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Microwave plasma chemical vapour deposition diamond nucleation on ferrous substrates with Ti and Cr interlayers

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Abstract

Diamond-coated steel is considered an important issue in synthetic diamond technology due to the great economical importance of enhancing the wear resistance and surface hardness of commercial Fe-based alloys. However, direct diamond coating by chemical vapour deposition (CVD) is rather problematic—adhesion and growth are seriously affected. The use of interlayers is a common approach to minimise these problems. This work reports an investigation on the establishment of good nucleation and growth conditions of diamond films by microwave plasma CVD (MPCVD) on ferrous substrates coated with Ti and Cr interlayers. Commercial grade ferrous substrates were pre-coated with commercial interlayers by sputtering (Ti, Cr) and electroplating (Cr) techniques. Steel substrates led to better results than iron cast substrates. The best films were obtained on Ti pre-coated steel substrate. The results on Cr interlayers pointed to the advantage of electroplating over the physical vapour deposition (PVD) sputtering. From the two selected parameter sets for diamond deposition, the one using lower power level conducted to the best results. Initial roughness and growth parameters were found to counteract on the uniformity of the diamond films. The morphology was studied by scanning electron microscopy (SEM), the roughness was estimated by profilometry, while diamond quality and stress state were evaluated by μ-Raman spectroscopy.

Keywords: Adhesion; Chemical vapour deposition diamond; Tool coatings

1. Introduction

Diamond thin films are very appealing for tribological applications, due to the excellent combination of diamond properties: very high hardness, low friction coefficient, high wear resistance, high thermal conductivity and chemical inertness. For tribological uses, strong film/substrate adhesion is necessary along with appropriate morphology for sliding contacts [1,2]. Chemical vapour deposition is a very attractive technique to integrate diamond with metals, although the direct deposition on ferrous substrates like steel or cast iron was found to be problematic: Fe catalyses graphite formation, carbon presents a very large solubility in most ferrous materials and the Fe vapour pressure affects the plasma. In fact, the nucleation process and diamond growth by microwave plasma CVD (MPCVD) on ferrous materials leads to the formation of a graphite and/or amorphous carbon layer, which severely compromises the adhesion. Besides, a strong diffusion of C into Fe occurs at the temperatures used in the process growth [3]. Along with this, the presence of Fe in the plasma delays the diamond formation, the growth rate being substantially decreased.

Until now, intermediate layers between the ferrous substrate and the diamond film has been the most common approach in order to solve these obstacles. An ideal interlayer should:

- have good chemical compatibility to carbon (carbide former) and adhesion ability with the substrate;

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Table 1
Interlayer R_a roughness and thickness

	Hard Cr	Ti (PVD)	Cr (PVD)
R_a roughness[a] (μm)	0.09	0.70	0.70
Thickness (μm)	0.8	1.8	1.0

[a] All samples starting with $R_a = 0.03$ μm uncoated substrates.

- be thermally stable-structurally and geometrically when submitted to temperatures of approximately 700–900 °C, typical of the CVD process;
- accommodate the thermal induced stresses developed during the growth and ramp down processes, due to thermal expansion coefficient mismatch;
- promote an effective diffusion barrier of C into Fe;
- afford adequate thickness and morphology; and
- be competitively priced and easy to produce.

Good adhesion requires both substrate/interlayer mutual diffusion and interlayer/carbon affinity (carbide formation) [4]. Hence, in order to obtain a strong coupling between the substrate and the interlayer (first interface), Fe must diffuse adequately into it. Iron is known to have low diffusion into W, Ta, Cr, medium into Cu, Ag, Au and high into Ti [5]. From this set, Cu, Au and Ag do not form carbides. However, carbon has a high diffusion into Ti, medium in Cr and Ta, and weak into W [5]. Diffusion depth calculations point W, Cr and Ta as excellent diffusion barriers against Fe, while Ti and Si need to be much thicker to be effective [6]. Both the use of single interlayers such as Mo [7], W [8], Si [9,10], Ti [11] and multi-layer structures such as Mo/Ni/Mo [7] or Mo/Ag/Nb [4] have been reported. The present work report on diamond film growth on steel and cast iron substrates when interlayers of sputtered Cr and Ti or electroplated hard Cr are used.

2. Experimental

Square samples with dimensions $10 \times 10 \times 2$ mm^3 were produced from two distinct materials of industrial interest: VANADIS 10 steel (2.9% C, 1% Si, 0.5% Mn, 8% Cr, 1.5% Mo, 9.8% V) and nodular iron cast (3.6% C+2.9% Si+0.35% Cu+0.1% Mn+0.01% P+0.04% Mg+0.0013% S). The unconventional VANADIS 10 steel is obtained by powder metallurgy. After being cut, all the metal squares were finished to ~0.03 μm of R_a roughness.

Electroplated (hard Cr) and sputtered (Cr, Ti) interlayers were used in this work, all of them having been applied by commercial companies, keeping all the characteristics of their commercial coatings. The interlayers were deposited according to an empirical adhesion/thickness compromise point. Although relatively thick interlayers (a few micrometres) would be desirable to avoid Fe diffusion to the surface [5], increasing thickness is known to build up stresses, reducing the adhesion strength. The interlayer thicknesses were assessed by cross-section scanning electron microscopy (SEM) observation, and are depicted in Table 1.

Prior to diamond deposition, all samples were scratched with 7-μm-sized diamond powder for ~2 min and ultrasonically cleaned in acetone and alcohol baths for 5 min. The CVD diamond deposition was performed using a commercial ASTeX PDS 18 machine. The CVD apparatus permits control of several parameters such as microwave power, gas pressure, partial gas flow (concentration), deposition time and substrate cooling. The process parameters were selected in order to avoid the substrate phase transformations, keeping moderate deposition temperatures. Also, by extending the time of the ramp-down step (after CH_4 supply cut), thermal shock was minimised along with its negative implications on the film adhesion.

Two different deposition parameter sets were used, as shown in Table 2 identified by shaded and white rows. Each set involved samples from the two kinds of substrate materials. While cast iron was pre-coated only with Ti, steel samples were produced with all available interlayers.

The 'hot' and 'cold' holder discrimination comes from different holder thermal conduction as a result of two distinct geometries. The 'cold' holder has an increased contact area with the cooled plate than the 'hot' holder, resulting in lower surface temperature for the same plasma conditions. Both holders are made of molybdenum.

Table 2
Deposition conditions for each sample

Sample	Substrate	Interlayer	Power (W)	Pressure (torr)	H_2 (sccm)	CH_4 (sccm)	Holder	Ramp-up (min)	Dep. time (min)	Ramp-down (min)
1	Steel	Hard Cr	2500	75	300	12	Hot	6	30	30
2	Steel	Cr (PVD)	2500	75	300	12	Hot	6	30	30
3	Steel	Ti (PVD)	2500	75	300	12	Hot	6	30	30
4	Iron cast	Ti (PVD)	2500	75	300	12	Hot	6	30	30
5	Steel	Hard Cr	1700	80	300	30/18	Cold	7	7+60	30
6	Steel	Cr (PVD)	1700	80	300	30/18	Cold	7	7+60	30
7	Steel	Ti (PVD)	1700	80	300	30/18	Cold	7	7+60	30
8	Iron cast	Ti (PVD)	1700	80	300	30/18	Cold	7	7+60	30

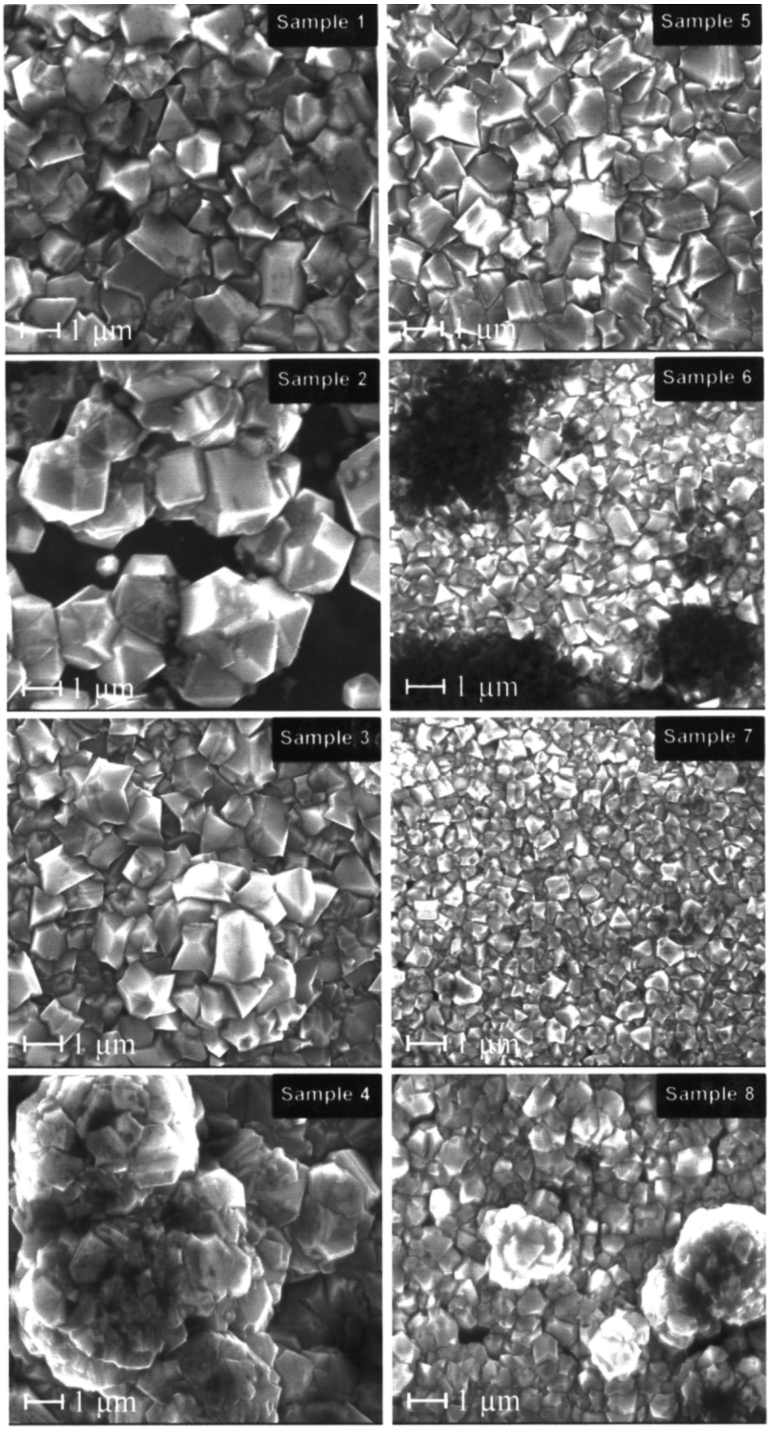

Fig. 1. Surface morphology of the diamond films on samples from 1 to 8. Left column corresponds to the first set of conditions, while the right one corresponds to the second set.

The roughness measurements were done with a Hommelwerke profilometer. Film morphology was characterised by SEM (Jeol JFM63 01 F, fitted with EDS analysis) and optical microscopy. Stress state and diamond quality were assessed by μ-Raman (Jobin–Yvon/SPEX T64000, 514 nm Ar^+, spectral resolution ~0.45 cm^{-1}). A highly transparent geological type IIa gem was used to calibrate the diamond peak position.

3. Results and discussion

A close observation of the micrographs shown in Fig. 1 points to systematic advantages of the second set of growth conditions (samples 5 to 8) compared with the first one (samples 1 to 4). This is true for each substrate and interlayer. Since the first set used an increased microwave power and 'hot' holder, the temperature at the sample surface is obviously higher than that obtained with the conditions imposed by the second set. This contributed to the visible differences on the increase of average diamond grain size in the first set of samples. The corresponding samples from the second set, which included a pre-growth step that used an increased methane concentration for ~7 min (Table 2), are better nucleated and present higher uniformity, these features being indispensable if tribological applications are to be addressed [12–15]. This is in agreement with the fact that lower nucleation density gives rise to bigger crystals, once these are free to grow until the space between them is overlapped [16].

These differences are not so obvious on samples 1 and 5 (electroplated hard Cr on steel), that correspond to the interlayer with the lowest roughness (Table 1). This illustrates that surface roughness must obviously play an important role on the film growth. Actually, the harsh growth conditions of the first set seemed to 'amplify' the non-uniformity found on rough interlayers in terms of diamond particle overgrowth. In fact, increased roughness promotes spontaneous nucleation in privileged spots, generally corresponding to peaks in the interlayers, allowing the crystals to grow freely to much higher dimensions. These instabilities are boosted by the growth conditions of the first set, to which correspond higher growth rates. Naturally, this effect results in extra final roughness, up to twice as much as the interlayers initial value. Actually, all samples registered roughness increment after diamond film growth. Thus, a compromise between high growth rates and initial surface roughness must be established if a dense and uniform diamond film is desired for tribological applications [13].

Curious dark formations can often be found, even when dense diamond films are obtained (Fig. 1, sample 6). These dark regions are related to conductive metal contamination from the ferrous substrate through 'channels' across the interlayer (Fe, V, Mn)—confirmed by energy dispersive spectrometry (EDS)—and metal co-deposition from its vapour pressure within the plasma. Although the roughness values are similar for Ti (PVD) and Cr (PVD) interlayers, the thickness is higher for the former, according to Table 1. This concurs to the differences on film morphology between the two types of interlayers, and it is valid for the two sets of growth conditions. Thus, being thicker than Cr, the Ti interlayer lead to better results once it constitutes a stronger diffusion barrier.

However, the diamond films obtained on Ti pre-coated cast iron substrates suffered from lack of uniformity and continuity, some zones being free of diamond nucleation while other regions present diamond conglomerates. In opposition, the diamond film on Ti pre-coated steel substrate was found to be dense, uniform and continuous. Actually, it is the sample that suits the best for tribological applications, due to its low roughness. The observations above indicate that, for the same interlayer, the detrimental effect caused by the diffusion of Fe to the surface is stronger in cast iron than it is in steel.

For all the samples containing portions of well-adhered diamond films the stress was very high, as confirmed by μ-Raman. A spectrum taken for sample 7 at the centre shows that the three-fold degenerated diamond peak (1332 cm^{-1}) splits in two (1340 cm^{-1} and 1350 cm^{-1}) with a positive shift (Fig. 3), as an evidence of a strong biaxial compression [17]. However, if one checks the same diamond film spot when released from the substrate (e.g. by indenting with a Knoop pyramid), a single diamond Raman peak at 1333 cm^{-1} with ~6 cm^{-1} full width at half maximum (FWHM) is observed. This is a clear indication that the stress state is extrinsic, with an intrinsic negligible contribution. The same overall behaviour is found for sample 5, although this one presents only ~4 cm^{-1} in FWHM for the referred indented zones, revealing higher crystalline quality. This may be due to the crystal size effect, which is bigger for sample 5. For the same laser spot area, the grain boundary concentration increases with decreasing average grain size. A μ-Raman analysis was performed all along the sample surfaces, confirming the stress presence which is higher near the edges. There, a locally increased temperature together with higher growth degree of freedom result in larger diamond crystals. The film surrounds the borders, giving raise to some delaminations initiated by cracks during the ramp down process (it was possible to observe them appearing looking to the sample through the reactors up window).

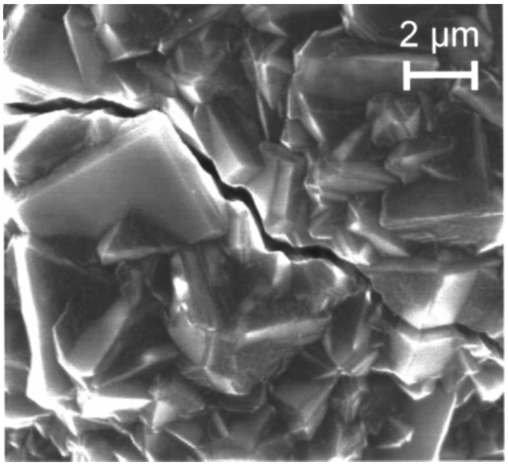

Fig. 2. Micrograph of a stress induced crack along the diamond film surface. Notice crack evolution across the grains.

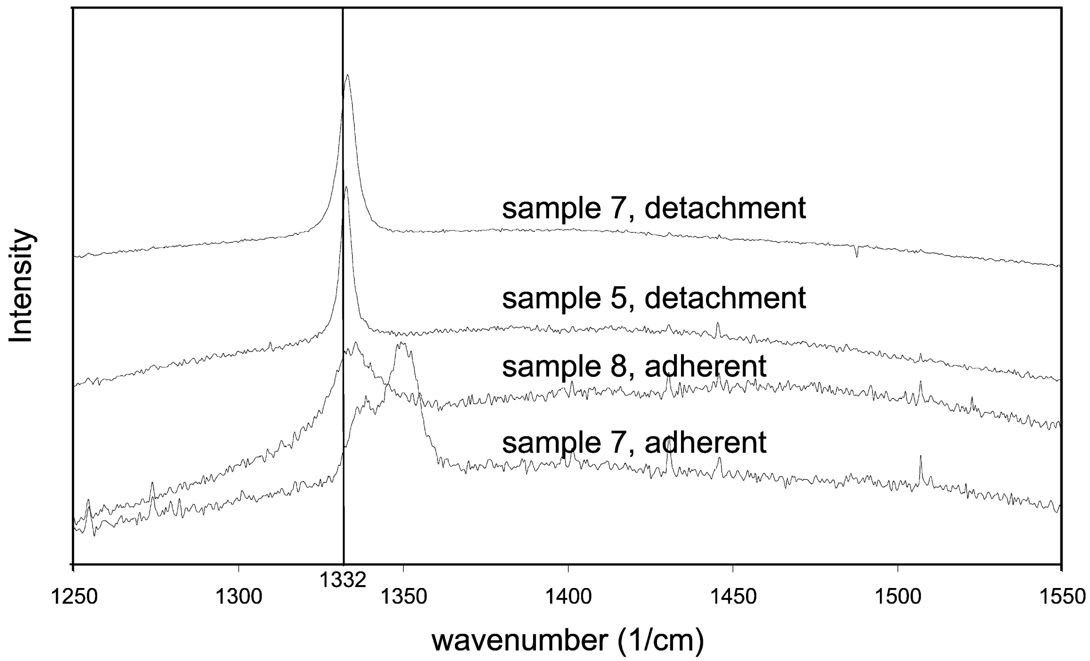

Fig. 3. Raman spectra taken on selected samples.

Unlike on the ductile materials, these cracks do not spread preferably along the grain boundaries [18]. Diamond crystals divided by such cracks can be observed (Fig. 2). For the Ti sputtered cast iron substrates, the Raman information (Fig. 3) correlates to the film morphology as depicted in Fig. 1: the film is not yet continuous (holes are clearly seen) therefore the stress (diamond peak shift) is not as strong as for sample 7, which is densely covered with diamond. Also, the existence of void spaces between diamond grains decreases the Raman diamond peak intensity, lowering the signal-to-noise ratio. This effect is reinforced by the Fe contamination which is stronger for cast iron samples, as referred before. In addition, Fe contributes to the Raman broad band that appears centred at ~1450 cm^{-1}, evidencing the presence of non-diamond carbon species.

4. Conclusions

This work concludes that:

1. lower substrate temperature, MW power and methane concentration leads to higher quality diamond films, with smaller grain size and better morphology;
2. the Cr (PVD) interlayer thickness proves to be insufficient to stop the Fe diffusion, leading to Fe contamination and poorly nucleated diamond films;
3. under similar conditions, cast iron substrates are more susceptible to promote Fe diffusion than steel substrates;
4. both Ti and hard Cr interlayers yield good diamond nucleation, this property being closely linked to adhesion, as demanded by tribological applications, but thinner Cr interlayers required lower surface roughness; and
5. a compromise between high growth rates and initial surface roughness must be established if a dense and uniform diamond film is desired.

Adhesion problems subsist still which will be addressed in future work. The thickness of well adhered interlayers should be reinforced to avoid diffusion processes, improving the diamond film adhesion. The use of multi-layer structures to form effective diffusion barriers will also be addressed. Another reference for future work is the search of standard industrially available methods to apply inexpensive interlayers compatible with MPCVD diamond deposition.

These results allow prediction of the use of this type of super-hard coatings in mechanical micro-components subjected to low loads and high number of work cycles.

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