

Figure 2 shows a typical set up used for microwave assisted CVD diamond synthesis and Table 4 gives typical operating conditions. The system

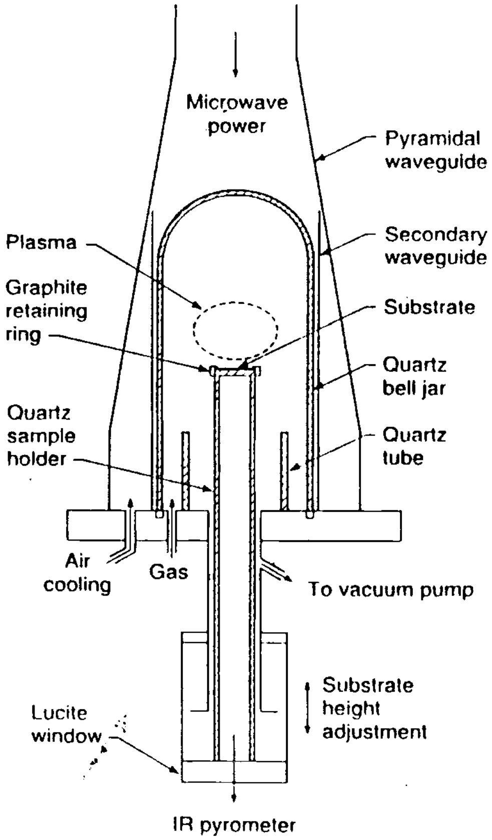


Figure 2 Schematic of a microwave assisted CVD (after Brewer et al, 1992)

Table 4 Typical Conditions for Diamond Deposition in Microwave CVD (after Klages, 1993)

Microwave Power, watts	100-1500
Substrate Temperature ,°C	800-1000
Pressure, torr	20-50
Flow rate of CH_4/H_2, sccm	0.5/99.5

consists of a 2.5 GHz magnetron power source for generating the microwave. A mixture of hydrogen and hydrocarbon gas, such as, methane is introduced into the reaction chamber. The gas mixture is ionized and excited by microwave power leading to the formation of a ball shaped plasma discharge (Brewer et al, 1992). The substrate is brought into contact with the plasma to obtain diamond deposition. The gaseous reactions and nucleation process in this method are similar to HF-CVD. Important process parameters include gas composition, pressure, flow rate, substrate temperature, and microwave power. The diamond growth rates in this method are similar to HF-CVD and are in the range of 1-2 µm/hr. The advantage of this method is that high quality diamond coatings can be produced since good control can be exercised over process parameters. However, this method can not be used for depositing diamond on large areas (>100 cm^2). Hence, microwave CVD is suitable for producing contamination free, uniform coatings on medium (30 cm^2) size substrates.

2.3 Combustion Synthesis

This method employs an oxyacetylene welding torch for diamond deposition (Nandyal, 1991). Figure 3 shows a typical setup used for the combustion synthesis of diamond and Table 5 gives the process parameters and conditions employed in combustion synthesis. The flame, in a welding torch has two regions, namely, the oxidizing flame region and the reducing 'acetylene feather' region. The diamond deposition occurs directly under the acetylene feather. Instead of acetylene, ethylene or ethane can also be used as carbon source in this method. Generally, the ratio of oxygen to acetylene is in the range of 0.9 to 1.1, ethylene to oxygen is in the range of 1.18 to 1.125, and ethane to oxygen is in the range of 1 to 1.63 for diamond deposition (Butler et al, 1990). Typical growth rates of diamond by this method are in the range of 50

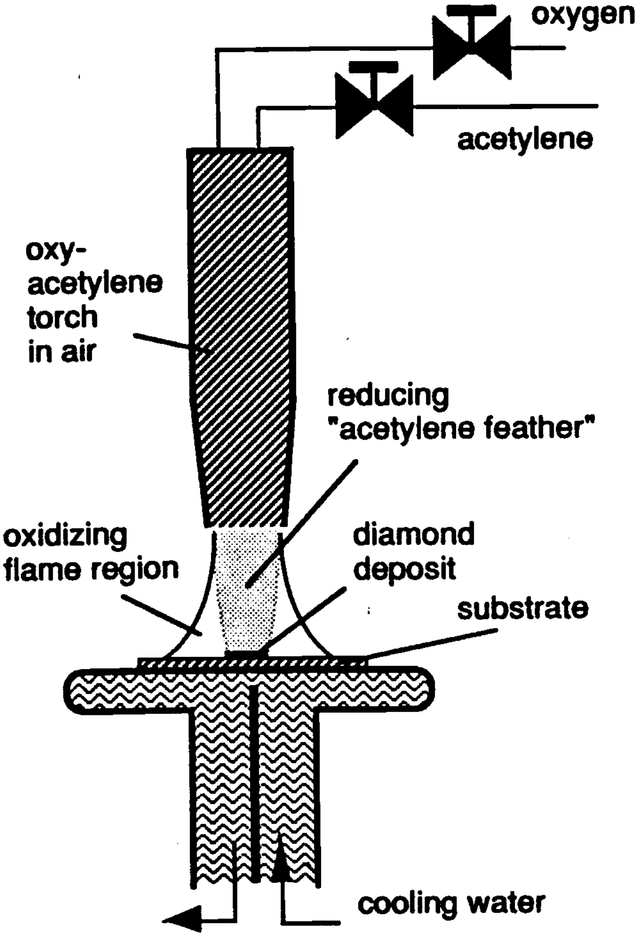


Figure 3 Typical Setup of the Combustion Synthesis (after Bachmann and Lydtin, 1991)

Table 5 Typical Conditions for Diamond Deposition by Combustion Synthesis (after Klages, 1993)

Flame Temperature, °C	3000
Substrate Temperature, °C	400-1100
Pressure, bar	1
Flow rate of $C_2H_4/0_2$, sccm	1000-2000

-150 μm/hr which is significantly higher than that of microwave or hot filament assisted CVD. This method can be employed when high growth rates are required and the contamination of the film is not a major consideration. The main advantages of this method are the following:

- simple set up
- high growth rates (50 - 150 μm/hr)

The main disadvantages are the following:

- control of substrate temperature is difficult
- inhomogeneous deposition
- contamination

3.0 LITERATURE REVIEW

3.1 Diamond Coatings on Cutting Tools

The requirements for diamond coatings on cutting tools are high hardness, wear resistance and strong adhesion to the substrate. The last requirement is posing the greatest challenge to the developers of this technology.

Cemented tungsten carbide tools, because of the wide range of hardness and toughness values, are widely used for cutting. Hence, this is an obvious substrate material for diamond coating. But, diamond coating on this materials suffers lack of adhesion. This is attributed to the presence of cobalt in the cutting tool as a binder (Okoli et al, 1989). Particularly, the presence of cobalt on the surface, leads to the formation of graphite and also the delamination of the diamond coating. To produce cobalt free surface, different techniques such as etching, use of interlayers, have been employed (Soderberg et al, 1991).

Peters et al (1993) employed different techniques including treating the substrate to sand blasting, etching with Murakami's reagent (Potassium hydroxide, Potassium ferricyanide, water in 1:1:10 ratio) to obtain adherent coatings on cemented tungsten carbide tool. They found the etched tools to have better adhesion when compared to depositing on the tool directly and also when compared to the sand blasted tools. Okes et al (1991), Hay and Dean (1991), and Kikuchi et al (1991) etched the surface of the tool with a solution of dilute nitric acid to obtain good adhesion.

Mitsubishi Metal Corp has been producing diamond coated carbide inserts (Mason, 1990). Toshiba Tungaloy (Japan), another tool manufacturer from Japan, found that by decarburizing the surface of the carbide by a hydrogen-oxygen plasma, best adhesion is achieved (Saijo et al, 1991). Toshiba Tungaloy tested these diamond coated cemented tungsten carbide milling inserts by machining Al-20%Si alloy in the 200 - 350 m/min speed range. These tests showed that the diamond coated tools performed better than the uncoated tools. However, the problem of microchipping of diamond film was observed. This was attributed to the collision of hard silicon particles on to the irregular surface of the diamond coating. Hence, Saijo et al polished the diamond coating to reduce the irregularities. This resulted in an increase in tool life by two times and microchipping was reduced.

Idemitsu Petrochemical CO (Tokyo), another manufacturer of cutting tools, has been test marketing the diamond coated inserts in Japan (Mason, 1990). Idemitsu had problems in the adhesion of diamond film to the cemented carbide substrate. This poor adhesion was attributed to the presence of cobalt. Hence, they replaced the substrate with silicon nitride. Diamond coated inserts produced by Idemitsu had a tool life 5 -10 times longer than uncoated silicon nitride insert. In the U.S Crystallume (Mason, 1990), Norton (Stephan, 1992) have achieved considerable success on coating diamond on silicon nitride.

Another cutting tool material which had been considered for coating diamond is SiAlON. Good quality diamond coatings have been obtain by Okoli et al (1989) and Bichler et al (1989).

3.2 Hot Filament CVD

The quest for making diamonds began as early as 1797 when Tennant showed that diamond is a form of carbon (Bridgman, 1955). But until 1954, these attempts to synthesize diamonds were not successful. In 1954, a group of scientists from General Electric successfully produced diamonds using HP-HT method. In this method, a pressure of 100 kbar and 1,500°C is applied simultaneously to convert graphite in to diamonds. Maintaining pressures and temperatures of this order is an expensive process. However, there were speculations since the early days that diamond can be synthesized at high temperatures but using low pressures (metastable conditions) by appropriate processing conditions (Bridgman, 1955).

In 1962, Eversole (1962) showed that the diamond can be grown under low pressures using methane as a precursor under metastable conditions. He used diamond crystals as seed material for growing diamond. The substrate temperature was in the range of 600-1100°C. Eversole, first subjected the diamond crystals to a methane atmosphere for approximately 60 hours. The pressure was in the range of 0.15-2 mm of Hg. After this, the diamond crystals were subjected to hydrogen cleaning. Similar method was employed by Angus et al (1968). But, they used a heated (1253°K - 1338°K) mixture of methane and hydrogen to produce diamond. They used diamond as substrate and the pressures were in the range of 0.15 to 458 Torr. In 1975, Derjaguin and Fedoseev (1975) showed that the diamond can be grown at the pressures and temperatures in the metastable region. They used carbon tetra-iodide as the carbon source in their experiments.

Matsumoto et al (1982) showed that diamonds can be grown on non-diamond substrates, such as silicon wafers and molybdenum plates, using hot filament CVD. This was based on 1912 work of Langmuir (1912), in which he showed that molecular hydrogen can be converted atomic hydrogen on a heated tungsten filament (1300°K - 2500°K). Subsequently, various aspects of hot filament CVD has been studied by many researchers. Harris et al (1989) studied the species in the reactor, Tankala et al (1992) and DebRoy et al (1990) worked on the heat transfer aspects of the hot filament CVD. Lux and his associates (Lux and Haubner, 1991 and Okoli et al, 1989) are working on use of HF-CVD to produce coatings on cutting tools.

Many modifications of the basic HF-CVD process have been attempted to obtain diamond at lower substrate temperatures. In one such method, the substrate was bombarded with electrons (Sawabe and Inzuka, 1986). With this method they were able to obtain diamond at lower substrates temperatures (< 700°K). In another method, the substrate was held at negative bias with respect to the filament (Glass, 1989). In 1992 Kondoh et al (1992) modified the hot filament process by introducing resistive heating of the substrate with water cooled electrodes. This resulted in greater control over the substrate temperature.

In the following sections, some of the important aspects of diamond deposition using HF-CVD will be discussed.

3.3 Effect of Hydrogen

As mentioned earlier, hydrogen gas when passed over a filament at high temperature (>2,000°C) is converted into atomic hydrogen. The amount of atomic hydrogen produced depends on such factors as the temperature and shape of the filament (Jansen et al, 1989) and pressure inside the chamber. Franklash (1989) summarized the effect of hydrogen on diamond deposition:

- preferential etching of graphite over diamond is the most important one. Both graphite and diamond are formed simultaneously. However, the graphite is removed by reaction with atomic hydrogen, as hydrogen etches graphite ten times faster than diamond (Franklash, 1989 and Banholzer, 1992).
- hydrogen atoms should be in superequilibrium for successful growth of diamond, and the reversible reaction,

  $C_{(s)} - H + H \rightarrow C_{(s)} \bullet + H_2$

  is the rate limiting step for diamond surface growth.
- Hydrogen satisfies the dangling bonds of surface carbon atoms, keeping them in the sp^3 configuration and thus preventing the diamond surface from reconstruction into graphitic sp^2 structure.
- Suppression of the formation of aromatic hydrocarbons by molecular hydrogen plays an important role in the formation of diamond.

3.4 Effect of Methane

Though different hydrocarbon gases can be used as a source of carbon in diamond synthesis (May et al, 1993), methane is the most widely used gas. Methane, when passed over the heated filament is converted into CH_3, or C_2H_2 (Celli and Butler, 1991 and Harris, 1989). Further, CH_4 and C_2H_4 are also present in the gas mixture. It has been shown (Harris,1989; Goodwin and Gavillet, 1990; and, Harris and Weiner, 1989) that CH_3 and C_2H_2 form the major part of the radicals present under the diamond deposition conditions. It is also shown that in filament assisted systems, CH_3 is the dominating contributor to diamond growth and C_2H_2 and other species contribute to a smaller extent.

Kondoh et al (1989) have shown that diamond nucleation and morphology are susceptible to changes in methane concentration. The diamond deposition occurs, when the concentration of methane in the mixture is 1-3%. Above this range, the deposition contains significant amounts of graphite. However, at higher filament temperatures (>2,200°C) the concentration of methane in the gas mixture can be increased to 5%.

3.5 Effect of Oxygen

Addition of oxygen facilitates increase in the growth rate of diamond (Chen and Huang 1989). The growth rate reaches a maximum at an O_2/H_2 ratio of about 2% beyond which it decreases to a level as though no O_2 is added. The tendency is more noticeable at lower CH_4/H_2 ratios. The increase in growth rates was attributed to a decrease in the ratio of $C_2H_2/CH4$ with oxygen addition (Celli and Butler, 1991 and Harris and Weiner, 1989). Harris and Weiner have attributed the effects of O_2 primarily to the following four causes (Harris and Weiner, 1989)

- formation of a more reactive surface,
- formation of additional radicals in the gas phase,
- destruction of gas phase pyrocarbon-forming species, and
- removal of non-diamond carbon from the surface.

However, O_2 can not be used in HF-CVD as it could lead to the oxidation of the filament and its destruction.

3.6 Effect of Various Parameters

Various parameters that affect the diamond deposition rate in HF-CVD are the following

- Pressure
- Substrate temperature
- Filament -substrate distance
- Filament temperature
- CH_4 concentration

The effect of each of these parameters is discussed in the following.

3.6.1 Pressure

In a study on the effect of pressure, Singh et al (1988), showed that diamond can be deposited in a wide range of pressure (2-250 torr). Experiments conducted by Kondoh et al (1989) using modified HF-CVD technique, which employs substrate bias, showed that good quality diamond deposition can be obtained between 30-300 torr chamber pressure. But, in the absence of substrate bias, the size of the deposited particles and the density of nucleation are critically dependent on the pressure. Figure 4 shows the variation of diamond particle size with pressure. It can be seen that, pressure in the range 20-50 torr yields large crystals. Haubner et al (1992) showed that at constant filament temperature and for a given filament-substrate distance, the substrate temperature decreases with increase in pressure (Figure 5). This is because, at higher pressures there is larger heat transfer to the gas. Hence, more power is required to maintain a constant substrate temperature. Similarly, at constant power input to the filament, temperature of the filament decreases with increase in power. Substrate temperature and filament temperature are

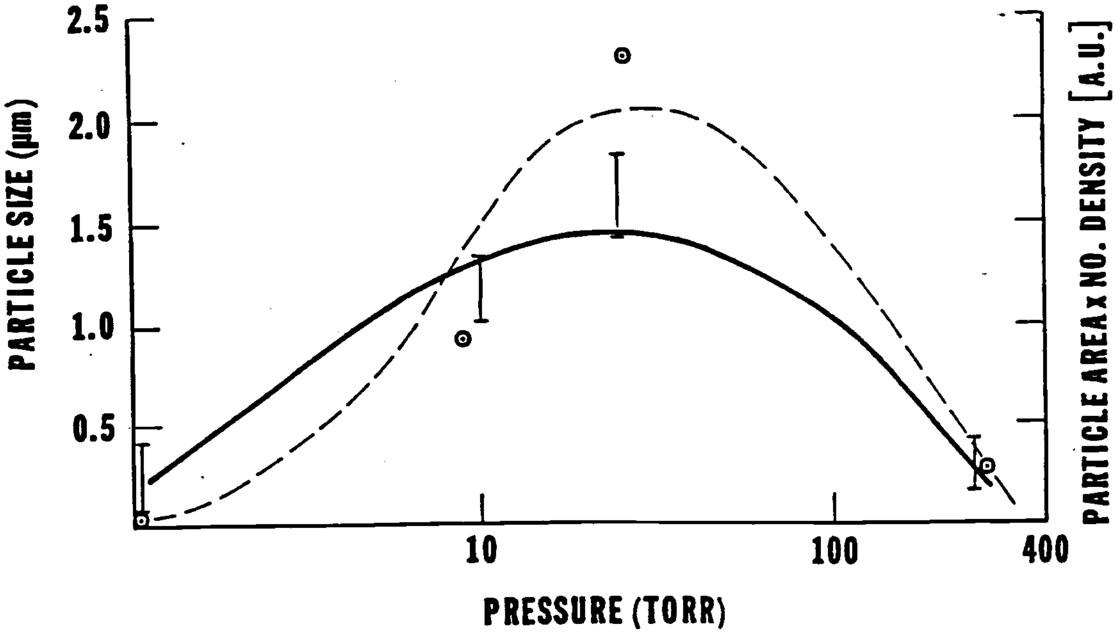


Figure 4 Variation of diamond grain size with pressure showing optimum pressure in the range of 20-50 torr (after Singh et al, 1988)

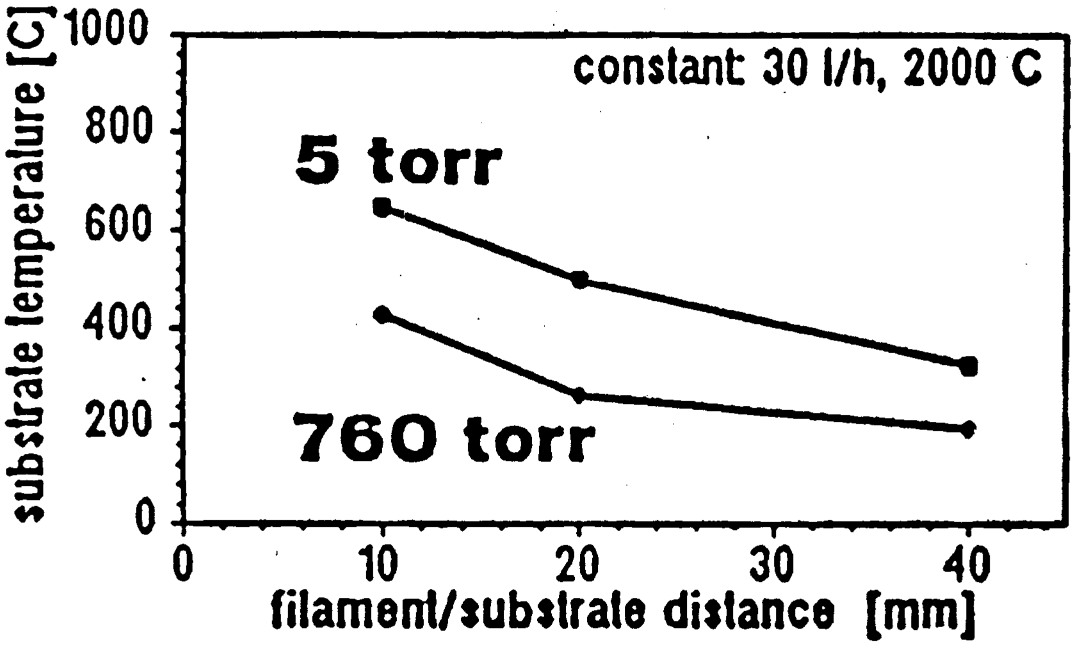


Figure 5 Variation of substrate temperature with substrate filament distance (after Haubner et al, 1992)

important factors in diamond deposition. As discussed above, pressure affects these factors.

3.6.2 Substrate Temperature

Singh et al (1989) has shown that grain size and amount of material deposited varies with substrate temperature. Figure 6 shows the variation of diamond grain size with substrate temperature. It can be seen that the optimum substrate temperature for diamond growth lies in the range of 700-1,000°C. Also, Singh et al has shown that diamond deposition will not occur above 1,300°C and below 650°C. Similar observations were made by Kondoh et al (1994). However, Bachmann (1991) showed that diamond deposition can be obtained at substrate temperature as low as 400°C in the presence of gas mixture containing carbon, hydrogen, and oxygen. But, the growth rates under these conditions are very low. Also, Bachmann considered the C-H-O phase diagram for different substrate temperatures stacked above each other as shown in Figure 7. It can be seen that the diamond growth occurs over a narrow range of gas ratios especially at high temperature. Further, the size of this region decreases with increase in substrate temperature, almost becoming zero at about 1300°C.

Also, the substrate temperature has an influence on the thermal expansion coefficient and hence on the adhesion of diamond coating to the substrate. Larger the difference in thermal expansion coefficients between the diamond coating and substrate material, higher the thermal stresses (Litos et al, 1989) leading to poor adhesion of diamond coating to the substrate.

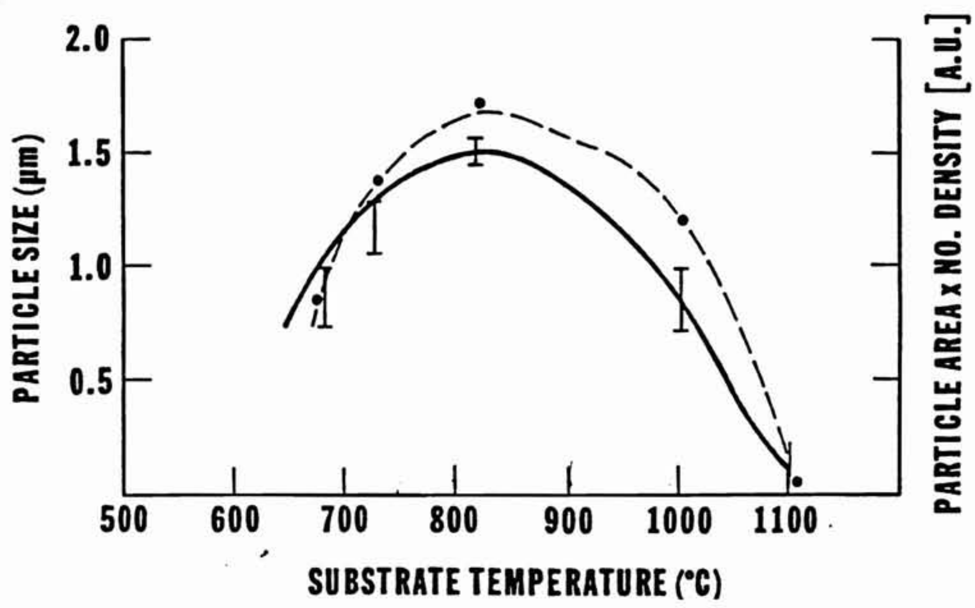


Figure 6 Variation of diamond grain size with substrate temperature showing optimum temperature in the range of 700-1,000°C (after Singh et al, 1988)

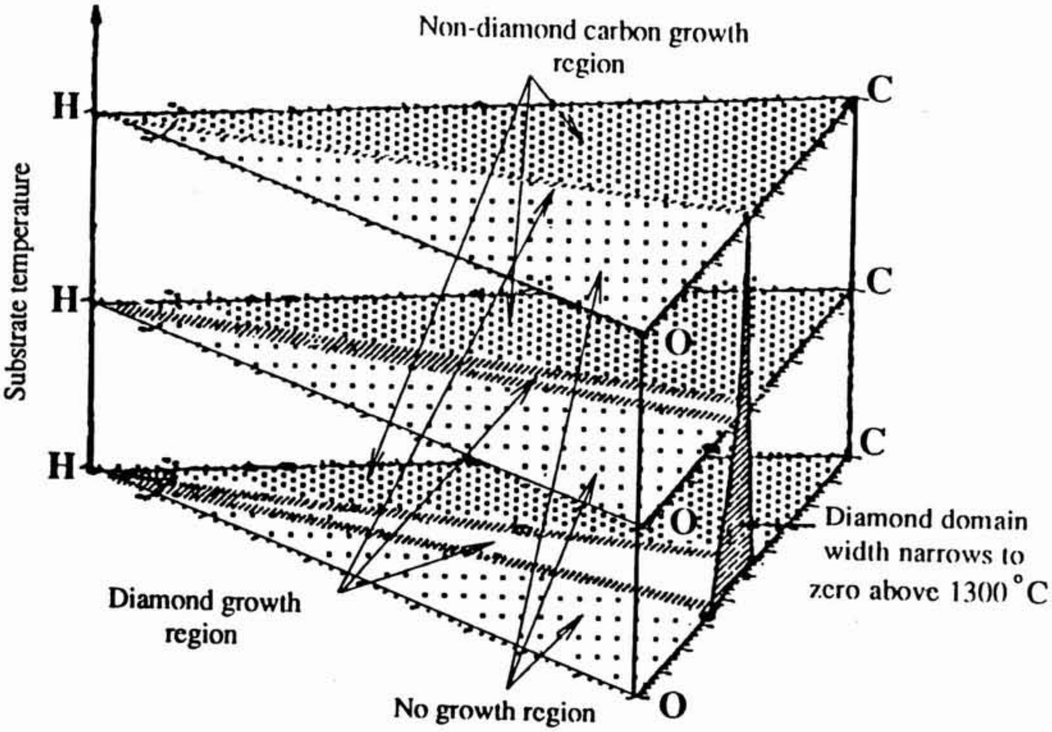


Figure 7 Stacked C-H-O diagrams for different substrate temperatures (after Bachmann, 1991)

3.6.3 Filament-Substrate Distance

The filament substrate distance influences crystal size, morphology, and homogeneity of diamond deposition. The morphology of the diamond is best directly under the filament and at small filament-substrate distance (Haubner and Lux, 1993; Kondoh et al, 1994; and Singh et al, 1988). At large filament-substrate distances, the deposit contains more diamond like carbon (DLC) and graphite. The is because, at small substrate-filament distances, the concentration of atomic hydrogen is more. As the substrate - filament distance increases, recombination of atomic hydrogen to molecular hydrogen increases. It has been shown that at a distance of 20 mm the recombination is complete and mostly graphitic deposit can be expected beyond this distance. Also, as the filament-substrate distance increases, the heat transfer from filament to substrate decreases, and hence the substrate temperature is lower (Haubner et al, 1992). This also leads to the formation of diamond like carbon and graphite. However, too small a filament distance makes the formation of diamond concentrated to a small region. Thus, there is an optimum distance which depends on factors such as flow rate and filament design.

3.6.4 Filament Temperature

Filament temperature plays an important role in the production of atomic hydrogen. Typically, the temperature of the filament is maintained in the range of 1,950-2,300°C. Many researchers have observed that below this range diamond like carbon and/ or graphite deposition occurs (Haubner and Lux, 1993; Singh et al, 1988, and Kondoh et al, 1994). With increase in filament temperature, the growth rate of diamond coating increases and the diamond crystal morphology improves. The size of the crystals also increase with increase in temperature. This is because, atomic concentration of hydrogen increases at higher temperatures. Also, the substrate surface temperature, which contributes to increased growth rates, increases because of higher heat radiation (Haubner et al, 1992). Filament temperature also affects the dissociation of methane. At higher filament temperatures, methane concentrations of up to 5% can be used, which may facilitate increased growth rates. Above 2,300°C, the stability of tungsten filament decreases.

3.7 Filament Selection

In HF-CVD, the energy required to dissociate the gas mixture into elemental species is supplied by the heated filament. Typically, a filament is required to operate in the temperature range of 1,900°C - 2,300°C. Though a wide range of materials satisfy this requirement, some constraints prevent the usage of some of them. Following are the requirements of a good filament material.

- High melting point
- Resistance to the action of hydrogen
- Good mechanical stability
- High binary eutectic temperature of the carbon-filament material system
- Low evaporation rate

These will be discussed briefly in the following.

3.7.1 High Melting Point

As mentioned earlier, the filament operating temperature should be in the range of 1,900°C-2,300°C. Hence, the melting point of the filament material must be greater than 2,300°C.

3.7.2 Resistance to the Action of Hydrogen (Anthony, 1991)

Atomic hydrogen has several important functions in the diamond deposition process. The molecular hydrogen present in the gas mixture is adsorbed by the surface of the refractory metal filament and dissociates into atomic hydrogen. These subsequently pass back into the surrounding gas. Hence, the selected material should be capable of dissociating hydrogen and should resist diffusion of hydrogen.

3.7.3 Good Mechanical Stability

The HF-CVD is typically run for 5 - 50 hours. The filament-substrate distance should be maintained constant during the deposition. Thus, the high temperature creep resistance of the material becomes an important factor.

3.7.4 High Binary Eutectic Temperature of the Carbon-Filament Material System

In the presence of carbon, the filament material will react with carbon and form carbides. Also, some of the carbon could dissolve in the material The melting point of the resulting eutectic system will be less than that of original filament material. Thus, the carbon-filament material eutectic point should be greater than the operating temperature; otherwise, melting and breakage of the filament will result.

3.7.5 Low Evaporation Rate

Diamond deposition in HF-CVD takes place under low pressure (20-50 torr) and high temperature. To ensure long filament life, the evaporation rate of the filament material under these conditions should be low. Electrically conductive, refractory metals satisfy most of the above conditions. A list of potential candidate materials is given in Table 6 (Anthony, 1991).

In Table 6, molybdenum and carbon filaments have marginal utility. This is because a hot spot on the filament may take it above the Mo-C eutectic temperature of 2,200°C and cause the filament to melt and fail before the filament is fully carburized. Carbon satisfies both the melting point and eutectic point requirements. But, it does not produce CVD diamond because, hydrogen reacts with carbon filament and releases hydrocarbon species into the surroundings rather than atomic hydrogen. Without atomic hydrogen at the substrate surface, graphite is deposited instead of diamond.

Of the remaining electrically conductive refractory materials rhenium, tantalum, and tungsten have been used as filament material for diamond deposition. It has been found that both tungsten and tantalum react with carbon forming carbides. Hence, tungsten and tantalum filaments quoted in the literature are in effect tungsten carbide and tantalum carbide filaments. These carbides are brittle and can result in the filament breakage. Carbide formation in tungsten to increases the volume by 70% (Banholzer, 1992) and leads to cracks in the filament. The formation of cracks in the outer carbide layer of tungsten and tantalum filaments can be seen in figure 8. Also, the cracks formed in tungsten filament are comparatively more. These cracks along with high resistivity cause fluctuations in power during the experiment. To ensure constant energy input, power supplies must operate under constant power. However, if the power is held constant the temperature of the filament will vary. According to Banholzer this is caused by changes in radiative heat transfer and

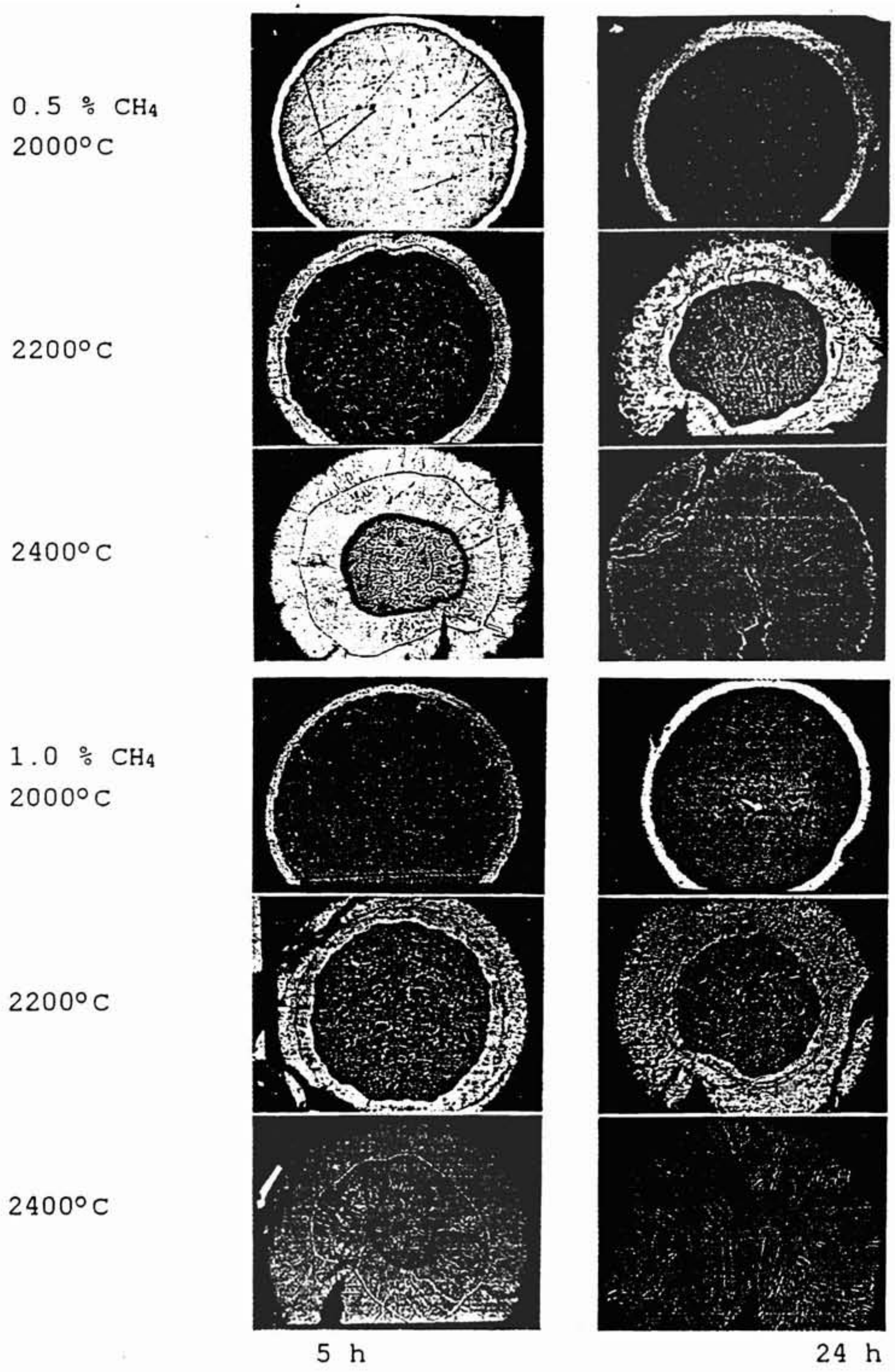


Figure 8 Effect of filament temperature and duration of carburization on tungsten and tantalum filaments showing cracks in the carbide layer (after Okoli et al, 1991)

Table 6 Candidate Filament Materials

Material	**Melting Point,°C**	**Evaporation Rate, gm/cm^2-s**	**Carbon Eutectic Point, °C**	**Resistivity, 10^{-8} Ωm**
Tungsten	3387	10^{-9}	2475	5.4
Carbon	3727	6×10^{-8}	3727	1375
Rhenium	3180	7×10^{-5}	2486	19.3
Tantalum	2996	10^{-8}	2800	13.15
Molybdenum	2610	4×10^{-7}	2200	5.34

changes in the amount of heat transferred by the combined reaction and diffusion. Carburization leads to changes in the diameter and also changes in the surface area which in turn influences the power used in hydrogen dissociation. Hence, in order to prevent the fluctuation of power during experiment, pre-carburization process is carried out to ensure conversion of tungsten and tantalum filaments to tungsten carbide and tantalum carbide, respectively. On the other hand, rhenium does not form carbides but dissolves considerable amount of carbon and becomes brittle. The cost of rhenium, when compared tungsten or tantalum filaments, is rather high. Hence, it is not widely used.

3.8 Substrate Selection

The nucleation and adhesion of diamond coating depends largely on the type of substrate used. Hence, while selecting a substrate for deposition the following aspects should be considered.

Chemical bonding characteristics of the substrate material and its carbide forming ability play an important role in the nucleation and adhesion (Lux and Haubner, 1991). Accordingly, it is typically observed that good quality diamond coatings can be formed on certain carbide forming substrates as well as on substrates having structures compatible with diamond (for e.g.,cubic boron nitride, tungsten carbide).

It has been found that the adherence of the diamond coating largely depends on the surface chemistry of the substrate (Murukawa and Takeuchi, 1990). In most of the cases, even after the film is formed, flaking of coating takes place due to poor adhesion. The poor adhesion of the film has been attributed to the differences in the crystal structure and thermal expansion between the substrate and the coating. This differential thermal expansion results in interface stresses within the layers.

The expansion of a material can be calculated using the equation

$$\Delta L = \alpha \, L \, \Delta T$$

where α is the thermal expansion coefficient, ΔT is the temperature difference, and L is the original length of the specimen.

To obtain a stress free interface, the expansion of diamond and substrate, should be equal. This is given by the relationship

$$\alpha_D \, L \, \Delta T_s = \alpha_T \, L \, \Delta T_B$$

where α_D and α_T are the thermal expansion coefficients of diamond and the substrate, T_S and T_B are surface and bulk temperatures of the substrate, and L is the length of the substrate. Using the above equations, the theoretical substrate surface temperature required to obtain a tension free interface after cooling can be calculated.

Figure 9 shows the thermal expansion coefficients of various substrates and the bulk temperature for which neither tension nor compression can be expected for a substrate surface temperature of 1,050°C (Lindlebauer, 1989). Figure 10 gives the theoretical substrate surface temperature needed to obtain a tension/ compression free interface after cooling. These figures facilitate in choosing a substrate with better adhesion properties, or in determining the substrate bulk temperature at which good adhesion can be obtained.

Another major criteria for the selection of a substrate is the type of application (Stephan, 1992). For example, the substrate selected for machining should have properties such as toughness, impact strength, and high temperature resistance. To date, silicon nitride is found to be the most compatible substrate material (cutting tool) for diamond coating. This is because the thermal expansion of silicon nitride is closer to diamond compared to most other candidate tool materials (Table 1). Chemically, silicon nitride is quite compatible with the diamond film growth, even though the normally contain 1-10% of oxide sintering aids (such as aluminium oxide, yttrium oxide, and magnesium oxide) which, by themselves are generally unsuitable for diamond films. Given moderately high CVD process temperatures (650°C-1,100°C) and the affinity of diamond with carbide formers at these temperatures, tool steels and carbides containing cobalt are basically incompatible substrates. This is due to the large difference properties of these materials compared to that of diamond, which results in stresses at the interface during cooling and increases the probability of film spalling.

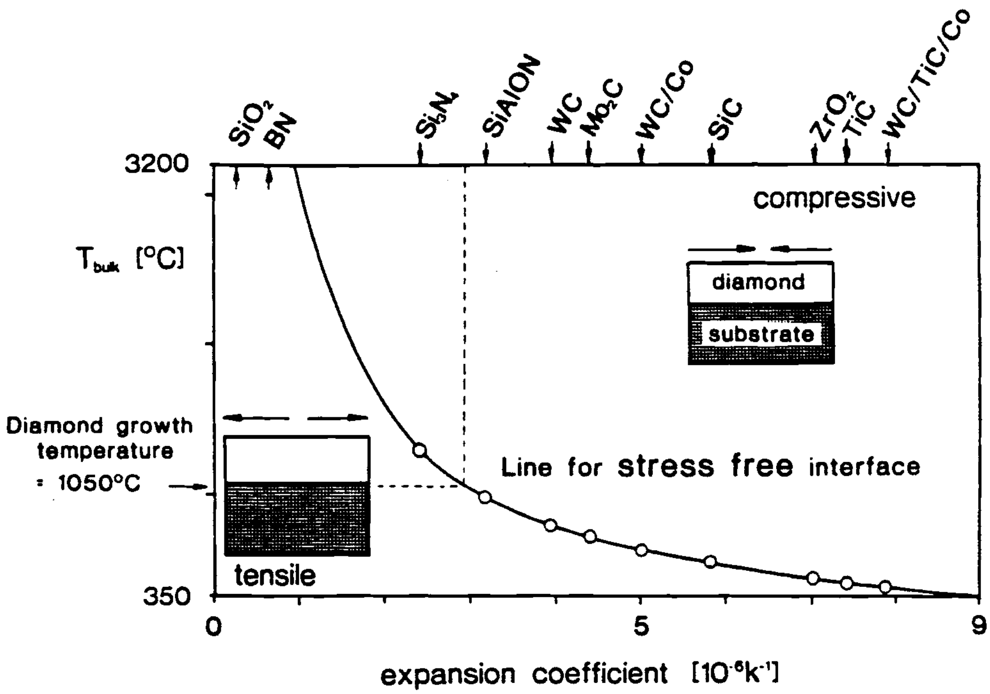


Figure 9 The thermal expansion coefficients of various substrates and the bulk temperature for which neither tension nor compression can be expected (after Lindlebauer, 1989)

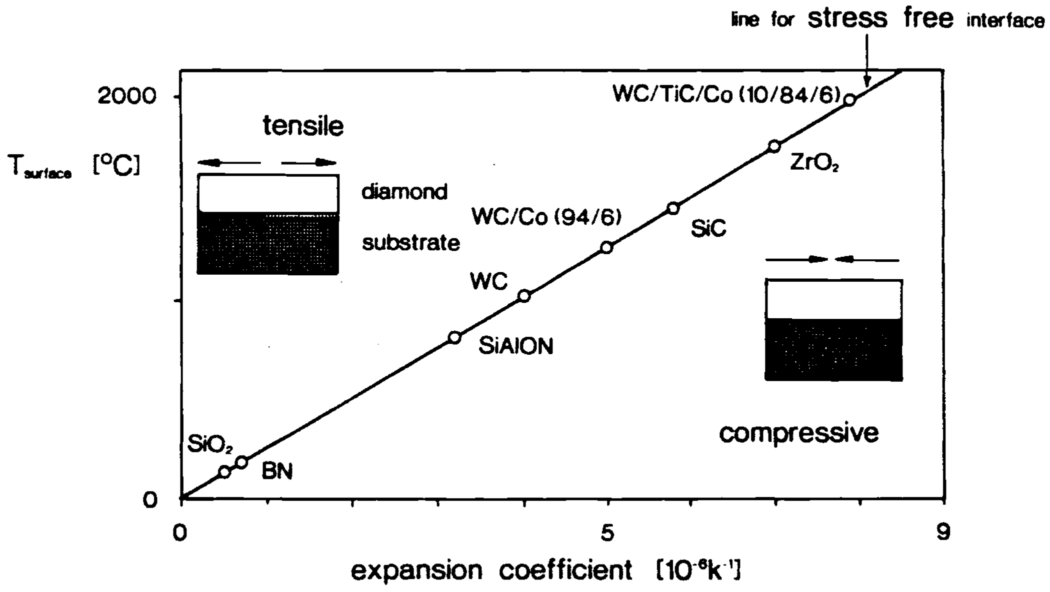


Figure 10 Theoretical substrate surface temperature needed to obtain a tension/ compression free interface after cooling (after Lindlebauer, 1889)

3.9 Effect of Different Substrate (Tool) Materials

Diamond being the hardest material has excellent wear properties. Hence, diamond coatings when applied to cutting tools should improve their wear resistance. Tool materials, such as cemented tungsten carbide and silicon nitride are being used as substrate materials for diamond coatings.

3.9.1 Tungsten Carbide

The delamination of diamond coating from the surface of tungsten carbide cutting tools is generally attributed to the presence of cobalt binder (Haubner et at., 1989). Cobalt does not form stable carbides, but dissolves carbon at high temperatures (a maximum of 3.9% at 1700°C and 0.1% at 900°C) (Kosolapova, 1971). Haubner et al (1993) observed that with cobalt as substrate, all carbon reaching the surface of the cobalt dissolves completely at the early stages of experiment and a large incubation time is required before diamond nucleation occurs. Further, at high methane concentrations, non-diamond carbon deposits were observed. Similar results were obtained on nickel substrates (Haubner et al, 1993). Haubner et al attribute this to the vapor phase reactions between cobalt vapor and CH_4 leading to graphite formation.

Bichler (1988) found the diamond nucleation rate to decrease with increasing cobalt concentration (3-10%). At cobalt concentrations higher than 6%, the nucleation rate reaches a minimum. Mehlmann (1992) reported that cobalt binder in tungsten carbide tools interacts with growing diamond crystals. Because of this interaction, partially dissolved diamond crystals and carbon saturated cobalt particles were found. If the deposition is continued, diamonds grow on these cobalt particles. Since cobalt saturated with carbon does not wet the surface, presence of these particles may result in delamination. Also, carbon containing cobalt may release graphite which also contributes to the decohesion of the film from the substrate. More recently, Mehlmann et al (1994) indicated that cobalt particles were observed on the surface of the cutting tool during deposition at lower surface temperatures (800°C) but not at higher temperatures (940°C). They showed that at higher temperatures cobalt is etched from the surface, in the presence of atomic hydrogen. They have shown using auger electron spectroscopy (AES) that as the deposition time increases the number of cobalt particles decreases, as some of the cobalt gets included in the diamond coating. Using a transmission electron microscope (TEM) to observe diamond films, they have shown that diamond - cobalt interaction results in the formation of small cobalt particles and disordered graphite.

Young (1961) reported that cobalt readily dissolves in HNO_3, HCl, and H_2SO_4. To reduce the effect of cobalt, Okes et al (1991) etched the substrates in Nitol (HNO_3 and water in the ratio 1:1) to remove cobalt. They have shown that good diamond film can be obtained on etched substrates and at lower substrate surface temperatures (700°C). The good adhesion found on etched substrates at lower temperatures was attributed to the lower cobalt mobility. For the same reason good adhesion was obtained at higher temperatures (900°C-1,000°C) on etched substrates.

Another method employed to obtain good adhesion involved etching of tungsten carbide from the surface of the substrate (Peters and Cummings, 1993) using Murakami's reagent (potassium ferri-cyanide, potassium hydroxide and water in the ratio 1:1:10). This reagent does not attack the cobalt phase but etches tungsten carbide. The cobalt appears as white or light-yellow patches along the grains of tungsten carbide. Subsequently the surface was treated with H_2SO_4 to remove the residue from Murakami's reagent and also to remove small amounts of cobalt. This method resulted in adherent film (Peters and Cummings, 1993).

Itoh et al (1991) studied the effect of grain size of the cemented tungsten carbide substrate. Etching of coarse (1 μm) and fine grained (0.5 μm) substrates by Murakami reagent and one hour diamond deposition showed that the fine grained substrate had 5 times more nucleation. Also, the nucleation increased with increase of diamond particle size in microflawing treatment. But, the nucleation decreased with increase in time of microflawing treatment.

To improve adhesion, Kubelka et al (1994) placed the substrate in a quartz ampule along with boron or silicon powder (grain size 100 μm) and sealed under vacuum. Subsequently, it was treated for 4-24 hours at a temperature of 700°C. The coatings in these experiments had good adhesion when the film thickness was less than 20 μm. But, films of 20 μm thick delaminated immediately. They claimed that the reason for good adhesion is the formation of stable cobalt compounds with boron and silicon. Also, by heating the substrate during diamond deposition, there will be lesser cobalt vapors since the vapor pressures of cobalt boride and cobalt silicide are lower than that of cobalt. Cobalt vapors decrease the crystal growth of diamond by catalyzing the formation of non-diamond carbon phases which lead to poor adhesion. Also, the growth rates in these experiments were higher compared to untreated substrates. Higher growth rates results in lower time for the interaction of cobalt with diamond. Hence, good adhesion can be obtained if the deposition is carried out for less number of hours.

Good adhesion was also obtained by ion-plating group IVa, Va, VIa metals and by heat treatment (Isozaki et al, 1993). They have shown that heat treated intermediate layer consists of tungsten but no cobalt. The good adhesion obtained is attributed to the absence of cobalt on the surface. Similar results were observed by Saito et al (1993).

Huang et al (1992) conducted indentation and friction experiments on tungsten carbide tools containing different cobalt content. They have observed that the adhesion of the diamond film decreases with increase in cobalt content. The friction coefficient increases with increase in cobalt content because finer diamond grains were observed in tools with lower cobalt content. Also, the rake face wear of the cutting tool during cutting tests is less with diamond coated tools with lower cobalt content.

3.9.2 Titanium Carbide

Titanium carbide (TiC) has the highest carbon diffusion rate among refractory metal carbides (Lux and Haubner, 1991). Hence, on TiC fewer diamond nuclei is formed at the beginning of the deposition. It is said that relatively high diffusion rate of carbon in TiC leads to continuous formation of nuclei with time (Lux and Haubner, 1991). The dissolution of carbon is said to continue at the diamond carbide layer interface as long as the substrate is heated during deposition and decrease with the increase in carbide thickness. Park and Lee (1991) conducted experiments on pure titanium and found that initially carbide layer forms and after a one hour the diamond nucleation begins. Along with the nucleation of diamond, the TiC layer continues to grow. Hence, it is said that diamond and TiC grow simultaneously and TiC does not contribute to diamond nucleation. According to them, the incubation time of the diamond and subsequent growth rate of diamond are dependent on the substrate preparation. Badzian and Badzian (1988) also conducted experiments on pure titanium by microwave CVD. After an initial incubation period, it was possible for them to grow good perfect diamond crystals. Perry et al (1993) conducted a study on the interface of diamond coatings and pure titanium by using Raman spectroscopy. They found Raman spectrum of the interface showed diamond, carbide, and amorphous carbon. Perry and Somorjai (1994) found the interface between the pure titanium and diamond exhibited a carbide layer. This study was conducted by delaminating the diamond film from the substrate. The delamination was found to occur near the nucleation layer of the diamond films. Also, small grain pullout of the carbide layer was observed, suggesting cohesive failure of the carbide layer. They also conducted similar studies on tungsten, copper, and molybdenum. Based on these tests, the degree of adhesion was ranked in the following order with titanium having best adhesion.

Ti >> Cu >> W >> Mo

Using HF-CVD Schachner et al (1987 and 1988) have coated diamond on titanium carbide using the conditions shown in Table 7. All these observations indicate that titanium carbide can be used as a inter-layer for obtaining good quality diamond coating on cemented tungsten carbide cutting tools (even with higher cobalt content).

Table 7 Conditions Employed for Diamond Coating on TiC Coated Tools (Schachner, 1988)

Filament Temp, ^{o}C	1700 - 2000
Substrate Temp., ^{o}C	800-1000
Pressure, torr	15
Duration, hours	10
Flow rate of CH_4/H_2, sccm	1.0/99.0

3.9.3 Silicon Nitride

Silicon nitride is the most suitable substrate material for diamond coating (Stephan, 1992, and Salvadori et al, 1992). This is because the properties of silicon nitride are close to that of diamond. It can be seen from Table 1 that the thermal expansion coefficients of silicon nitride and diamond are almost the same. Also, the crystal structure of the silicon nitride being tetrahedral (diamond also has tetrahedral structure) makes it conducive to diamond growth. Commercially, it has been possible to coat diamond on silicon nitride and the adhesion in all the cases is said to be good (Destefani, 1993). Diamond coated cemented tungsten carbide can be used for machining aluminum and aluminum alloys even after the coating is worn. However, silicon nitride, when compared with carbides, lacks toughness and impact strength (Sprow, 1995, and Salvadori et al, 1992), which inhibits its wide usage. Diamond coated silicon nitride while machining aluminum fails catastrophically, at the point of contact when the coating is worn (Destefani, 1993).

3.10 Nucleation of Diamond During Hot Filament CVD

The low-pressure synthesis of diamond takes place under the conditions of temperature and pressure conditions where diamond is metastable with respect to graphite. It is said that the crystalline diamond can be grown at low pressure if the precursor gas is 'activated' prior to deposition. According to Singh (1993), the nucleation of diamond involves:

- Formation of carbon clusters
- Conversion of sp^1-sp^2-sp^3 bonding
- Crystallization of amorphous phase
- Growth of diamond crystal
- Secondary growth of diamond

4.0 PROBLEM STATEMENT

The objective of the present investigation is to obtain adherent diamond coatings on cutting tool materials such as cemented tungsten carbide and silicon nitride using hot filament CVD technique. Following sub-goals were identified to accomplish this.

- construction of a state-of-the art hot filament CVD reactor.
- deposition of diamond coatings on various cutting tools.
- parametric studies to determine operating conditions suitable for diamond growth.

The following features were identified as essential in the construction of the reactor:

- Selection of the filament material and design of a filament heating system that enables temperatures in the range of 1950-2300°C for a prolonged period of time.
- Selection of a substrate heater system which can heat the substrate upto 1000°C.
- Selection of suitable vacuum system to evacuate the chamber up to $5X10^{-3}$ Torr.
- Selection of the gas flow system that monitors and controls the flow rates desired.

The important parameters of the hot filament CVD reactor are the following:

- Substrate-filament distance
- Filament temperature
- Substrate temperature

- Methane concentration
- Duration of deposition
- Pressure

Some of the above parameters have been studied in the present investigation to obtain optimum conditions for diamond deposition on cutting tools.

Diamond deposition has been carried out on various cutting tool materials including cemented tungsten carbide (different cobalt content), titanium carbide and titanium nitride coated carbide tools, and silicon nitride. Also, different substrate surface preparation techniques have been studied towards an improvement in the adhesion between cutting tool substrate and diamond coating.

5.0 HOT FILAMENT CVD REACTOR

Figure 11 is a schematic and Figure 12 is a photograph of the Hot Filament CVD reactor employed in the present study. It is an integration of the vacuum system, gas flow system, filament heating system, and substrate heating system. A quartz bell jar, used as the reaction chamber, is mounted on an aluminum base plate. Each of these components will be briefly discussed in the following.

5.1 Vacuum System

Typically pressures in the range of 20 - 50 torr are used in diamond deposition. This is achieved by evacuating the chamber to a pressure of 5×10^{-3} torr using a mechanical pump and by back filling the chamber with CH_4 and H_2. The pressure inside the chamber is monitored continuously using a pressure transducer (MKS Type 222) and is maintained constant using a pressure controller (MKS Type 250). The specifications of the instrumentation used are given in appendix A.

5.2 Gas Flow System

The gases required for the diamond deposition, i.e CH_4 and H_2, are introduced into the chamber near the filament. All the gas connections are made using stainless steel tubes. The flow rates of gases are monitored and controlled using mass flow meters (MKS Type 1159B) along with mass flow controllers (MKS Type 250). Typically, the total flow is about 100 sccm with 0.5 to 3% CH_4 in H_2.

5.3 Filament Heating System

The gases introduced into the chamber are dissociated by the hot tungsten filament (1950°C- 2300°C). The filament is supported on a block of h-BN and thick copper wires are used as electrical leads. A DC power source [Electronic Measurements, EMS II 20-30, with a maximum capacity of 20 V and 30 A (i.e., 600 W)] is used for heating the filament. The temperature of the filament is measured using an optical pyrometer (Williamson, T8120ps-G-C). Temperature of the filament is set by adjusting the current and voltage.

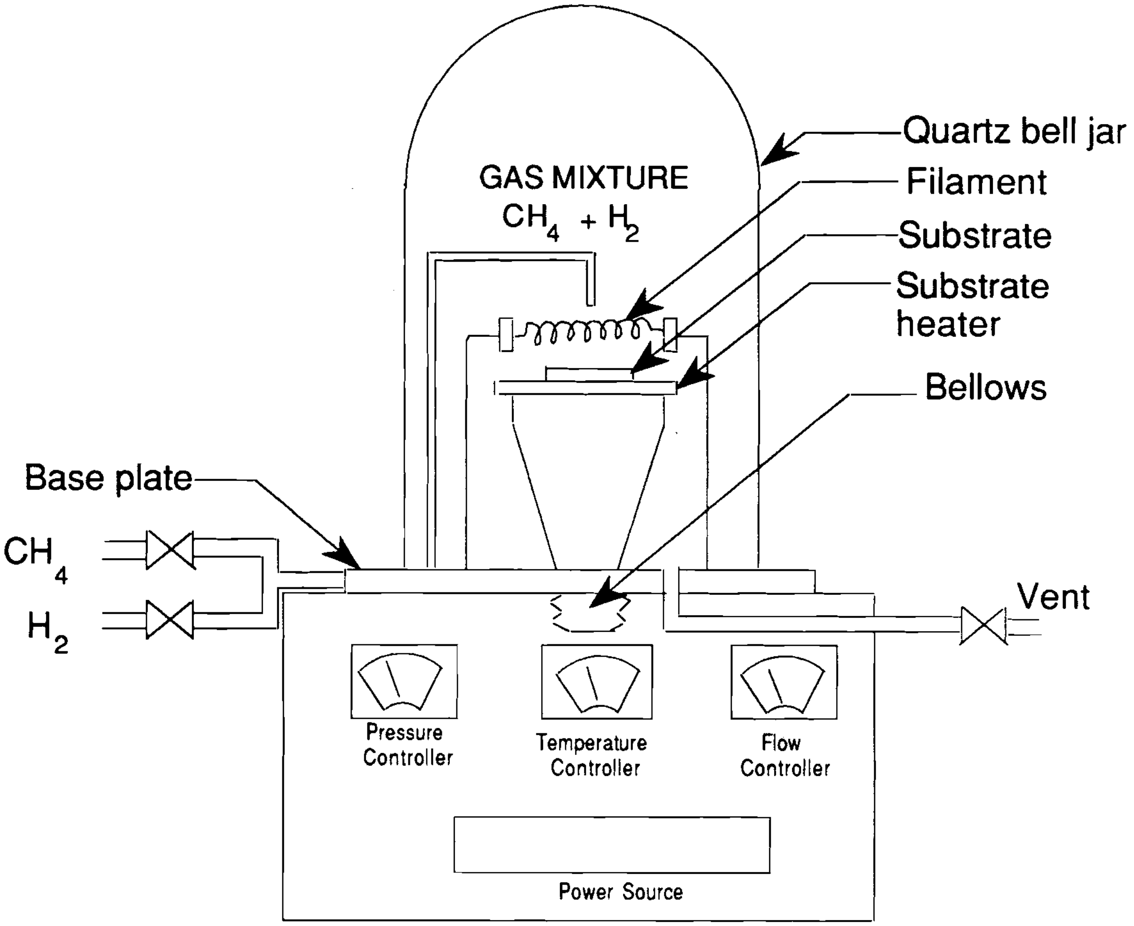


Figure 11 Schematic of the experimental setup

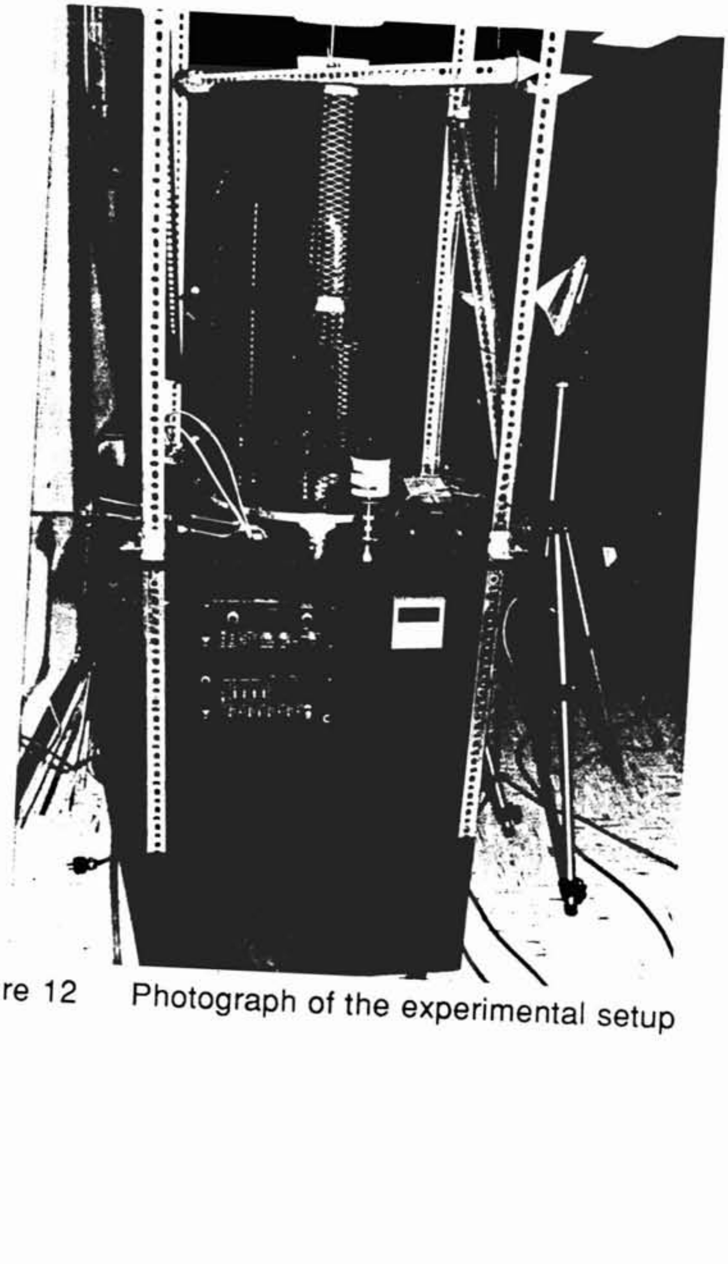


Figure 12 Photograph of the experimental setup

5.4 Substrate System

The substrate (cutting tool) is placed on the substrate heater in the center of the chamber directly below the filament. Figure 13 shows the top view of the substrate heater. The substrate heater consists of a graphite heating element in the form of coil. This graphite heating element is coated with a non-conducting layer of h-BN. Temperatures up to 1100°C can be obtained with this heater. Power is supplied to the heater by molybdenum heater. These leads also act as supports to the heater. Hence, molybdenum is used instead of copper, because copper becomes soft at high temperature causing a drift in the substrate - filament distance.

The heater can be moved up or down with the help of bellows located at the bottom of the aluminium plate (Figure 11). Hence, the distance between the substrate and the filament can be controlled by adjusting the position of the substrate heater. The range of movement that can be obtained is 15 cm. The temperature of the substrate heater is measured by a W - 26% Re thermocouple and controlled by a PID controller (Omega, CN3000).

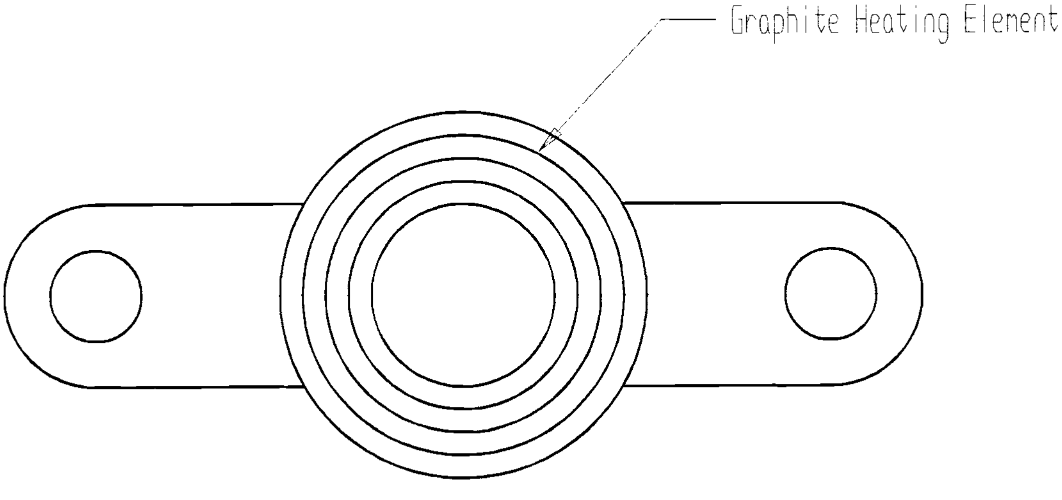


Figure 13 Top view of the substrate heater

6.0 EXPERIMENTAL PROCEDURE

Following are the various steps involved in the HF-CVD process for depositing diamond coatings on cutting tools.

- Initially the tungsten filament is carburized in order to prevent fluctuations in power
- The substrate is cleaned with acetone ultrasonically to remove dirt
- Substrate treatment (for e.g., etching of the substrate, scratching with diamond) is then performed
- The specimen is placed on the substrate heater
- The chamber is evacuated to 5×10^{-3} torr pressure and then back filled with CH_4 and H_2 gases
- The gas flow rates, chamber pressure, substrate-filament distance, and substrate temperature are set to the desired values
- The filament is brought to the required temperature (1,950°C - 2,000°C)
- Experiment is carried out for the desired duration.
- The methane flow is stopped 10 minutes prior to the end of the experiment
- Power supply to the filament is switched off at the end of the experiment
- Hydrogen flow and substrate heater are turned off and the system is allowed to cool

6.1 Carburization of Filament

Thoriated (0.5%) tungsten is used as filament material in all the experiments. Tungsten begins to react with carbon at 1,000°C. During such reactions WC is formed on the surface and W_2C is formed in the core. The densities of these two compounds along with that of tungsten is shown in Table 8. It can be seen that the compounds have lower densities than tungsten. This results in an increase in filament diameter leading to a reduction in resistance and consequently lower heating power. This leads to a continuous decrease in filament temperature. This decrease can be avoided by pre-carburization of the filament, the details of which are given in the following:

Table 8 Densities of Carbides of Tungsten

Carbide Type	Density, g/cc
WC	15.5-15.7
W_2C	17.2-17.3
W	19.35

6.1.1 Carburization Procedure

Following are the various steps involved in the carburization of the filament.

- A tungsten filament of 0.5 mm in diameter, 14.5 cm in length is fastened to the copper leads
- The chamber is evacuated to 5×10^{-3} torr and is back filled with methane to the required pressure.
- The methane flow is turned off.
- The filament power is switched on and the temperature is maintained at 1,950°C - 2,050°C for 30 minutes.
- At the end of 30 minutes the filament power is switched off and the filament is allowed to cool.

Carburization of the tungsten filament (0.5 mm diameter) was carried out in a methane atmosphere for 30 minutes. Carburization pressures of 5, 10, and 20 torr were used. The temperature of the filament was maintained at 2,000°C. While the experiment was in progress various parameters such as current, voltage and filament temperature were recorded at regular intervals. Also, the diameter of the filament was measured before and after the experiment.

6.1.2 Results

Figure 14 shows the change in resistance with carburization time for different pressures. It can be seen that resistance increases with time for first 15-20 minutes before reaching a constant value. The rate of increase decreases with the pressure of carburization. In Figure 15, the power required to maintain a constant filament temperature of 2,000°C with time is shown for different pressures. It can be seen that the power consumption is constant for pressures in the range of 5-10 torr, while at 20 torr a continuous increase is noticed. In Figure 16, the diameter of filament after the treatment is plotted with respect to filament pressure. It can be seen that for up to 10 torr, the change in diameter is negligible while beyond 10 torr there is an increase in diameter, such that at 20 torr the diameter is nearly doubled.

6.1.3 Discussion

As mentioned earlier, carburization of the filament leads to the formation of WC and W_2C. This will result in an increase in the electrical resistance. This effect is seen at 5-10 torr. However, at 20 torr this increase is offset by decrease in resistance due to increase in diameter of the filament. This leads to constant resistance for 20 torr carburization. Therefore, the increase in diameter leads to an increase in power needed to maintain a constant filament temperature. In

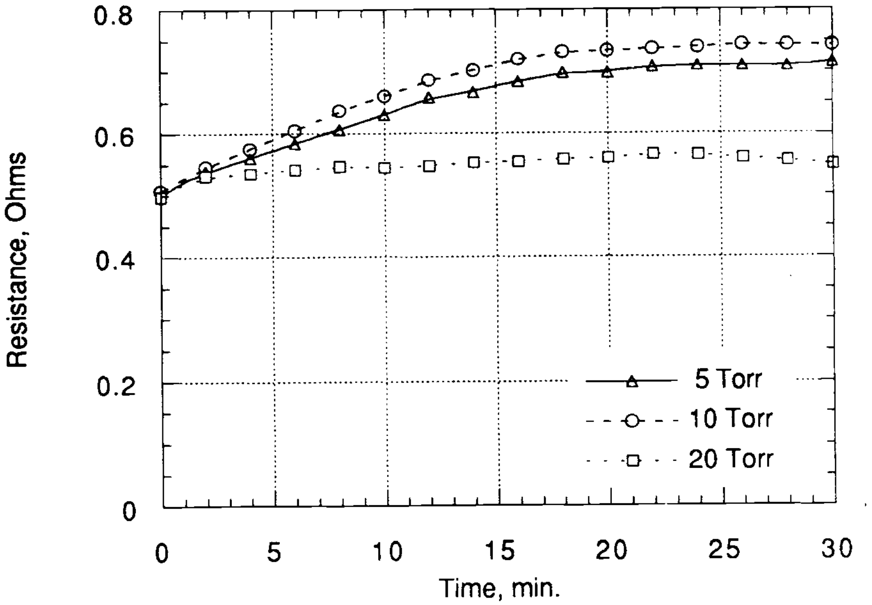


Figure 14 Change in resistance with carburization time for different pressures showing the optimum pressure in the range of 5-10 torr

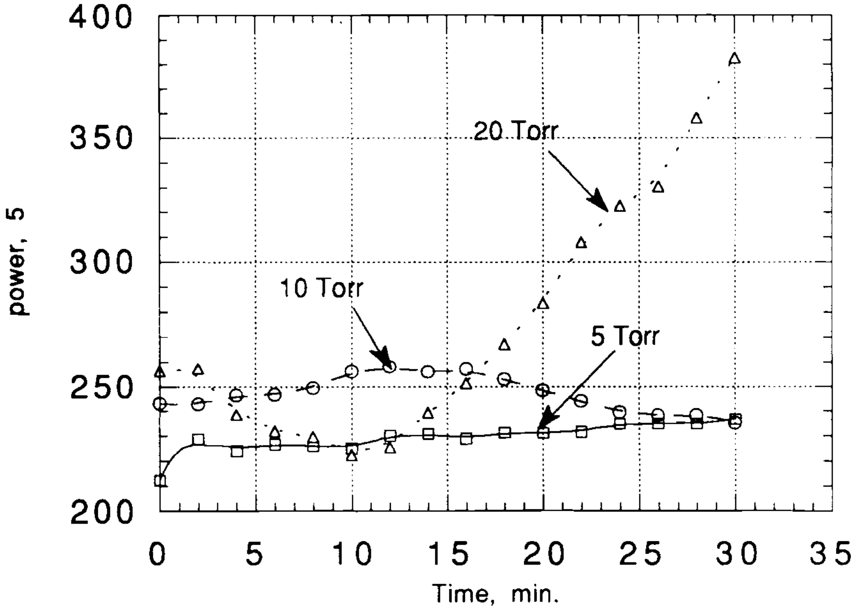


Figure 15 Variation of power with time for different pressures showing 5 torr to be the best condition for carburization

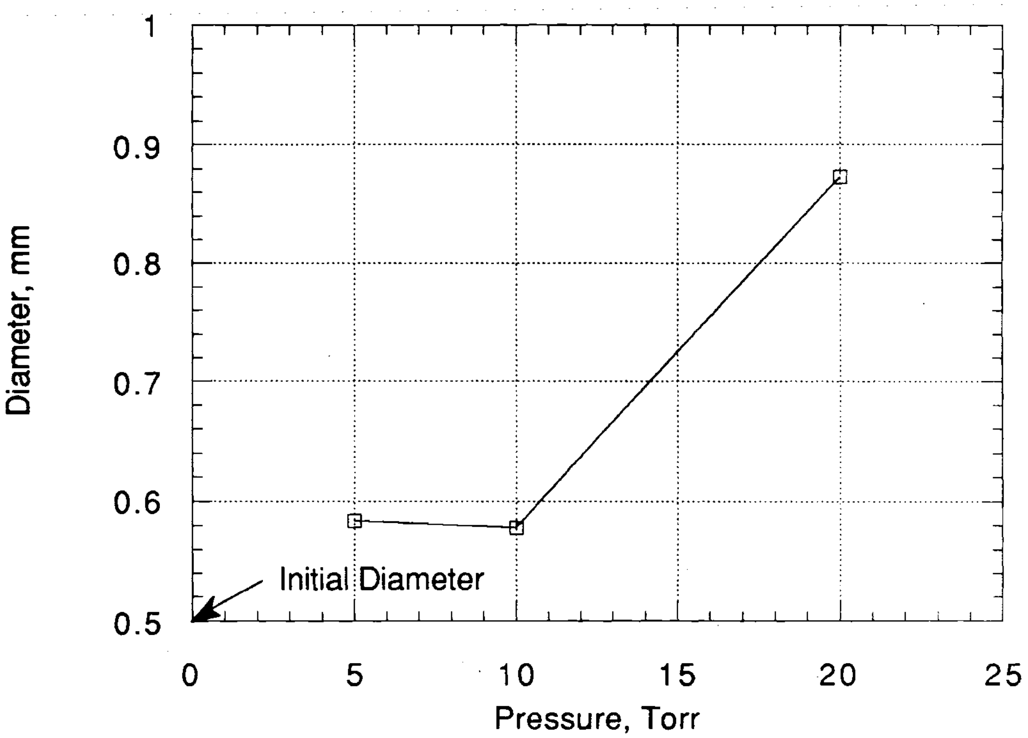


Figure 16 Variation of filament diameter with carburization pressure showing the change in diameter to be minimum at 5 torr

the case of 20 torr, the power continuously increases. Hence, if the diamond deposition is carried out without carburization, the power supply will be saturated in a short time. After this, the filament temperature will begin to fall. On the other hand, if the filament is carburized at 5-10 torr, the increase in diameter is negligible; also the power consumption remains constant. Hence, such filament can be used for diamond deposition for a long time (~300 hours).

6.2 Test Procedure

The present study is concerned with obtaining high quality, adherent diamond coatings on cutting tools. The quality of the film was assessed by diamond morphology, coating continuity, and absence of non-diamond carbon. The tools used for the substrates were obtained from 3 suppliers and are designated as A, B, and C in this investigation.

Chamber pressure, substrate temperature, and filament substrate distance were varied to study the nucleation of diamond by short duration experiments. In these tests the filament temperature was kept at 2050°C and hydrogen to methane ratio at 99.5:0.5. A flow rate of 100 sccm and test duration of 5 hours was used. Later, the duration of the experiment was varied to study the effect on coating continuity.

The filament temperature and amount of methane in hydrogen were not changed in the present work. Generally, diamond is formed when the filament temperature is in the range of 1,900°C to 2,300°C. If the temperature is below this range graphite deposition will occur (Haubner and Lux, 1993). Also, tungsten which is used as filament material will soften significantly at temperatures above 2,300°C. This causes a loss of mechanical strength and creep of the filament, thus altering substrate-filament distance and the possibility of filament breakage.

The amount of methane in hydrogen should be in the range of 0.5 to 3%. If the amount is less than 0.5%, diamond growth will not occur, whereas, if the amount is greater than 3%, deposition of diamond like carbon or graphite occurs. Since, the growth rate is influence by the concentration of methane, the best value from the literature (0.5 sccm) was selected.

To improve adhesion of the coating to the substrate, various substrate preparation techniques were considered including

- Microflawing
- Etching
- Use of inter-layers

In some cases, the substrate temperature was varied in order to study the effect of thermally induced interface stresses on adhesion. Also, according to Oles et al (1991), the cobalt mobility and migration to the surface can be affected by temperature. Cobalt has been indicated to have detrimental effect on the adhesion of coating (Mehlmann et al, 1992 and 1994), due to the formation of carbon rich cobalt particles, which do not wet either the surface or the coating due to the promotion of graphite. In order to study the effect of cobalt, tools with different cobalt contents were used. In the following, details of various substrate surface treatments are given briefly.

6.2.1 Microflawing

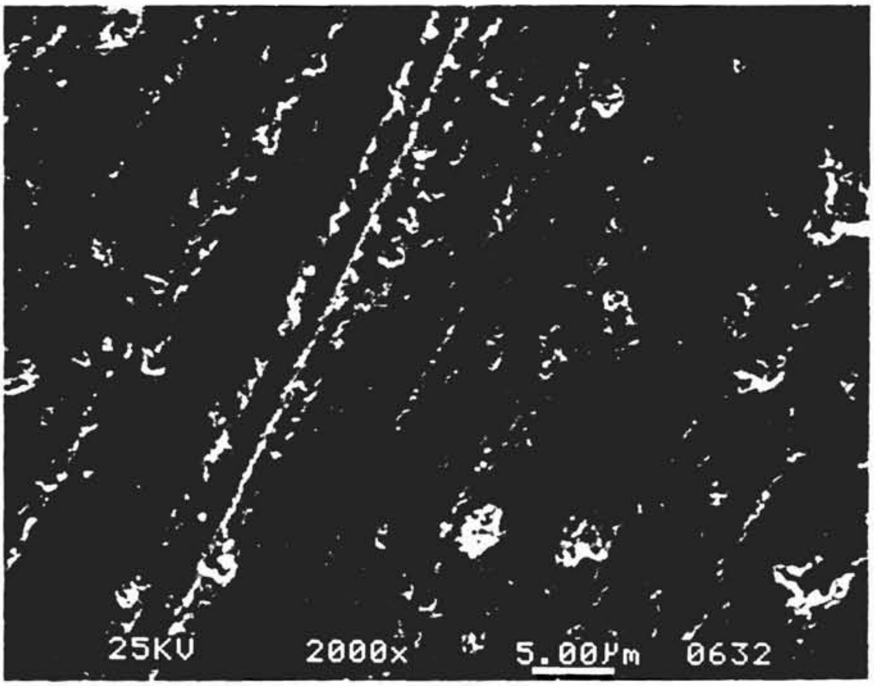
This involves scratching the substrate with diamond powder (0.25 μm). In this method, diamond is suspended in acetone. The substrate (cutting tool) to be treated is placed inside this solution and ultrasonically cleaned for 5-10 minutes. This results in micro-scratches on the surface and some diamond crystals will remain on the surface. These crystals are known to act as nucleation sites which increase the nucleation of diamond.

6.2.2 Etching

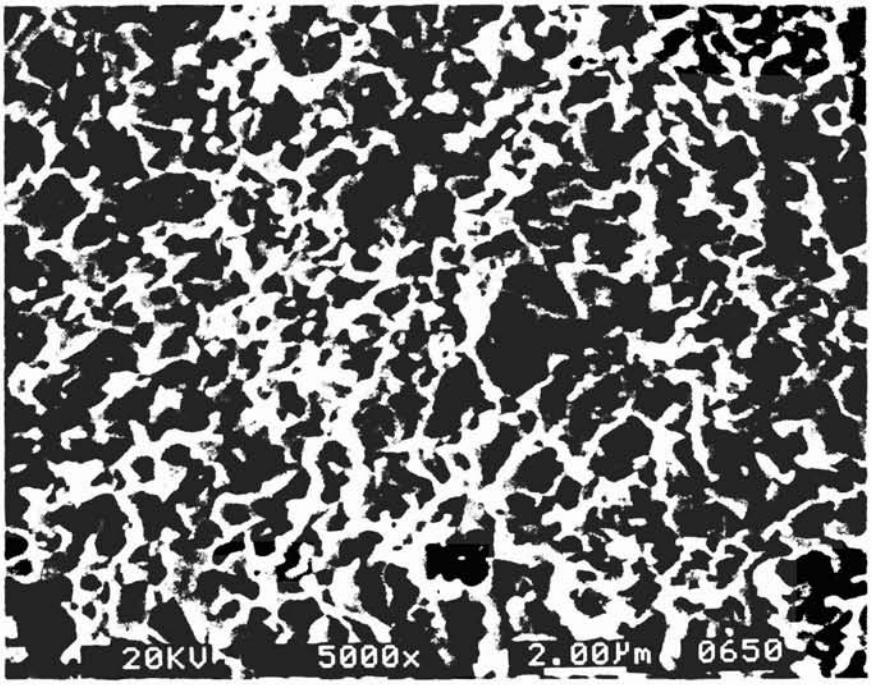
In etching, first a of tungsten carbide is etched and then the cobalt is removed from the grain boundaries near the surface. This involves treating the substrate with a solution of 1:1:10 potassium hydroxide, potassium ferricyanide, and water for 6-25 minutes and subsequently with 30% H_2SO_4 in hydrogen peroxide for 6 seconds (Peters and Cummings, 1993). This treatment has significant effect on micro-roughness of the surface. Figure 17 is the surface of the tool before etching and after etching. It can be seen that the scratch marks due to grinding has been removed and is replaced by isotropically rough surface.

6.2.3 Use of Interlayers

It has been suggested the that use of graded interlayers will improve adhesion of diamond coatings to the substrate (Braza and Sudarshan, 1992). Materials, such as titanium and silicon may reduce the mismatch in the properties between diamond and the substrate. Hence, commercially available tools coated with titanium carbide were used to investigate the effect of interlayers on adhesion of diamond coatings.



(a) Before etching



(b) After etching

Figure 17 SEM micrograph of the surface of tungsten carbide tool before and after etching showing isotropic roughness in the etched tool

7.0 RESULTS

Short duration deposition experiments were conducted to study the effect of process parameters on nucleation of diamond on cemented tungsten carbide tools. Deposition for longer duration was carried out to obtain adherent coatings. For this, cemented tungsten carbide tools with different cobalt contents were used. Different substrate temperatures and different methods of pre-treatment were also used. Some tests were also conducted on commercially available titanium carbide coated cutting tools. The diamond coatings obtained from these experiments were characterized using a scanning electron microscope (SEM).

7.1 Effect of Filament Substrate Distance

Experiments were conducted at 2, 4 and 7 mm filament - substrate distances. The test conditions employed are given in Table 9. The micrographs of the diamond coatings for these conditions are shown in Figures 18, 19, and 20, respectively. It can be seen from the micrographs that at 2 mm filament-substrate distance, well defined crystals of diamond are obtained but the nucleation is sparse. At 4 mm, the nucleation density is higher and the structure of the diamond is not well defined. At 7 mm, the nucleation of diamonds is negligible.

7.2 Effect of Pressure

Table 10 lists the process parameters used in a study on the effect of pressure. Figures 21, 22 and 23 are micrographs of diamond deposited at chamber pressure of 20, 30, and 40 torr respectively. It is clear from the Figures

Table 9 Process Parameters Used to Study The Effect of Filament Substrate Distance

Filament Temp, °C	2050
Substrate Temp, °C	500
Pressure, torr	20
Flow rate of CH_4/H_2, sccm	0.5/99.5
Duration, hours	5

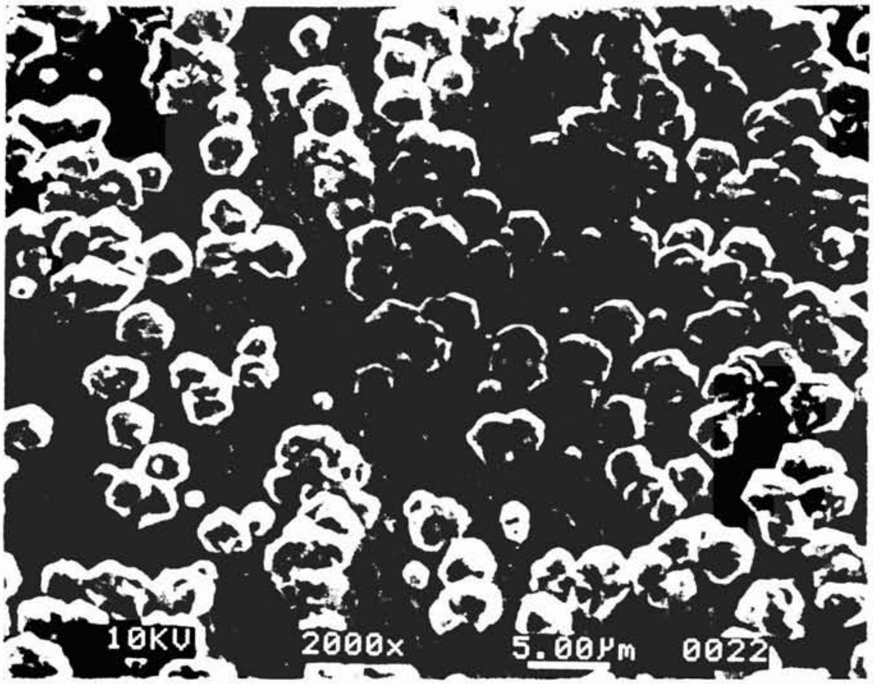


Figure 18 SEM micrograph of diamond coating at 2 mm substrate filament distance showing crystalline structure

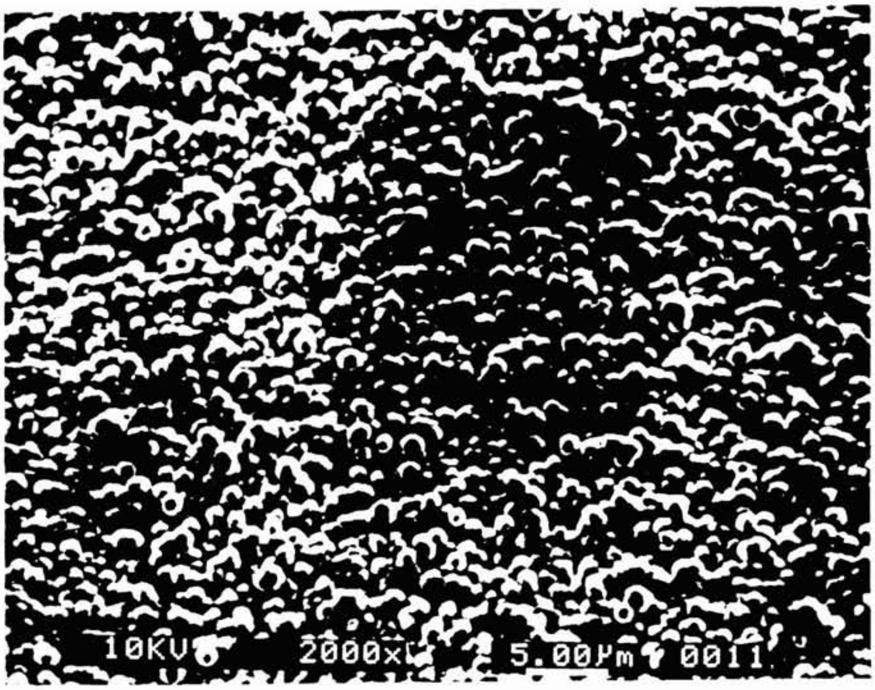


Figure 19 SEM micrograph of diamond coating at 4 mm substrate filament distance showing ball like structure

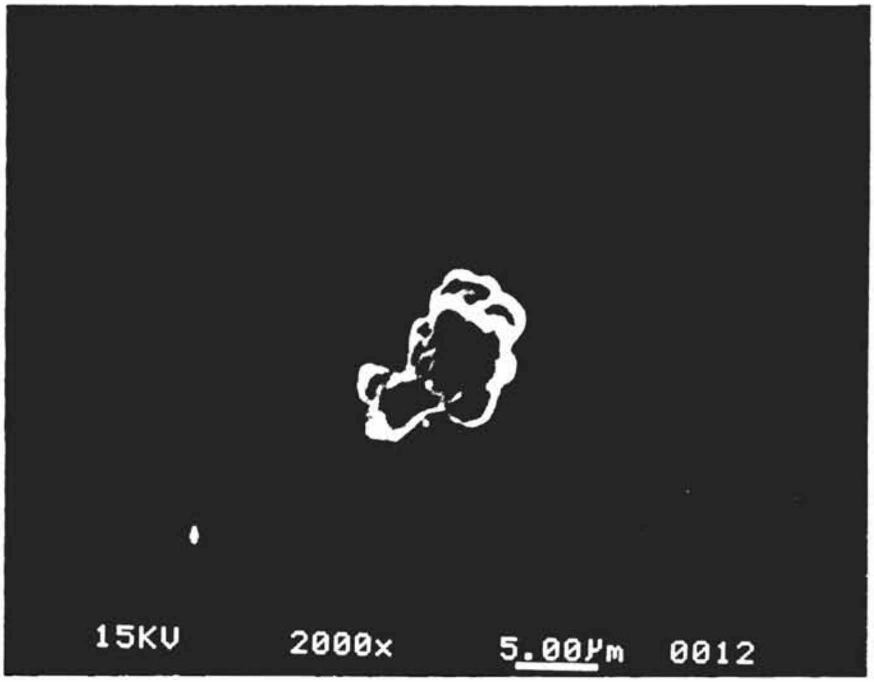


Figure 20 SEM micrograph at 7 mm substrate filament distance showing sparse nucleation

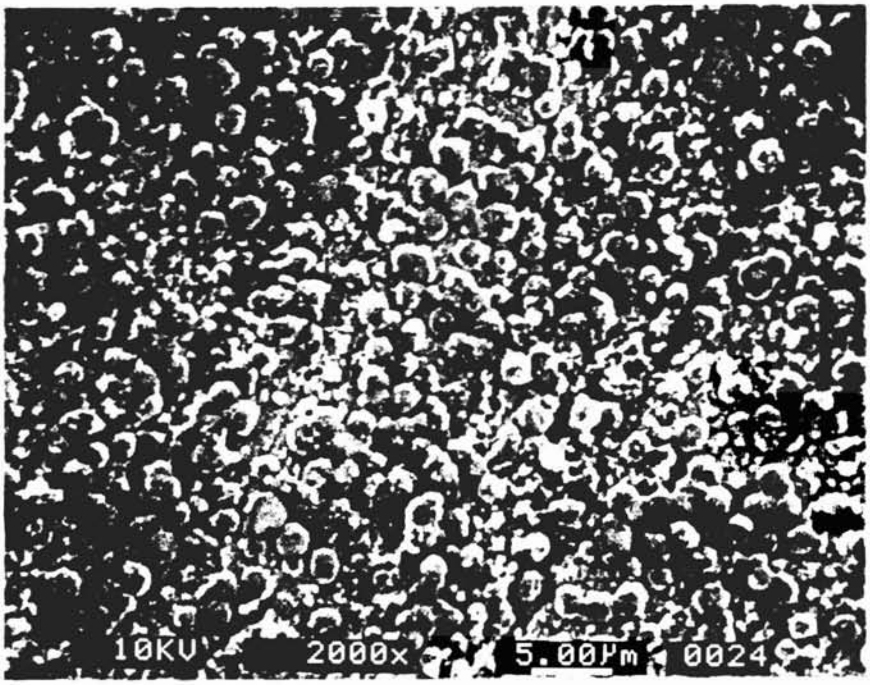


Figure 22 SEM micrograph of diamond coating at 30 torr pressure showing ball like structure

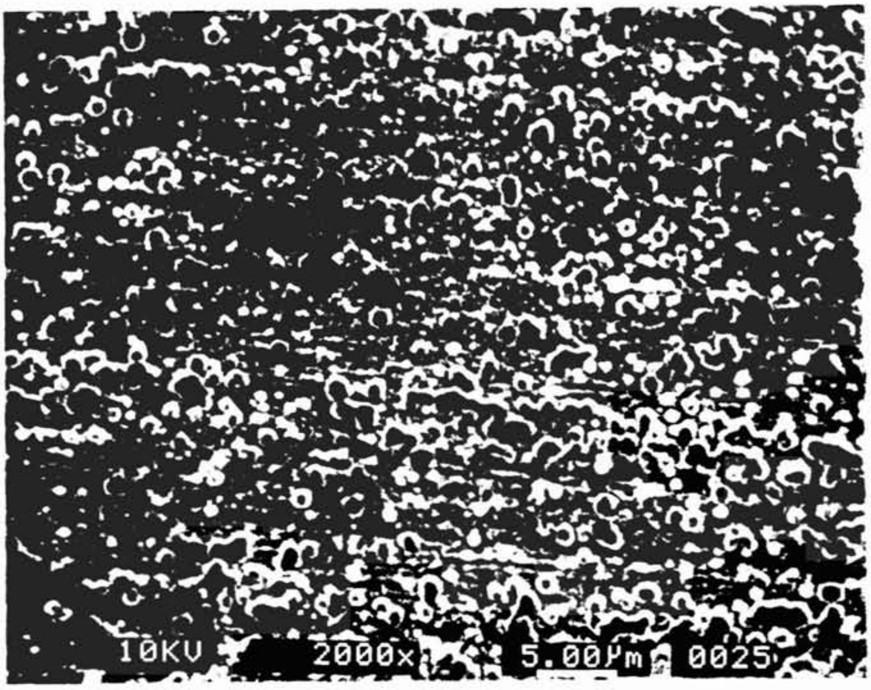


Figure 23 SEM micrograph of diamond coating at 40 torr pressure showing ball like structure and lower density of nucleation

21, 22, and 23 that the nucleation density decreases with increase in pressure. Thus 20 torr appears to be the best pressure to obtain maximum nucleation.

7.3 Effect of Duration

Experiments were carried out for 5, 10, and 25 hours to study the effect of duration on deposition. Table 11 gives the parameters employed. Figures 19, 24, and 25 are SEM micrographs for these tests. It can be observed from the micrographs that at 5 hours only nucleation of the diamond takes place. At 10 hours a continuous coating with predominantly ball like structures, similar to diamond like carbon, is seen. After 25 hours a continuous film with crystalline diamond structure is obtained. Also, it can be seen that some of the facets are not completely developed. Coating thickness was measured on delaminated coating using an optical microscope. The thickness of the coating was found to be about ~5 µm after 10 hours and 40 µm after 25 hours.

Table 11 Process Parameters Used to Study the Effect of Duration

Filament Temp., ^oC	2050
Substrate Temp., ^oC	500
Pressure, torr	20
Flow rate of CH_4/H_2, sccm	0.5/99.5
Fil-Subst. Dist., mm	4

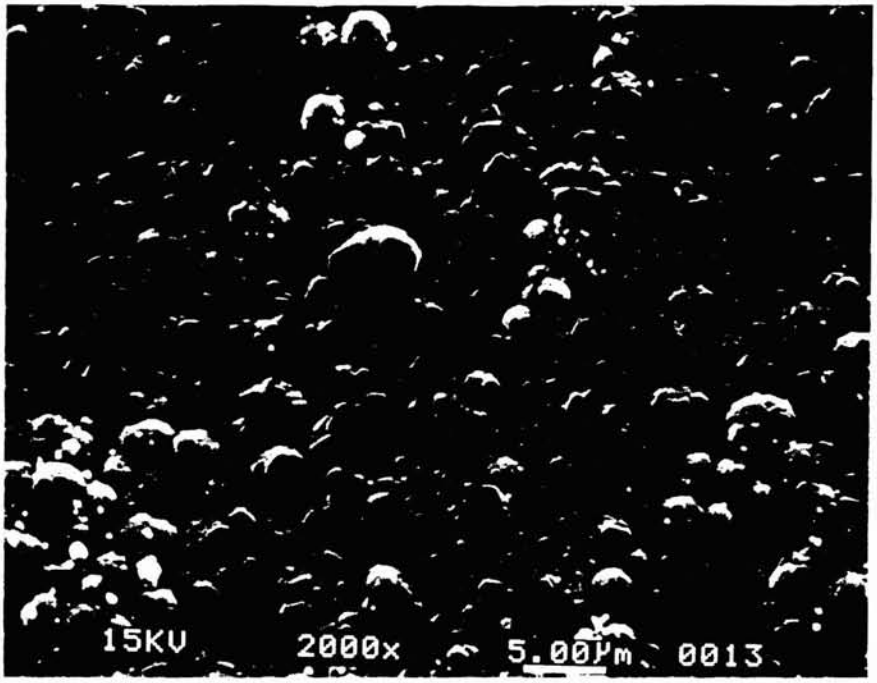


Figure 24 SEM micrograph of diamond coating at 10 hours showing ball like structure

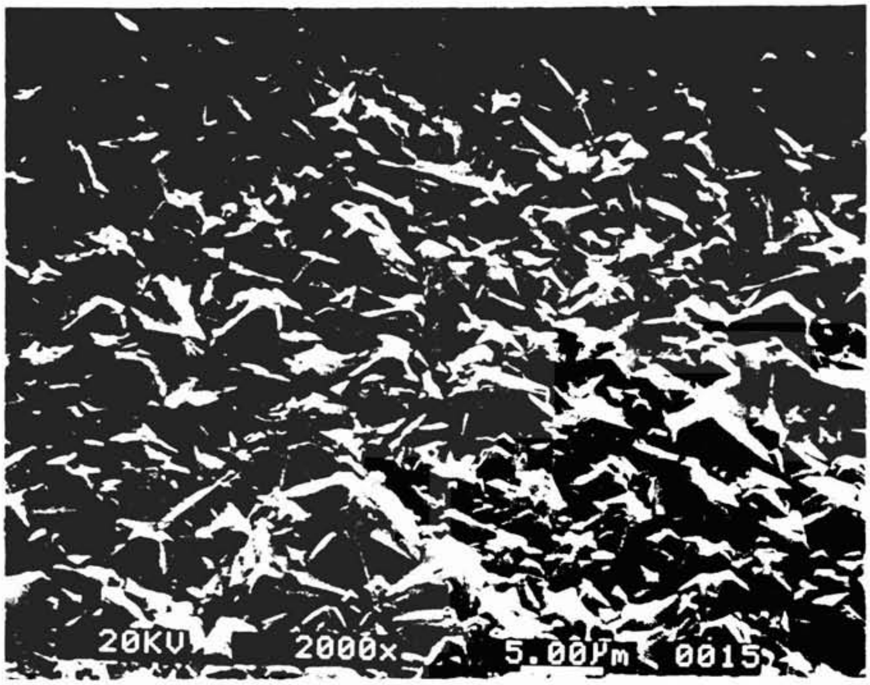


Figure 25 SEM micrograph of diamond coating at 25 hours showing crystalline structure

7.4 Effect of Cobalt

To study the effect of cobalt content experiments were conducted on tools with 3%, 6%, and 12% cobalt. In the first set of experiments tools were subject to microflawing. The parameters used in these experiments are given in Table 12. It was observed that the adhesion of diamond film was good with 3% and 6% cobalt tools. On the other hand, diamond coating on 12% cobalt tools delaminated. Figure 25 is a SEM micrograph of the diamond coating on a 6% cobalt tool. Figures 26 and 27 show the top and the bottom view respectively of the delaminated coating. The bottom of the coating corresponds to the interface between tool and coating. It can be seen from Figure 26 that the coating consists of ball like structures, mostly amorphous carbon. On the other hand with the 6% cobalt cutting tool a crystalline diamond coating was obtained (Figure 25). The bottom of the delaminated coating for the 12% cobalt tool (Figure 27) appears like a replica of the grinding marks on the surface of the cutting tool. Also the coating appears amorphous in nature.

Table 12 Process Parameters Used for Diamond Deposition after Microflawing Treatment

Filament Temp., ^oC	2050
Substrate Temp., ^oC	500-700
Pressure, torr	20
Flow rate of CH_4/H_2, sccm	0.5/99.5
Duration, hours	25
Fil-Subst. Dist., mm	4

In the second set of experiments, the tools were subjected etching. Table 13 gives the other parameters used. Figures 28, 29, and 30 are the SEM

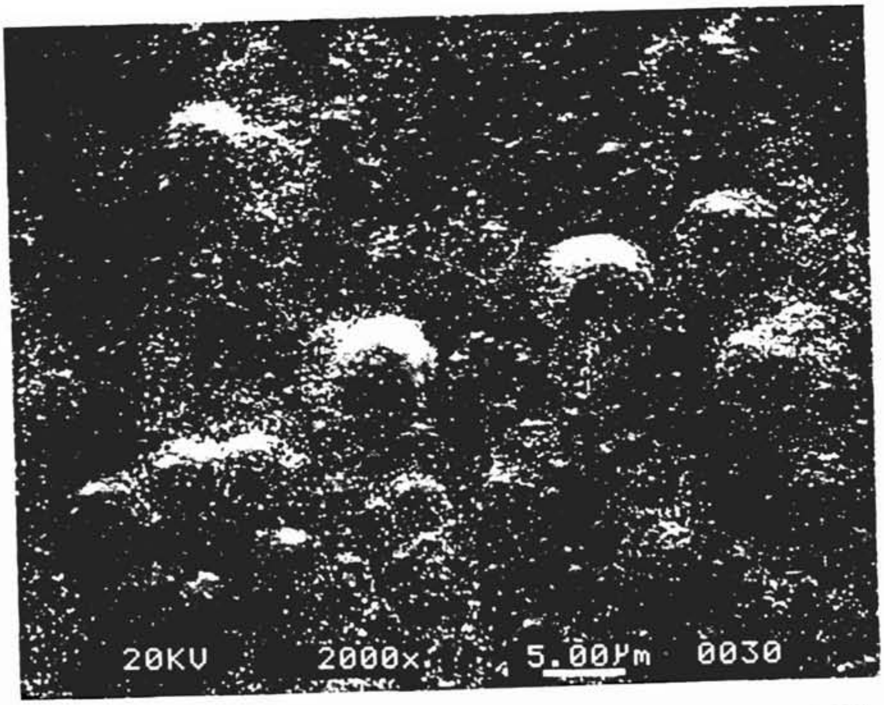


Figure 26 SEM micrograph of top surface of diamond coating on 12% cobalt tool showing amorphous structure

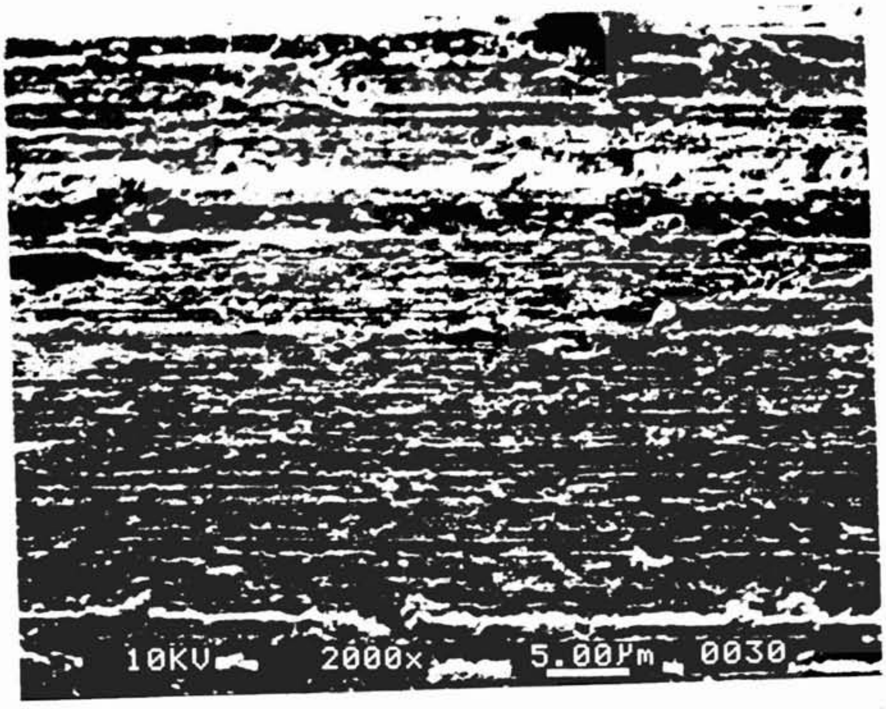


Figure 27 SEM micrograph of the interface of diamond coating and 12% cobalt tool showing grinding marks

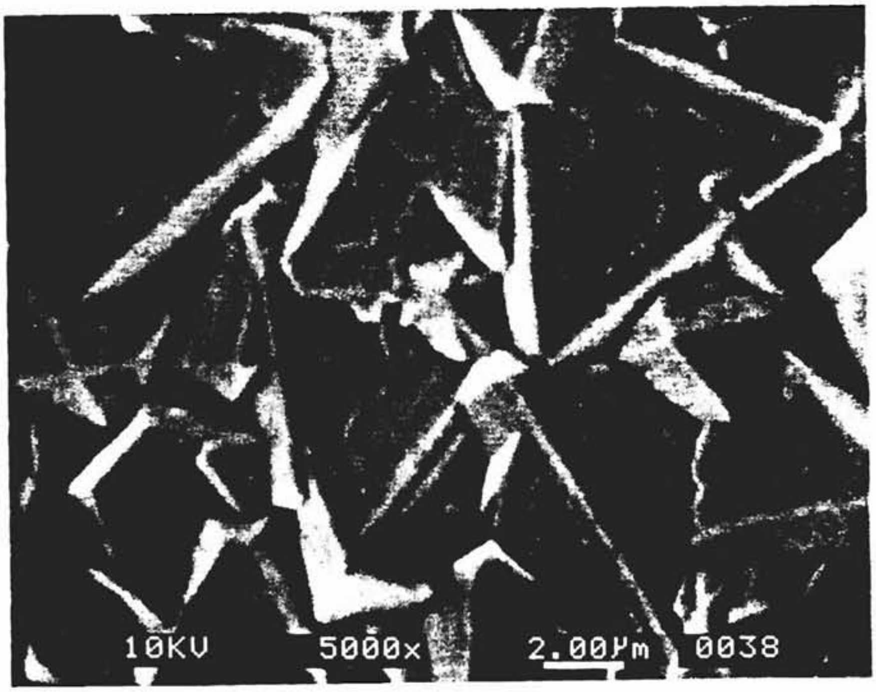


Figure 28 SEM micrograph of diamond coating on 3%cobalt tool showing octahedral structure

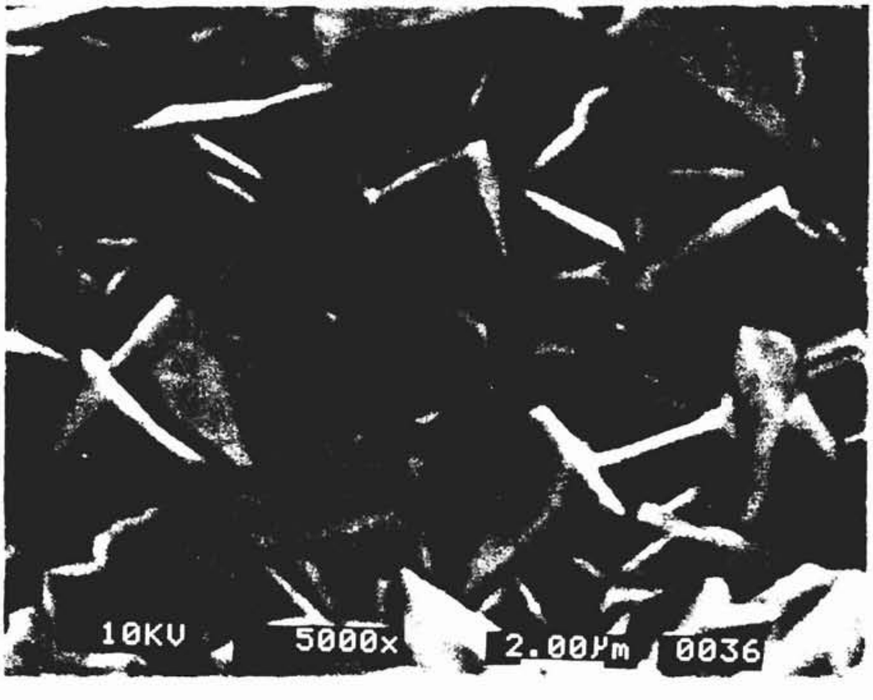


Figure 29 SEM micrograph of diamond coating on 6%cobalt tool showing octahedral structure

Figure 30 SEM micrograph of diamond coating on 12% cobalt tool showing octahedral structure

micrographs of diamond coatings for etched 3%, 6%, and 12% cobalt tools, respectively. In these experiments the coating had good adhesion and the morphology of the diamond was octahedral in all the cases. Deposition was carried out at a lower substrate temperature (700°C) on a 12% cobalt tool subjected to etching. The coating delaminated after the deposition. Figure 31 is a SEM micrograph of the diamond coating for this test. The diamond in this coating exhibits defects in the crystal structure and incompletely formed facets.

Table 13 Process Parameters Used for Diamond Deposition After Etching

Filament Temp., °C	2050
Substrate Temp., °C	900
Pressure, torr	20
Flow rate of CH_4/H_2, sccm	0.5/99.5
Duration, hours	25
Fil.-Subst. Dist., mm	4

7.5 Effect of Interlayers

Generally interlayers are applied between the diamond coating and substrate to provide a graded interface to improve the chemical compatibility including matching of the thermal expansion coefficients. It is suggested that carbide forming materials such as titanium and silicon can be used as inter layers to improve adhesion (Braza and Sudarshan, 1992). This is because carbide forming materials provide chemical compatibility. During diamond deposition titanium is first converted to titanium carbide and then diamond nucleates on top of this titanium carbide (TiC) layer. Therefore, use of TiC coated tools, which are commercially available, can reduce the time required for

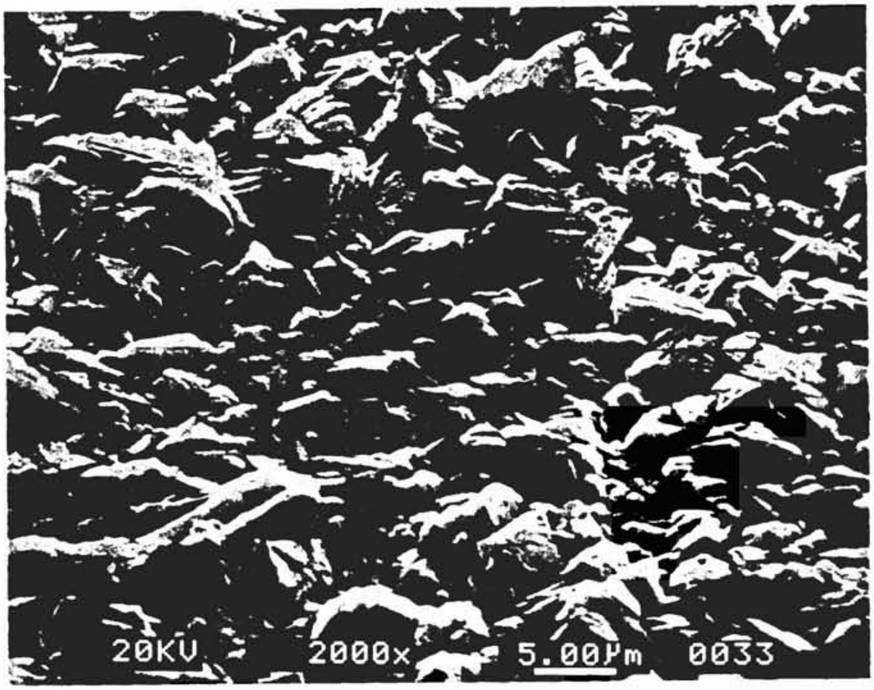


Figure 31 SEM micrograph of diamond coating on 12% cobalt tool at 700^{o}C substrate temperature showing imperfect crystals

diamond nucleation. Hence, in the present study titanium carbide (TiC) coated tungsten carbide cutting tools from three commercial tool manufacturers were used as an interlayer. Based on SEM examination of the coatings, the morphology of TiC coatings has been found to be different depending on the manufacturer. Figures 32, 33, and 34 are the SEM micrographs of the titanium carbide coatings of manufacturers A, B, and C, respectively. It can be seen that coatings from manufacturers A and C (Figures 32 and 34) are smooth, whereas the coating from manufacturer B(Figure 33) has a crystalline structure. This difference in structure may be due to differences in stoichiometry of TiC coating and the process conditions used.

Initially, experiments were conducted on the TiC coated tungsten carbide tools from manufacturer A. Table 14 gives the details of the various process parameter used for deposition (Tests 1-5). All substrates were subjected to microflawing surface treatment before deposition. As mentioned earlier, the theoretical substrate temperature required for obtaining stress free interface between TiC and diamond is around 450°C. But, it is not possible to grow diamonds at such low temperatures. The minimum possible bulk temperature is about 500-600°C in the present experimental set up, at a distance of 4 mm from the filament. Also, the growth rate is higher at higher substrate temperatures. Hence, the substrate temperature was varied from 600-1050°C. In all cases, the coating delaminated at the end of deposition. Therefore, it appears that in the range of substrate temperatures investigated, substrate temperature does not really seem to play much role in improving adhesion of diamond coating on TiC coated tools.

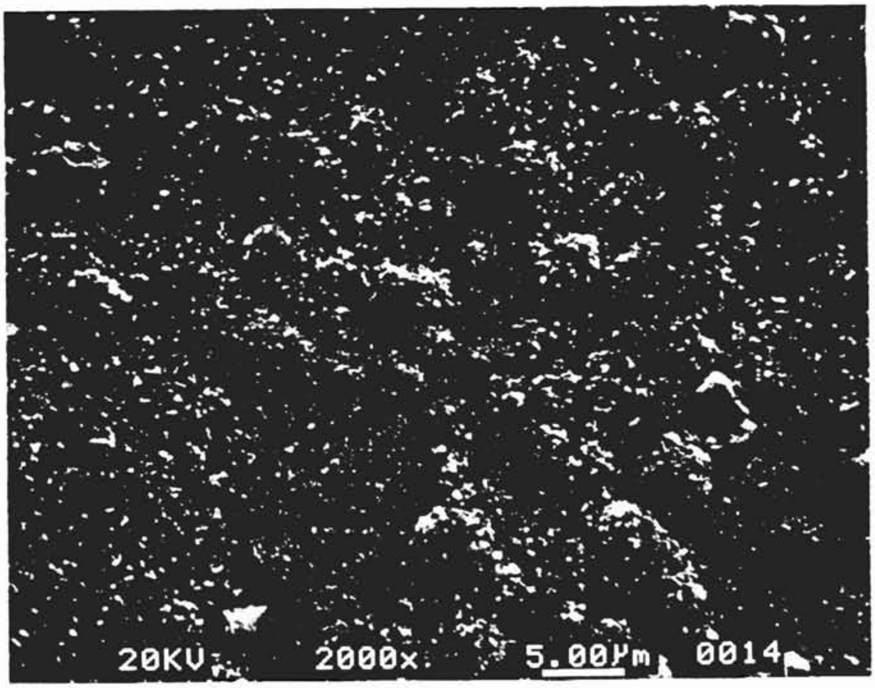


Figure 32 SEM micrograph of TiC coating from manufacturer A

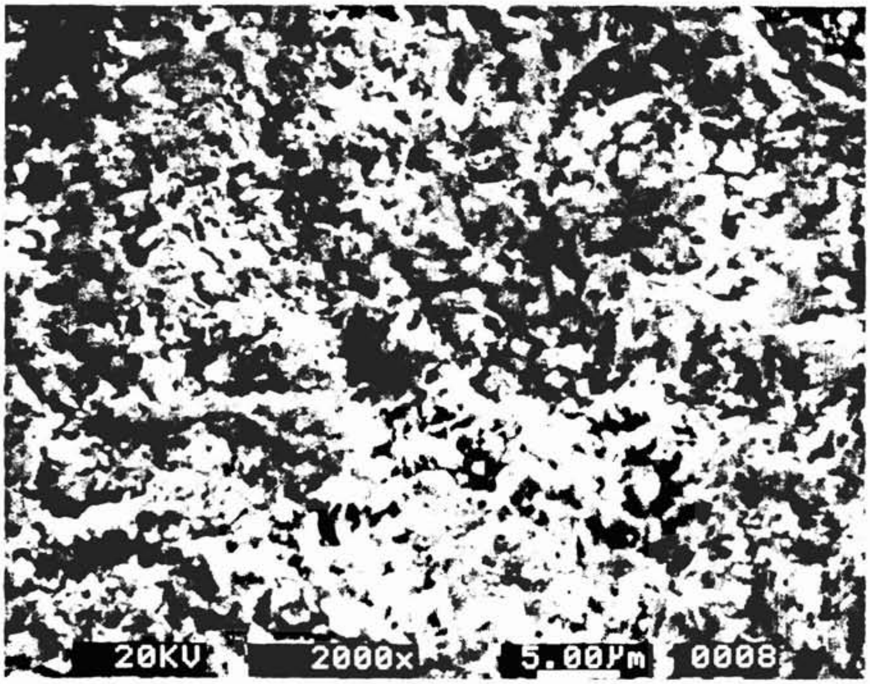


Figure 33 SEM micrograph of the TiC coating from manufacturer B

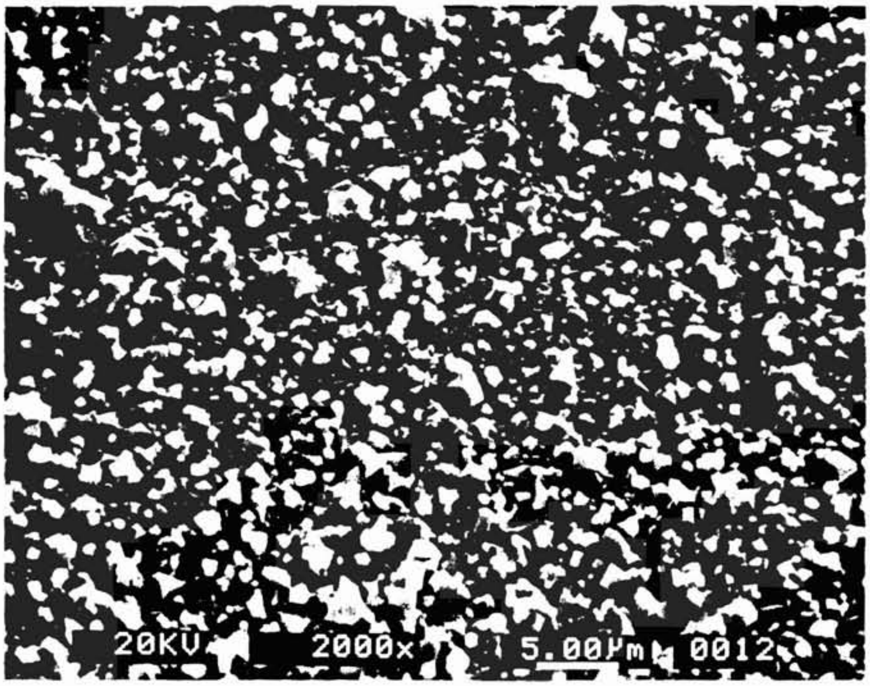


Figure 34 SEM micrograph of TiC coating from manufacturer C

Since, increase in the substrate temperature did not improve adhesion of diamond coating, other factors were considered including pre-treatment for altering the surface morphology. To investigate the effect of cleaning, tool from manufacturer A was subjected to a pre-treatment using activated hydrogen (Test 6). In this test, the substrate was heated to a temperature of 1000°C. The tungsten filament was heated to 2050°C and hydrogen gas was passed over it to obtain atomic hydrogen. The atomic hydrogen was used to clean the surface. Subsequently, the diamond deposition was carried out at a substrate temperature of 900°C. As with the earlier cases with tool A, the diamond coating delaminated.

The surface material in the TiC coating was etched for 3 minutes using aqua regia (Test 7). Subsequently diamond deposition was carried out at a substrate temperature of 900°C. Even in this case the diamond coating delaminated. In the next experiment, the etching time was increased to 10 minutes (Test 8). Figure 35 is a SEM micrograph of the etched surface showing *that the crystalline titanium carbide is exposed at the surface along with patches* of the base material. The presence of Ti was confirmed using the energy dispersive X-ray (EDAX) analyzer of the SEM, indicating that etching has not completely removed the TiC layer. In this case, the diamond coating was adherent. Figure 36 is a SEM micrograph of the coating showing octahedral morphology.

Tool from supplier B was subjected to microflawing surface treatment and diamond deposition was carried out at a substrate temperature of 900°C (Test 9). In this case the diamond coating was found to delaminate at the edges.

Table 14 Conditions Employed for Diamond Coating on TiC Coated Tungsten Carbide Tools

No	Tool	Pr, torr	Fil-temp, °C	Dist, mm	sub-temp, °C	Surface Treatment	Remarks
1	A	20	2050	4	600	Diamond	Peeled
2	A	20	2050	4	700	Diamond	Peeled
3	A	20	2050	4	900	Diamond	Peeled
4	A	20	2050	4	950	Diamond	Peeled
5	A	20	2050	4	1050	Diamond	Peeled
6	A	20	2050	4	900	Diamond 1/2 hr H_2 at 1000 °C	Peeled
7	A	20	2050	4	900	3 mins aqua regia Diamond	Peeled
8	A	20	2050	4	900	10 mins aqua regia Diamond	Adherent
9	B	20	2050	4	900	Diamond	Adherent (peeled at corner)
10	B	20	2050	4	900	20 mins aqua regia Diamond	Peeled at corners
11	B	20	2050	4	700	Diamond	Adherent
12	B	20	2050	4	700	Diamond	Adherent
13	C	20	2050	4	700	Diamond	Peeled
14	C	20	2050	4	700	1 hr aqua regia Diamond	Adherent

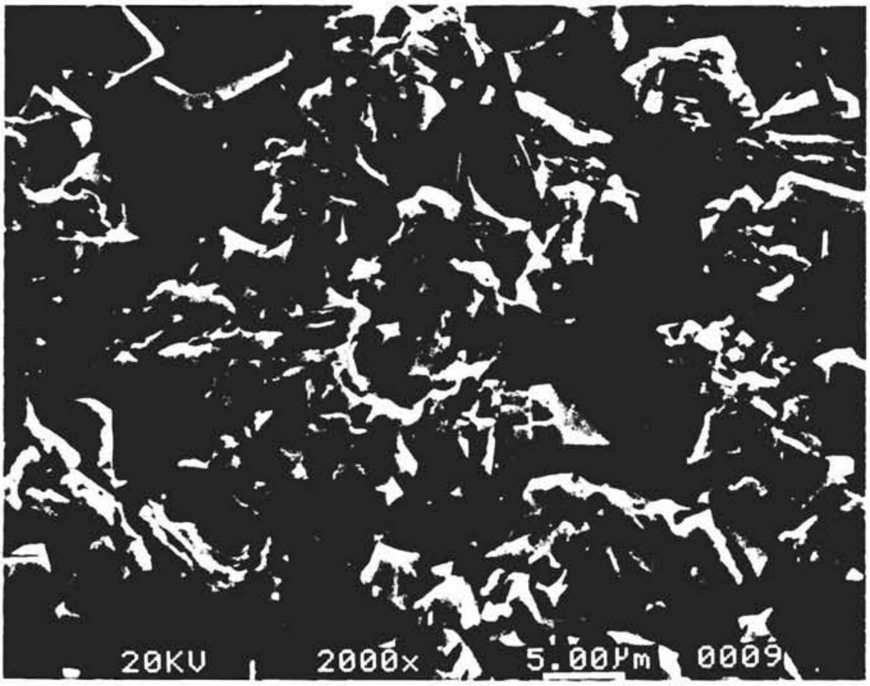


Figure 35 SEM micrograph of TiC coating from manufacturer A after 10 minutes etching

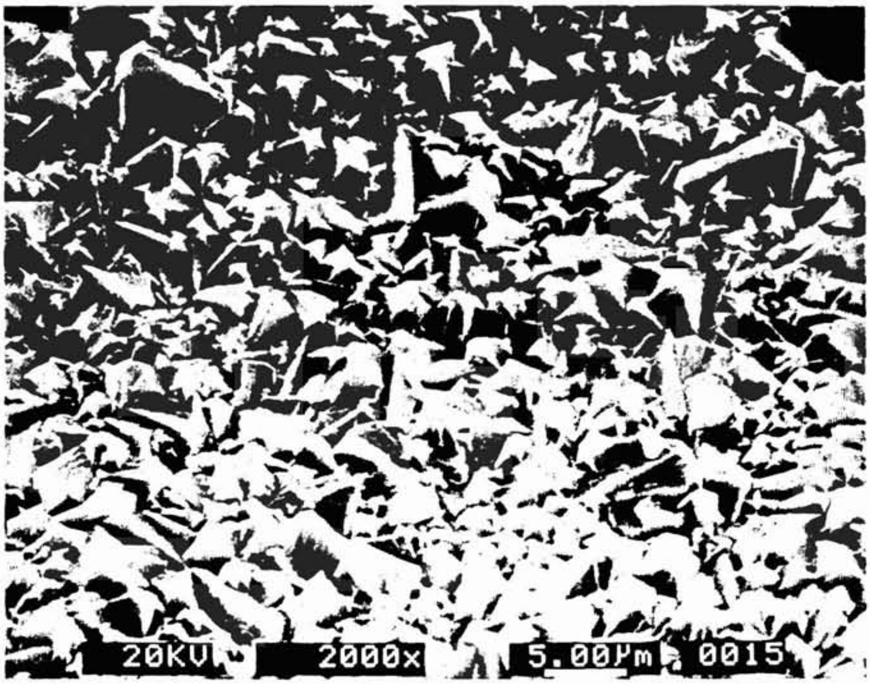


Figure 36 SEM micrograph of diamond coating on etched TiC coated tool from manufacturer A

Figure 37 is a SEM micrograph of delaminated coating near the edges. About 5 μm thick coating is seen after 10 hours of deposition. Etching for 20 minutes with aqua regia and subsequent diamond deposition at 900°C substrate temperature (Test 10) also resulted in delamination of the coating at the edges. The delamination of the coating could be due to thermal stresses caused by the mismatch in the thermal expansion coefficients. Hence, diamond deposition was carried out at a substrate temperature of 700°C on a surface subjected to only microflawing treatment (Test 11). In this case, an adherent diamond coating was obtained. Figure 38 is a SEM micrograph of this coating showing diamonds with cubic morphology, with cube faces visible on the top. The coating is continuous and the grain size is 2-3 μm. This test was repeated (Test 12) and the coating was again found to be adherent.

Based on the results with tools supplied by B, diamond deposition was carried out on tool from C at a substrate temperature of 700°C (Test 13). In this case, the tool surface was subjected to microflawing treatment before diamond deposition. The diamond coating was found to delaminate. Hence, etching with aqua regia was used as surface pre-treatment (Test 14), as it had given good results with tools from A. In the case of tools from C, it was determined that one hour of etching in aqua regia was needed to alter the surface morphology. Figure 39 is a SEM micrograph of the etched tool from manufacturer C. It is not clear why 1 hour etching was needed in the case of tool from C, while 10 minutes was sufficient for tool from A. Also, it is not clear why the morphology of the etched surfaces is different. It is possible that this could be due to differences in the stoichiometry of coating. An adherent diamond coating was obtained in this case. Figure 40 shows the diamond coating on this tool. It can be seen that the coating has about 4 μm size grains.

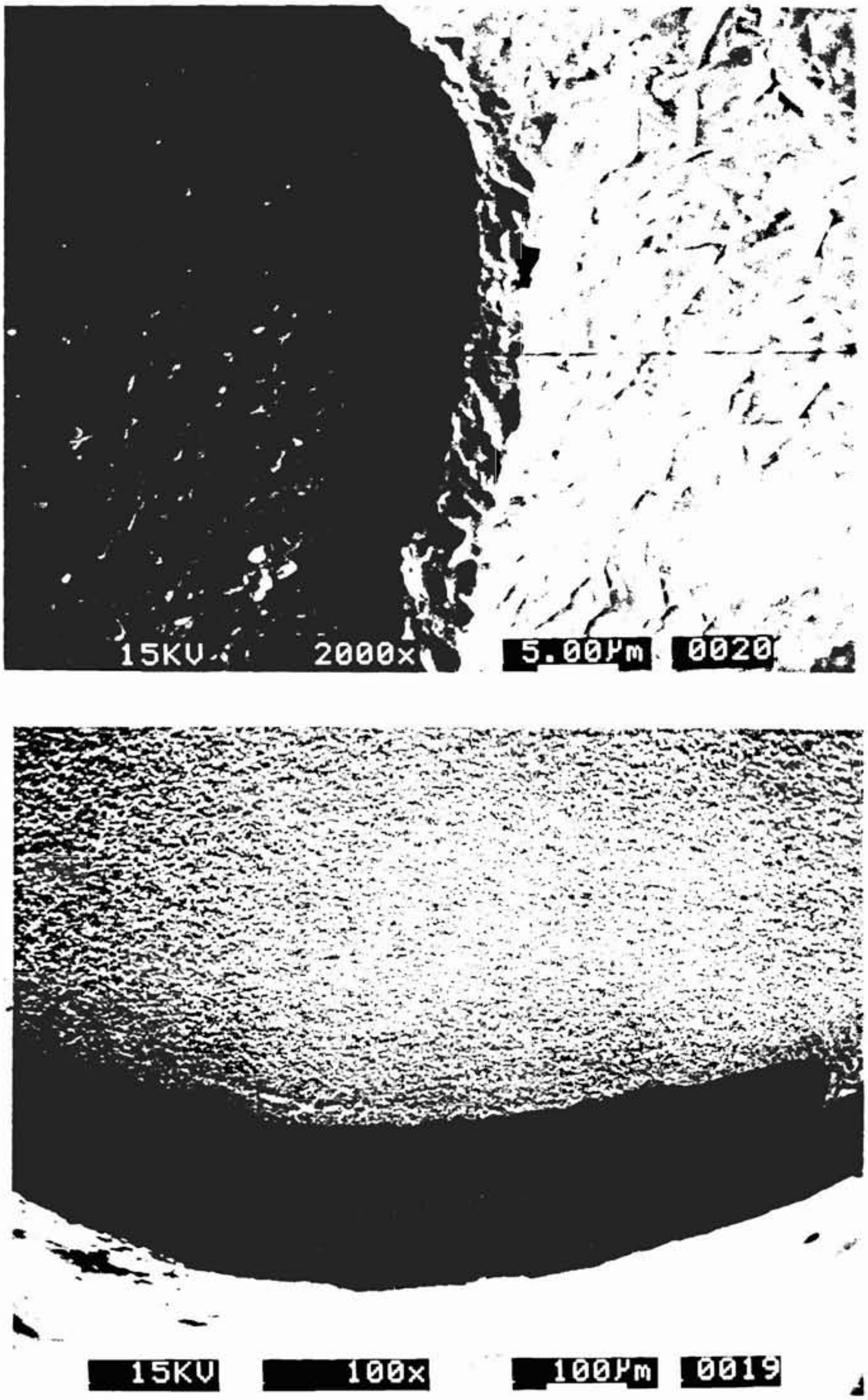


Figure 37 SEM micrograph of diamond coating on TiC coated tool from manufacturer B showing delamination at the corner

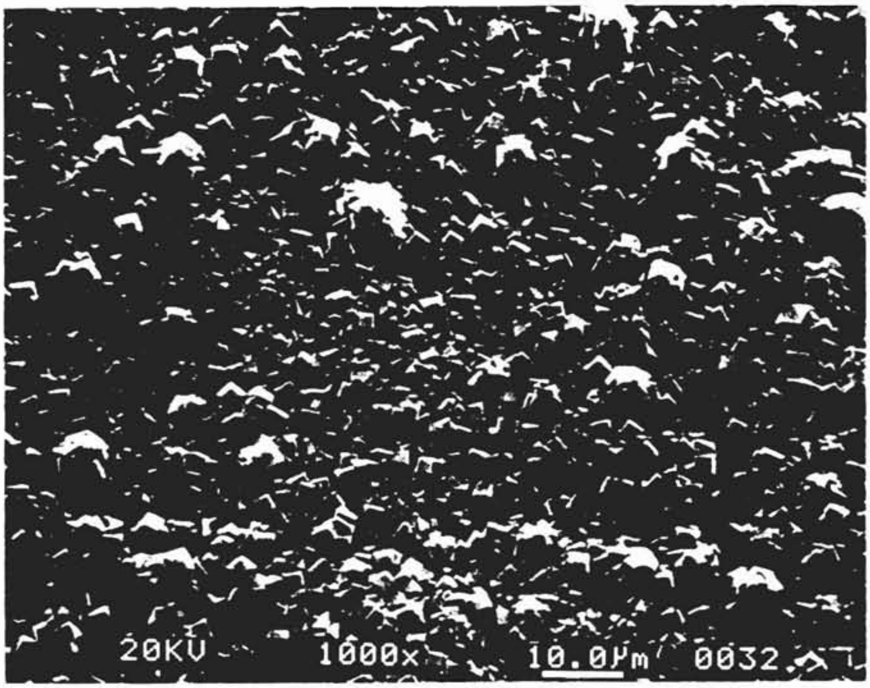


Figure 38 SEM micrograph of adherent diamond coating on tool from manufacturer B showing cubic structure

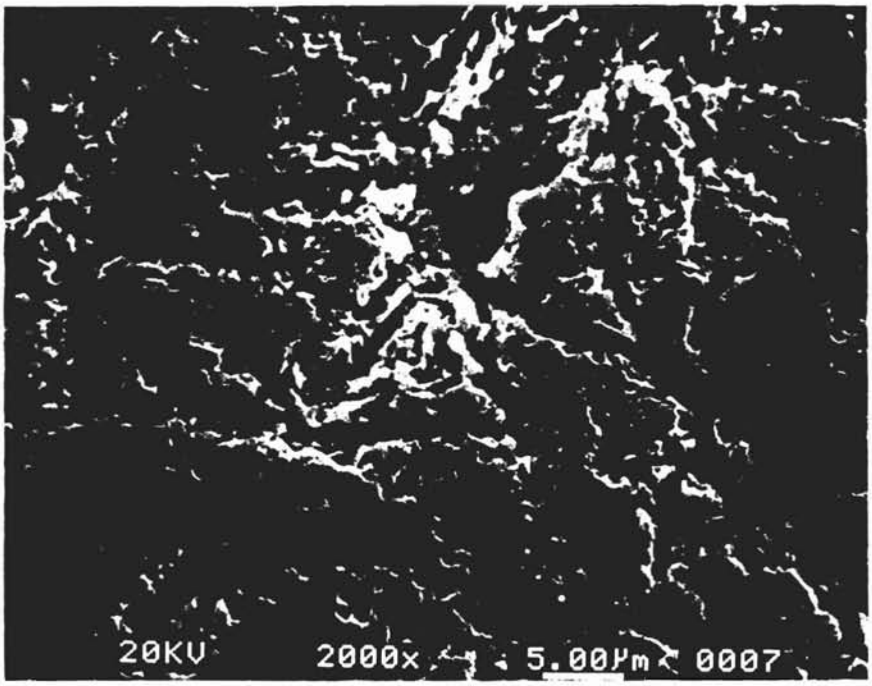


Figure 39 SEM micrograph of etched TiC coating from manufacturer C showing pits

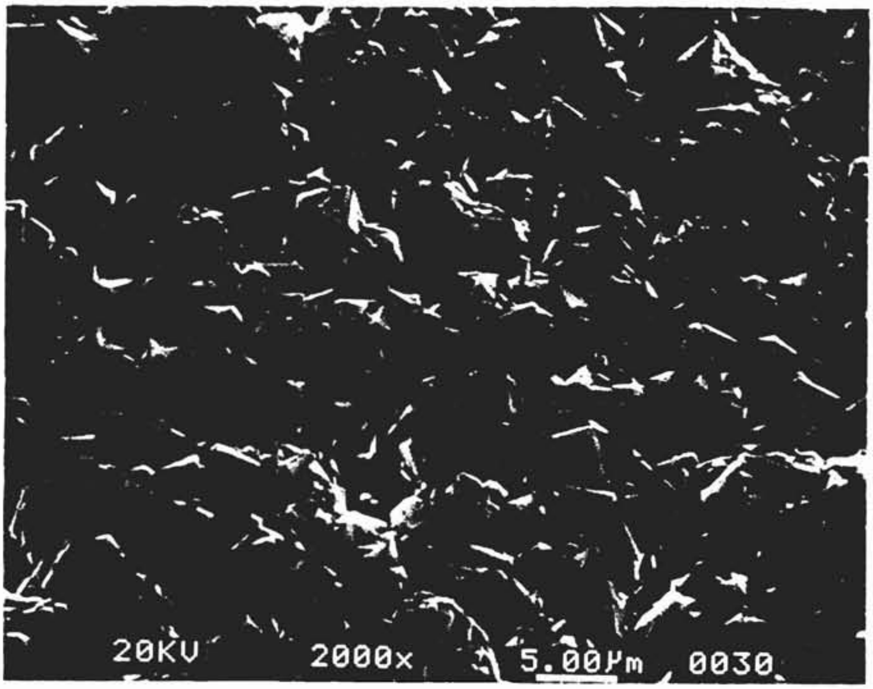


Figure 40 SEM micrograph of diamond coating on etched tool from manufacturer C showing an adherent coating with a grain size of ~4µm

7.6 Effect Of Substrate Materials

The most widely used tools are cemented tungsten carbide, titanium carbide coated cemented tungsten carbide, silicon nitride, and titanium nitride coated cemented tungsten carbide. Of these materials, diamond deposition on cemented tungsten carbide was discussed in detail in section 7.4 with emphasis on the effect of cobalt content. In section 7.5 diamond growth on titanium carbide coated tungsten carbide tools was discussed. In this section the results from deposition experiments on silicon nitride and titanium nitride coated cemented tungsten carbide are given. In all the tests, the substrate was subjected to microflawing treatment and the substrate temperature was maintained at 700°C. Other conditions employed for these tests are shown in Table 15. In Table 15 tests on cemented tungsten carbide and titanium carbide coated tungsten carbide are also given for comparison. It was found that it is possible to obtain adherent diamond coatings on tungsten carbide (with different cobalt content), titanium carbide coated cemented tungsten carbide (procured from 3 manufacturers), and silicon nitride, whereas, diamond coating on titanium nitride coated cemented tungsten carbide exhibited delamination. All these experiments were conducted at least two times for repeatability. Figures 25, 38, and 41 are SEM micrographs of diamond coating on tungsten carbide, titanium carbide coated cemented tungsten carbide, and silicon nitride respectively. It can be seen that coatings on tungsten carbide and silicon nitride exhibit similar structure and have grain size in the range of 3-4 μm. As mentioned earlier diamond coating on titanium carbide coated cemented tungsten carbide showed cubic structure and had grain size of ~2 μm. But, further experimentation suggested on TiN coated tungsten carbide tools to improve the adhesion of the diamond coating.

Table 15 Process Parameters Used in the Study of the Effect of Substrate Material

No	Tool	Press torr	Fil-temp °C	Dist mm	Sub-temp °C	Treatment	Remarks
1	Tungsten carbide (6%)	20	2050	4	600	Diamond	Adherent
2	Titanium carbide (supplier B)	20	2050	4	700	Diamond	Adherent
3	Silicon nitride	20	2050	4	700	Diamond	Adherent
4	Titanium nitride	20	2050	4	700	Diamond	Peeled

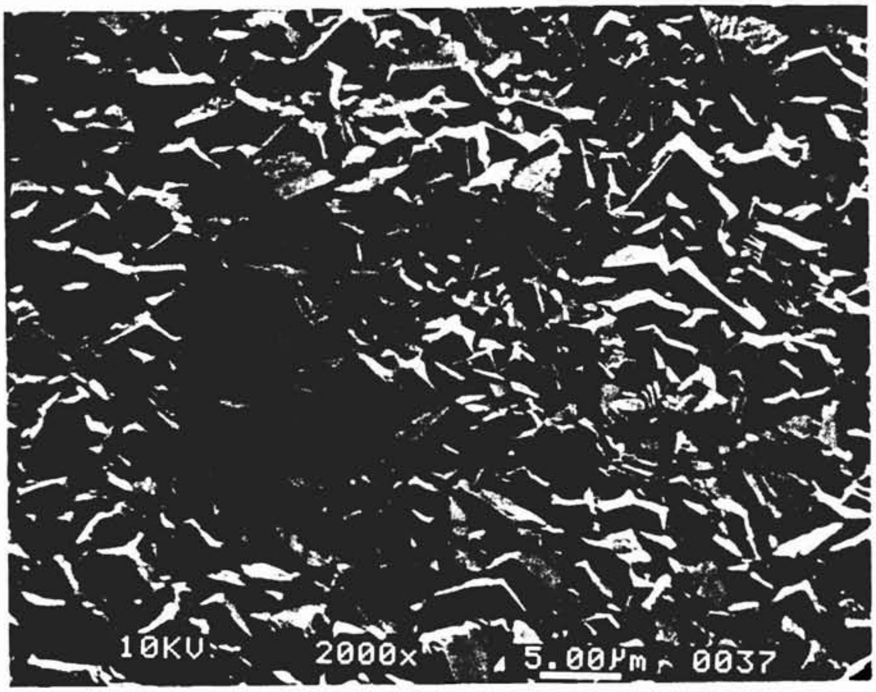


Figure 41 SEM micrograph of diamond coating on silicon nitride tool showing octahedral structure

8.0 DISCUSSION

8.1 Effect of Filament-Substrate Distance

It can be seen from Figures 19 to 21 (chapter 7) that filament substrate distance has a major influence on the nucleation rate. At very small distances, the nucleation is low and confirmed to region directly underneath the filament, as the active species do not have sufficient time to spread out and cover the whole surface. On the other hand, at large distances, the active species may diffuse into the chamber again resulting in reduced nucleation. Also, there is sufficient time for recombination of active species to form methane and hydrogen. This again leads to a reduction in the amount of nucleation and there is possibility of formation of diamond like carbon. Thus, it can be seen that there is an optimum distance at which the nucleation is high and uniform over the entire surface. This distance will vary depending on other parameters such as filament shape, filament temperature, substrate temperature, substrate area, flow rate, and methane concentration. For the present setup and conditions used, the optimum filament-substrate distance was determined to be 4 mm.

8.2 Effect of Pressure

Pressure is one of the important parameters which control nucleation density. It can be seen from Figures 22 to 24, the amount of nucleation varies with pressure. At higher pressures, the energy required for dissociation/ creation of active species is high. Also, the probability of recombination of gases is more because of more collision among the molecules. This leads to a reduction in nucleation density and also contributes to the formation non-diamond carbon (graphite). Such graphitic deposition could lead to delamination of the coating. On the other hand, at very low pressure though the recombination is less, number of active species available for the diamond formation may be very low. This would lead to reduced growth rate. Thus there is an optimum pressure, which was determined to be 20 torr in the present study. At this pressure, good nucleation density is obtained with reduced formation of non-diamond carbon. It should be noted that other process parameters will have an influence on the value of optimum pressure.

8.3 Effect of Duration

It takes about 1 hour for the experimental conditions to stabilize and the nucleation to begin. The nucleation stage continues for about 5 hours after which the film growth begins. The morphology of the diamond coating at this stage is small, ball like structure. As the deposition progresses, the morphology changes and is more crystalline. After 10 hours, a continuous coating of diamond with distinct crystalline structure is obtained (Figure 25). The thickness of the coating is ~5 μm. After 25 hours (Figure 26), about 40 μm thick diamond coatings are obtained. The diamond morphology is crystalline and there is little change in the crystal size as compared to 10 hours. If a thicker coating is required the coating duration can be further increased. For most metal cutting applications thin coatings of the order of few microns (~5 μm) is sufficient. Also, thicker coatings lead to higher thermal stresses and higher possibility of delamination of coating. This is true both during deposition and at the time of usage. In the present investigation, coatings of about 40 μm were deposited so that by obtaining adherent coatings of this thickness we can assure the adherence of thinner coatings.

8.4 Effect of Cobalt Content

In the present investigation adherent coatings were obtained on 3%, 6% and 12% cobalt containing cemented tungsten carbide tools. However, tools with 12% cobalt content had to be subjected to etching to obtain adhesion, while microflawing was sufficient for tools with 6% cobalt content. Also, when microflawing was used on 12% cobalt cutting tools amorphous coating with ball like structure was obtained. Lux and Haubner (1991) reported that cobalt in the cutting tool leads to graphitization of the diamond coating and consequently poor adhesion of the coating to the substrate. Thus, it appears that about 6% cobalt content is the limit for obtaining adherent diamond coating, when only microflawing is used.

As indicated earlier in the case of 12% cobalt tools, it was necessary to etch the surface of the substrate to get adherent coatings. The etching results in

- Increased surface roughness
- Isotropic surface as compared to directional grinding marks
- Reduction of surface stresses
- Removal of cobalt at or near the surface

All these factors are beneficial in the improvement of adhesion of coating to the substrate. With etched tools, it was found that higher cobalt content gives better diamond structure. Further, it was seen in the case 12% cobalt tools, higher temperatures (compare Figures 31 and 32) and etching (compare Figures 26 and 32) give better diamond morphology and adhesion.

Based on these results, it can be concluded that tools with 6% or lesser cobalt content can be used to obtain adherent coatings with only microflawing treatment. For tools with higher cobalt content chemical etching is useful in improving adhesion. Lower cobalt content, etching (on tools with higher cobalt content), and higher substrate temperature lead to better adhesion and better diamond morphology.

8.5 Effect of Interlayers

Another method for obtaining good adhesion is to use graded interlayers. Lux and Haubner (1991) suggested titanium carbide as a suitable material. But the thermal expansion coefficient of titanium carbide is double that of diamond. This can lead to delamination of coating. The delamination can be prevented by having mechanical bonding between the coating and the substrate by increased surface roughness. Also, lower substrate temperatures would decrease the thermal stresses induced. In the experiments conducted it was shown that the tool with crystalline structure exhibited good adhesion of diamond coating, where as, the coating delaminated on titanium carbide coating with amorphous structure. Since etching creates isotropically rough surface, it is possible to get good adhesion on the titanium carbide coating with amorphous structure. Also, it was found that at higher substrate temperatures, even the tool with crystalline morphology exhibited delamination of coating. Therefore, it is necessary to have the substrate temperature in the lower range to obtain adherent coatings.

8.6 Effect of substrate materials

The properties of various tool materials employed in the present study is given in Table 1. It is known that the thermal expansion coefficient of materials play an important role in the adhesion of coatings. Since silicon nitride has thermal expansion coefficient closest to that of diamond (Table 1) and it appears that adherent diamond coatings can be obtained on this material. Similar observation has been reported in the literature (Sprow, 1995). Tungsten carbide, with a thermal expansion coefficient of $5 \times 10^{-6}/^{o}C$ should also give good adherence. However, cobalt used as binder in tungsten carbide cutting tools has a thermal expansion coefficient of $12.3 - 18.1 \times 10^{-6}/^{o}C$ which makes obtaining good adhesion difficult. With titanium carbide, low temperatures and specific surface morphology are needed to obtain good adhesion due to high thermal expansion coefficient . Due to large mismatch in the thermal expansion coefficient between titanium nitride and diamond, it would be difficult to obtain adherent diamond coatings as found in the present investigations.

9.0 CONCLUSIONS AND FUTURE WORK

9.1 Conclusions

1. A state-of-the art hot filament CVD reactor was designed and built for diamond synthesis.

2. In this investigation adherent diamond coatings were obtained on cemented tungsten carbide (with 3%, 6%, and 12% cobalt), titanium carbide coated cemented tungsten carbide (from 3 manufacturers), and silicon nitride.

3. Three types of substrate surface treatments, namely microflawing, etching and use of interlayers, were used with cemented tungsten carbide tools. Microflawing was sufficient for tools with less than 6% cobalt content. Tools with 12% cobalt content had to be subjected to etching to obtain adhesion. Table 16 shows the conditions at which adherent coatings can be obtained on the substrate materials (tools) used in this study.

4. When titanium carbide coating was used as an interlayer, it was possible to obtain adherent diamond coatings. The titanium carbide coated tools exhibited either a crystalline or smooth surface depending on the manufacturer. In the case of smooth titanium carbide coating, etching which produces isotropically rough surface, was found to be necessary for the adhesion of diamond coating.

5. Adherent diamond coatings were obtained on silicon nitride cutting tools at substrate temperature of 700°C.

6. When titanium nitride coating was used as interlayer, the adhesion of diamond coating was found to be poor. One reason for this can be due to very large mismatch in the thermal expansion coefficients of titanium nitride and diamond. However, further investigation is needed to study the effect of factors such as etching and substrate temperature.

7. Filament pre-treatment was found to be necessary for maintaining constant temperature and prolonged filament life. This is because the filament temperature (without pre-treatment) was found to decrease with time during deposition. This is due to carburization of the filament, which leads to an increase in the filament diameter and consequently increase in power required to maintain the filament temperature. Pre-carburization of the filament by heating the filament to 2000°C in an atmosphere of methane was found to eliminate this problem. It was found that carburization at 5-10 torr methane pressure results in best performance of the filament.

8. Parametric studies were conducted to determine the optimum operating conditions for diamond deposition. From these experiments, it was found that the following conditions are suitable for diamond deposition.
   Pressure: 20 Torr
   Filament-substrate distance: 4 mm
   Deposition time: 10 hours

Table 14 Conditions Employed for Diamond Coating on Tool Materials Used in the Present Investigation

No	Tool	Pr, torr	Fil-temp, °C	Dist, mm	sub-temp, °C	Surface Treatment
1	WC (3%)	20	2050	4	900	Etching + Diamond
2	WC (6%)	20	2050	4	900	Etching + Diamond
3	WC (12%	20	2050	4	900	Etching + Diamond
4	TiC (Supplier A)	20	2050	4	900	Etching +Diamond
5	TiC (Supplier B)	20	2050	4	700	Diamond
6	TiC (Supplier C)	20	2050	4	700	Etching + Diamond
7	Si_3N_4	20	2050	4	700	Diamond

9.2 Future Work

Following are the aspects that need to be addresses in future:

- Further research is needed to establish a physical/ chemical basis for the beneficial results obtained by etching of 12% cobalt cemented tungsten carbide tools.
- Surface morphology of the substrate seems to affect the adhesion of diamond coating for both cemented tungsten carbide and titanium carbide coated cemented tungsten carbide. This effect needs to be studied further.
- Several studies have shown that smooth diamond coatings will enhance tool life during machining. Possibility of obtaining smooth diamond coatings by appropriate process control has to be explored.

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APPENDIX

1. **DC Power Supply**

   Manufacturer: EMS Power Supplies Inc.,

   Feature: A high frequency switching power supply with constant current/constant voltage With automatic crossover.

   Rating : 600 W (20 V, 30A)

   Model No: EMS II 20-30

2. **Pressure Controller**

   Manufacturer: MKS Measurements Inc.,

   Feature: Closed loop PID controoler with a 0.25% of Full scale accuracy

   Model No: Type 250

3. **Mass Flow Meter**

   Manufacturer: MKS Measurements Inc.,

   Feature: 4 channe;l controller with channels either operating independently or in ratio

   Model No: Type 247

5. **Mass Flow Controller**

   Manufacturer: MKS Measurements Inc.,

   Feature: Closed loop PID controoler with a ±1.0% of Full scale accuracy

   Model No: Type 1159B

6. Substrare Temperature Controller

Manufacturer: Omega

Feature: Microprocessor based, programmable closed loop PID controoler (ON/OFF)

Model No: CN3001

VITA

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Master of Science

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