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A Comparison Study of Diamond Films Grown on Tungsten Carbide Cobalt Tool Inserts with CH₄ and CF₄ Gas Sources

by

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ABSTRACT

The results of a comparison study of continuous diamond coatings deposited on tungsten carbide-6% cobalt tool inserts using CF₄ and CH₄ gas sources are presented. The CH₄ grown diamond film utilizes a thin (1200 Å) amorphous silicon interlayer for adhesion while the CF₄ diamond film is deposited directly onto the tool insert. Diamond films produced with CF₄ gas have much higher growth rates and better adhesion than diamond films grown with CH₄ gas. The films are characterized by scanning and transmission electron microscopy, and Raman spectroscopy to determine film crystallinity and quality. Macroscopic indentation tests have been conducted to determine the adhesion of the films to the substrate, and an aluminum-17% Si alloy is machined with the diamond-coated tool inserts to determine their performance in a machining environment. A mechanism for the growth of diamond on tungsten carbide-cobalt using CF₄ gas is postulated.
I. INTRODUCTION

The unparalleled physical properties of diamond have driven researchers to synthesize diamond crystals and thin films. Recently and more specifically, the chemical vapor deposition (CVD) method, in forms such as microwave plasma CVD\(^1\), RF plasma CVD\(^2\), hot filament CVD\(^3\), electron assisted CVD\(^4\), laser assisted CVD\(^5\), DC plasma CVD\(^6\), and plasma jet CVD\(^7\), has received intensive investigation due to the possibility of the direct deposition of diamond films on a variety of substrates. Research and development interests are found in the electronics, aerospace, cutting tool, and related industries. For the cutting tool industry, the high hardness and thermal conductivity of diamond as well as the possibility of coating a variety of cutting tool shapes, a notable deficiency in polycrystalline diamond (PCD) technology, make CVD diamond an attractive alternative. Materials likely to be machined include Al-Si alloys, composites, ceramics, and various wood-based products. In fact interest in diamonds is escalating rapidly, and the average market for abrasive diamond, not to mention diamond's electronic or tribological markets, is expected to be $200 million by 1995\(^8\). While the forecasts look promising, many issues and problems remain to be solved.

In this paper, we present our research results on the CVD of diamond on tungsten carbide - cobalt (WC-Co). One of the most serious problems to be solved concerns the poor adhesion of the diamond film to the WC-Co substrate. Recent work on diamond
coating of cemented carbides has focused on two main issues: 1) Removal of near-surface cobalt by chemical\textsuperscript{9} or plasma\textsuperscript{10} etching to allow diamond deposition to proceed and 2) improvement of the coating substrate adhesion by various means. Adhesion strength improvement is accomplished by diamond seeding\textsuperscript{11,12} and pre-decarburization of the WC.\textsuperscript{13} These methods serve to increase the nucleation density thereby improving the bond between the substrate and the coating. Soderberg et al.\textsuperscript{14} have concluded three reasons account for the poor adhesion: void formation during growth, non-diamond material formation at the interface, and high residual compressive stresses in the deposited film. The ability to improve the interface adhesion depends upon the type of interface found and/or needed. Chalker et al.\textsuperscript{15} depict three main types of interfacial zones occurring between a coating and a substrate. The first results from pseudo-diffusion brought about by monolayer by monolayer deposition. Secondly, an interlayer is used to promote bond formation between the two regions, and finally, a rough interface causes mechanical keying and locking between the coating and the substrate. In this research, a comparison study of the improvement of the interface adhesion of unseeded diamond coating on WC-Co has been undertaken by using an a-Si interlayer for CH\textsubscript{4} growth and chemical pre-treatment for CF\textsubscript{4} growth.
II. EXPERIMENTAL

Diamond growth in this experiment utilized a microwave plasma enhanced CVD setup described previously. No independent substrate heating was used; the plasma itself heated the substrate to the growth temperature of approximately 900°C. No substrate pre-treatment with diamond powder was used in any of the experimental samples. The typical diamond growth conditions are listed in Table I.

To determine what effect the etchants have on subsequent diamond growth, the tool inserts (Ingersoll Cutting Tools grade 110) of WC-Co (6% Co) have been treated either by cobalt etching, (FeCl₃·H₂O 1:33 by weight) tungsten carbide etching, (K₃Fe(CN)₆·NaOH·H₂O 1:1:10 by weight) or both cobalt and tungsten carbide etching. Subsequent diamond growth proceeded for 1/2 hour with 3% CF₄ or 1/2% CH₄. For continuous diamond coatings, tool inserts were initially prepared in two groups. One group received a surface roughening treatment while the other group acquired an amorphous silicon interlayer on the tool insert surface. The roughening treatment consisted of sequentially etching the tungsten carbide and the cobalt. An amorphous silicon interlayer (approx. 1200 Å thick) was deposited by RF decomposition of a 2% silane balance hydrogen gas mixture.

The analysis of diamond coatings was conducted by a variety of techniques. Auger electron spectroscopy (AES) determined the surface elements present during the various steps in the etching
of the tool inserts and growth of the diamond on the tool inserts. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to visually observe the nucleation density, the grain size and structure of the diamond. The purity/crystallinity of the films was determined by Raman spectroscopy with the 488 nm Ar⁺ line.

To evaluate the macroscopic adhesion of the films to the substrate, indentation tests were conducted with loads ranging from 15 kg to 60 kg in 15 kg increments utilizing a "N" Brale indenter and associated hardness tester similar to tests performed by Jindal et al. For each indentation, crack lengths were measured at 45° intervals around the indentation; the eight values were averaged to yield an average crack length value for that indentation. Seven to nine indentations were made for each data point. Finally, a real cutting test was conducted on 390 aluminum, an alloy containing 17% Si, to evaluate the coatings in a real machining environment. The machining conditions are listed in Table II. After the cutting tests, the wear lands, wear land lengths, and wear depths were measured with an optical microscope and profilometer respectively. Using these measurements, the volume wear rate of the tool insert during the cutting test is determined by plotting the wear volume versus the cutting time.
III. RESULTS

1. Diamond Nucleation and Growth

Fig. 1 details the nucleation densities for the various combinations of etchants and source gases without diamond pre-seeding. In the first case, the cobalt has been etched away and diamond nucleated using 3% CF$_4$ (Fig. 1a) and 1/2% CH$_4$ (Fig. 1b). It is found that the diamonds in Fig. 1a are much denser and larger with a wide variety of crystal sizes evident when compared to Fig. 1b. One may argue that six times more carbon in the CF$_4$ than the CH$_4$ case may have enhanced nucleation of the larger and denser crystals; however, an identical test conducted with 3% CH$_4$ yielded no diamond crystals but a continuous layer of soot on the surface. Apparently different nucleation and growth mechanisms are at work for the two gas sources.

In the second case, the WC crystals of the tool inserts were preferentially etched. This etching produces a wide variety and quantity of sharp edges, steps, and crevices, all ideal places for diamond nucleation. Compared to the previous case, the nucleation density is reduced on both samples. The 1/2% CH$_4$ sample (Fig. 1d) exhibits practically no diamond crystals while the CF$_4$ sample (Fig. 1c) has some diamond crystals. This indicates that a different mechanism is taking place to allow nucleation to occur in the presence of surface cobalt.

Using the two etchants concurrently to remove the cobalt and roughen the tungsten carbide results in typical nucleation densities shown in Figs. 1e and 1f. The CF$_4$ growth sample (Fig. 1e)
le) contains a dense pattern of very small crystals, much smaller than either of the other CF<sub>4</sub> grown samples. This high nucleation density implies, in the long run, a better film-substrate adhesion due to the increased contact area between the film and the substrate as well as fewer voids as the crystals grow to form a continuous film. Nucleation to this degree without a pre-treatment indicates that some substrate-plasma interaction is occurring that aids in the diamond nucleation. Relatively few crystals are seen in the sample grown with 1/2% CH<sub>4</sub> (Fig. 1f). This is not surprising because of the lack of a diamond powder pre-treatment as a conventional diamond growth pre-treatment.

On a longer time scale, diamond coatings on tool inserts etched as in Fig. 1e and 1f have very different appearances. A continuous film 3-4 μm thick is deposited after two hours with CF<sub>4</sub> while 8 hours of growth with CH<sub>4</sub> yields a discontinuous film with a large graphitic component.

Fig. (2) gives the Auger spectra of an etched tool insert and an etched tool insert exposed to a 3% CF<sub>4</sub> diamond growth plasma for 5 minutes. Upon etching the tungsten carbide and cobalt, a variety of elemental species is found. The resultant Auger spectrum is shown in Fig. 2a. Peaks identified include tungsten at 169 and 179 eV with chlorine at 181 eV, overlapping the 179 eV tungsten peak. Other peaks of interest include the carbon fine structure at 252, 260, and 271 eV showing the carbidic nature of the sample, nitrogen at 379 eV, and oxygen at 468, 483, and 503 eV. Metallic species, other than tungsten,
present on the surface are iron at 598, 651, 703, and 716 eV, and cobalt at 775 eV. All of these new elements, except for oxygen, are residues from the etching process. The oxygen peak is due to both etching and environmental adsorption. The etching process yields adherent residue films (i.e. films not easily removed from the substrate by methanol or acetone rinsing.) The cobalt is bound with the chlorine to form cobalt chloride, while the tungsten most likely forms tungsten oxides, with tungsten pentoxide (\(W_2O_5\)) being stable to around 800°C.

A tool insert with a WC and Co etch followed by an exposure to a diamond growth plasma for 5 minutes has a typical Auger spectrum shown in Fig. 2b. This spectrum exhibits tungsten, carbon, and oxygen peaks all at the characteristic energy values found in Fig. 2a while the cobalt, iron, chloride, and nitrogen peaks associated with the chemical etching have disappeared. The highly reactive hydrogen atoms in the plasma readily remove the surface and near-surface layer of contaminants paving the way for commencement of diamond growth.

Having some idea how etching affects the surface of the tool inserts, continuous films were grown and characterized for crystallinity and purity. The results of the TEM analysis conducted on films grown with \(CH_4\) and \(CF_4\) are found in Fig. 3. This figure contains plan-view, bright-field TEM micrographs and corresponding electron diffraction patterns for diamond grown with \(CH_4\) (Fig. 3a) and \(CF_4\) (Fig. 3b). Large, well-faceted crystals (> 1μm) are found when growing with a \(CH_4\) precursor.
The selected area electron diffraction pattern gives a polycrystalline pattern with diffraction rings from the diamond (111), (220), and (311) planes (1st, 3rd, and 4th rings from the center) and from the graphite (1012) plane (2nd ring) indicating that a significant amount of graphite exists in this film. Smaller crystals are seen in the CF$_4$ grown diamond in Fig. 3b. This is consistent with the results shown in Fig. 1e. The electron diffraction pattern in Fig. 3b shows only the well-defined rings of spots indicative of polycrystalline diamond; no graphite ring is found. The explanation for the absence of the graphite ring when growing with CF$_4$ could be due to a more efficient etching of the graphite when growing with CF$_4$ or a different growth process. The discussion section details these possibilities.

2. Growth of Continuous Diamond Coatings

Due to the slow growth of diamond on WC-Co when using CH$_4$, an interlayer of a-Si was deposited to aid in diamond nucleation. The thought is to use the a-Si to create a thin layer of silicon carbide and then have the diamond grow on top of the silicon carbide. A continuous film is grown over the entire substrate. Using CF$_4$ on an a-Si interlayer results in destruction of the interlayer because CF$_4$ plasmas etch silicon quite readily. As a result, diamond growth with CH$_4$ source gas on a substrate with an interlayer, is compared to diamond growth with CF$_4$ source gas on a chemically etched substrate. In the
remainder of the paper, the reference to CH₄ refers to diamond growth on an a-Si interlayer deposited on WC-Co while CF₄ refers to diamond growth on a chemically etched WC-Co substrate.

The crystallinity of the films determined by Raman spectroscopy is shown in Fig. 4a for the CH₄ grown diamond and Fig. 4b for the CF₄ grown diamond. For the CH₄ sample, the characteristic diamond peak at 1332 cm⁻¹ is present but it is very broad and weak in intensity. The FWHM value of the peak is 19 cm⁻¹ indicating deviations from a perfect crystal lattice. This broadening can be attributed to defects in the diamond crystals brought about during the growth process. This small peak also indicates the difficulty in nucleating and growing diamond on an unseeded substrate. It is not surprising that a large graphite peak is found centered around 1580 cm⁻¹, which dovetails with the electron diffraction pattern shown previously.

For the CF₄ grown samples, the Raman spectra (Fig. 4b) is somewhat different. The characteristic diamond peak at 1332 cm⁻¹ is much stronger in intensity and more narrow (FWHM = 8 cm⁻¹) when compared to the CH₄ diamond. Some graphitic components are also detected as seen by the small, broad "hump" centered around 1580 cm⁻¹, but the quantity of graphite is small when the intensities of the graphite and diamond peaks and the scattering coefficients of graphite and diamond (50:1) are taken into consideration.

Shown in Fig. 4 are two SEM micrographs examination of
the deposited coatings which reveal a different crystal morphology for the two samples (a: CH₄ b: CF₄). Both were grown at the same measured substrate temperature (900 C), but for different times as listed in Table I. The (111) facets are found for the CH₄ case and (100) facets for the CF₄ case. The preponderance of (100) facets on the CF₄ sample is rather surprising at this carbon concentration. An investigation of the growth of diamond on silicon using CH₄ source gas indicates that the (100) morphology terminates around a concentration of 1.2% CH₄. In the CF₄ diamond case, (100) facets are still found at a carbon concentration 2.5 times higher. Even higher concentrations of CF₄ (6%-9%) produce a microcrystalline morphology. Reasons for this occurrence are not entirely clear at this time.

3. Adhesion and Machining Performance of the Diamond Coatings

The micrograph inset into figure 5 is a low magnification view of an indentation. The circular area in the center of the film is the point of contact between the indenter and the film. Around this contact zone is the portion of the film that has delaminated due to the applied load. The scale of the figure gives an indication of the macroscopic nature of this indentation test.

Figure 5 is a plot of the crack lengths of indentations vs. the load depicting the wide adhesion disparity between the CH₄
and CF$_4$ grown diamond. The test results from diamond grown on a-Si deposited on the tool insert (curve a) and literature values of diamond grown with pre-seeding$^{11-12}$ (curve b) exhibit rather large crack lengths. The crack length in the CF$_4$ grown diamond coating (curve c) monotonically increases with the load approaching 150 microns at 60 kg of load compared to 400 microns at 45 kg of load in the CH$_4$ case. Throughout this test the adhesion of the CF$_4$ films is found to be a factor of two or more better than for the CH$_4$ films.

Fig. 6 shows optical micrographs of tool insert wear cf a virgin tool insert (a), an uncoated insert machined for 8 minutes (b), and a diamond coated insert machined for 8 minutes (c). A long, narrow wear land appears on the uncoated sample (Fig. 6b) while a shorter but somewhat wider wear pattern is found on the diamond coated insert (Fig. 6c). Initially the diamond coating along the cutting edge provides protection and shifts the wear pattern back along the top face of the tool insert. With no diamond coating, wear can proceed quite easily in the vertical direction as well as back down along the cutting tool.

The volume of tool insert abraded away by the material being cut is plotted versus the cutting time, shown in Fig. 7. Each data point is the result from one tool insert machined for a specified length of time. Four tool inserts of the same type were used for each curve resulting in some spread of the experimental data. A least square fit was performed to find the trend of the data. All three curves start in the same general
vicinity. After one minute, very little difference is seen in the abraded wear volume. After a longer cutting time, differences begin to appear. The volume wear rates (slope of each curve) are as follows: $0.31 \mu m^3/min$ for the uncoated sample (a), $0.24 \mu m^3/min$ for the CH$_4$ diamond coated sample (b), and $0.20 \mu m^3/min$ for the CF$_4$ diamond coated sample (c). A 50% improvement in the volume wear rate is seen between an uncoated and a CF$_4$ diamond coated tool insert. Correlating the wear rate to the indentation results, one realizes that a better indentation adhesion value corresponds to a better wear volume.

Further improvements in cutting performance may be possible by thoroughly understanding how CF$_4$ nucleates and grows diamond on WC-Co without a diamond powder pre-treatment.

Comparison with other researcher's experimental data is difficult due to the variability in cutting materials and conditions. For example, in other papers cutting depths and speeds range from 0.5 mm and 450 m/min on an Al-11.7% Si rod to 0.1 mm and 250 -350 m/min on an Al-11% Si rod. Still others used 0.5 mm and 200 m/min on an Al-20% Si alloy and 1.5 mm, 300 m/min on an Al-18% Si alloy. Comparison with other types of materials is clearly inappropriate (i.e. Al-11% Si), but similar materials (i.e. Al-18% Si & Al-20% Si) have higher cutting speeds (33-100% higher) and a lower depth of cut in one case and slightly higher in another. To allow for comparison among researchers, it seems to be necessary to standardize some type of testing procedure for machining diamond coated tool inserts.
IV. DISCUSSION

Our experiments have shown that high quality diamond coatings can be grown with 3% CF$_4$ compared to diamond grown with 1/2% CH$_4$ on an a-Si interlayer. Knowing some facts about the film composition, structure, and morphology as well as previous work different growth mechanisms can be postulated for CH$_4$ nucleation on a-Si and CF$_4$ diamond nucleation directly on the WC. The probable growth mechanism when using CH$_4$ gas involves conversion of portions of the a-Si to form silicon carbide and tungsten silicide. The WSi$_2$ forms at the interface between the a-Si and the WC serving as an adhesive layer while the silicon carbide forms from a reaction of the gaseous carbon species and the a-Si. This nascent SiC then serves as a nucleation site for the diamond growth in much the same way as diamond nucleation on single crystal silicon where a thin silicon carbide layer is formed before diamond nucleation and growth begins$^{22-23}$. The large size of the crystals, as indicated by TEM micrographs, implies a low initial nucleation density. The low nucleation density also means a long growth period will be needed to allow the crystals to coalesce into a continuous film. While the crystals are growing to form a continuous film, the gaps between the crystals are still subjected to a carbon flux. Unable to attach to a diamond nuclei, the incoming carbon is deposited as graphite and amorphous carbon. As a result, a two phase region is initially
formed in the film. The amount of oxygen used is obviously unable to remove all of the graphite co-depositing on the continuous diamond film. The end result is a diamond film containing diamond crystals as the majority constituent, but also some graphite and amorphous carbon components.

Little work has been done regarding the mechanism for the growth of diamond with CF$_4$ source gas\textsuperscript{24-25}, and certainly no work has been done regarding CF$_4$ growth of diamond on WC-Co tool inserts. Based on our experimental results the mechanism of growth is postulated. Plumb and Ryan\textsuperscript{26-27} have conducted several experiments to determine the species present in a CF$_4$-H$_2$ and CF$_4$-O$_2$ discharge. For the CF$_4$-H$_2$ experiment the dominant reaction was as follows:

$$CF_3 + H \rightarrow CF_2 + HF$$

The CF$_3$ came from the dissociation of CF$_4$ either from electron impact or from the reaction with atomic hydrogen in the plasma. In the CF$_4$-O$_2$ discharge, the CF$_4$ is dissociated into CF$_3$ and CF$_2$. Through a complex reaction sequence, the CF$_3$ and CF$_2$ react with oxygen in the discharge and form the following stable carbon-containing species: COF$_2$, CO$_2$, and CO. The concentration of these stable species varies according to the ratio of CF$_4$ and O$_2$ in the discharge. Growing diamond on WC-Co with a combination of H$_2$, O$_2$, and CF$_4$ results in a variety of plasma species, and these species may be a combination of the species found separately in
the CF$_4$-H$_2$, and CF$_4$-O$_2$ plasmas described above. Work is in progress to identify the species present in the plasma, their concentrations as well as the role of the carbon containing species in the nucleation and growth of diamond films.

Several reasons may explain the better adhesion strength. Smaller crystal sizes for the CF$_4$ grown diamond means fewer voids and more film-substrate interface area implying better film-substrate adhesion. Less non-diamond component for the CF$_4$ grown diamond may also result in improved adhesion strength. Should the proposed growth mechanism detailed in the above be proven correct, CF$_4$ grown diamond results in a strong bond between the WC substrate and the diamond film itself.

V. CONCLUSION

Interlayers of a-Si for CH$_4$ diamond growth and surface chemical pre-treatment for CF$_4$ diamond growth have been used to improve the adhesion between the diamond film and the WC-Co tool insert. In both cases, no pre-seeding with diamond powder is required. Analytical characterization of the films shows the CF$_4$ film to contain small crystals and less graphite when compared to the CH$_4$ grown film. Diamond films grown on WC-Co with CF$_4$ also have a growth rate approximately four times faster than diamond films grown on WC-Co with CH$_4$. Indentation testing shows an increased adhesion strength by a factor of two or more for the CF$_4$ grown film. Machining tests on 390 aluminum depicts the increased durability of the CF$_4$ grown films when compared to the
CH₄ grown films and plain, uncoated inserts. Further understanding of the CF₄ growth mechanism may result in additional adhesion improvements.

ACKNOWLEDGEMENT

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TABLE I. EXPERIMENTAL DIAMOND GROWTH CONDITIONS

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<th>Parameter</th>
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<tr>
<td>Substrate:</td>
<td>WC/ 6% Co</td>
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<td>Surface Modification:</td>
<td>Chemical etching with $K_3Fe(CN)_6:NaOH:H_2O$ 1:1:10 or an a-Si interlayer</td>
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<td>Feed Gases: (1.)</td>
<td>1/2% CH$_4$, 1% O$_2$, balance H$_2$</td>
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<tr>
<td>Feed Gases: (2.)</td>
<td>3% CF$_4$, 1% O$_2$, balance H$_2$</td>
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<tr>
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<tr>
<td>Growth Time:</td>
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<tr>
<td></td>
<td>2 hrs. for 3% CF$_4$</td>
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TABLE II. CUTTING TEST PARAMETERS

Machine Parameters:
- Speed: 152 m/min
- Feed: 0.254 mm/revolution
- Depth of cut: 1.27 mm
- Cutting Time: 1, 2, 4, and 8 minutes
- Coolant: None

Workpiece:
- Material: 390 Aluminum
- Hardness: < 20 HrC (as cast)
- Actual Material Composition: Shown in table below (%)

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8 Diamond and Structural Carbon News, Vol 1, No. 1, June 1991, p. 3.


FIGURE CAPTIONS

Figure 1. SEM micrographs showing diamond nucleation densities after various chemical etching and growth procedures. (a) and (b) are etched for 4 hrs in FeCl₃, (c) and (d) for 2 min. in Murakami's etchant, and (e) and (f) are etched with both. In terms of growth, (a), (c), and (e) are grown with 3% CF₄ for 1/2 hr, and (b), (d), and (f) with 1/2% CH₄ for 1/2 hour.

Figure 2. Auger spectra of (a) WC-Co etched with Murakami's etchant for 2 min. and FeCl₃ for 4 hrs., and (b) a WC-Co sample with the same etching treatment as (a) but exposed to a 3% CF₄ diamond growth plasma for 5 min.

Figure 3. Plan-view bright-field TEM micrographs and corresponding electron diffraction patterns for diamond film grown with CH₄ precursor (a), and CF₄ precursor (b).

Figure 4. Raman spectra and SEM micrographs of diamond films grown with (a) 1/2% CH₄ and (b) 3% CF₄.

Figure 5. Indentation adhesion test results for various diamond films grown on WC-Co tool inserts. (a) 1/2% CH₄, (b) experimental data from Ref. 12, and (c) 3% CF₄.

Figure 6. Optical micrographs of tool inserts after machining Al-17% Si for various times. (a) uncoated, unmachined, (b) uncoated, machined for 8 minutes, (c) diamond coated, machined for 8 minutes.

Figure 7. Amount of tool insert volume worn away with respect to cutting time for various coated and uncoated tool inserts. The curves are (a) uncoated insert (+), (b) 1/2% CH₄ diamond coating(○), (c) 3% CF₄ diamond coating( ).
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