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Structural investigations of protective polycrystalline diamond coatings on titanium substrates

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Abstract

Thick titanium substrates were coated with conductive polycrystalline diamond films by means of the microwave plasma assisted CVD method. In general, the obtained films showed good adhesion and did not peel off the substrates regardless of residual stresses. These were released from the titanium specimens during the deposition process and gave rise to a noticeable deformation of the samples. The structural properties of the deposits were found to be depending on the substrate pre-treatment procedures (sandblasting) as well as the deposition conditions (carbon oversaturation). No evidence was found for the formation of titanium hydrides from the use of the hydrogen-rich plasma. Structural continuities (heteroepitaxy) in the Ti/TiC/Diamond interfacial layer as well as the key role of titanium oxide for the diamond nucleation are discussed.

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1. Introduction

Titanium exhibits the best strength to weight ratio among the reactive metals. Unfortunately, the susceptibility to oxygen, nitrogen and hydrogen makes titanium more brittle. On the other hand, a thin oxide overlayer is known to protect the pure metal against corrosion in normal conditions. In many advanced applications such protection is insufficient, e.g. during the electrochemical recycling of wastewater, where titanium electrodes suffer from strong oxidising agents [1,2]. To improve the wear and corrosion resistance of titanium and its alloys, the electrodes are usually covered with thin diamond coatings.

However, several factors are found to limit the use of diamond-coated titanium substrates, the most disadvantageous being: poor adhesion due to the mismatch of the diamond and titanium thermal expansion coefficients [3], residual stresses induced within the titanium substrates during their metallurgical fabrication and then released during the deposition process at high temperatures [4], and rapid in-diffusion of light elements forming non-diamond species (mainly carbides and hydrides) [5]. The latter has a three-fold detrimental effect on the obtained structures: a degradation of the mechanical properties of the Ti substrates (hydrides formation), a reduction of the density of diamond nuclei at the start of the diamond film growth, and a decrease of the diamond phase purity (TiC formation). At the same time, fortunately, an interfacial TiC layer also minimizes the residual thermal stresses between substrate and film thereby enhancing the necessary adhesion strength. As a result, an optimal growth process appears to be a compromise between an acceptable coating quality and the mechanical integrity of the covered parts.

This paper aims at examining several modifications to the standard CVD growth process so that evolution and structural

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dependencies between substrate, interfacial layer and diamond coating become visible. It involves the investigation of the influence of sandblasting of the Ti substrates on the diamond nucleation density, the impact of a thin sputtered titanium film to establish the effect of a spontaneously oxidised substrate surface, and finally, a two-step deposition process to reveal the interfacial carbide evolution.

2. Experimental

Pure titanium plates $(20 \times 20 \times 1 \text{ mm}^3)$ were used as substrates for diamond deposition. Half of the substrates were sandblasted prior to deposition. Each substrate was mechanically seeded with 0.25 µm sized diamond powder followed by ultrasonic cleaning in isopropyl alcohol and deionised water. The growth process was carried out in an ASTEX AX6500 microwave plasma assisted CVD system using a standard diamond growth gas mixture containing methane diluted with large amounts of hydrogen. The deposition parameters were as follows: hydrocarbon concentration 1–5% (vol.) except for the two-step process, in which the concentration was maintained at 15% for the first 15 min, substrate temperature 630–800 °C measured by a two-colour pyrometer, gas pressure 40–70 Torr, microwave power 3 kW and deposition time 2–5 h.

The titanium overlayer was deposited by DC-pulsed magnetron sputtering. The titanium target (4 in. in diameter, 99.99% purity) was held on the water-cooled magnetron cathode, being sputtered by accelerated argon ions. The substrate was not heated and its temperature was dependent only on the plasma heating. According to the profilometry measurements the obtained overlayer was ~1 μ m thick.

The surface morphology of the films was investigated by scanning electron microscopy (FEI Quanta 200F FEG-SEM), while their quality was studied with Raman scattering spectroscopy (Jobin-Yvon U1000 spectrometer) using a 514.5 nm argon laser beam. The crystal structure was investigated using XRD spectra recorded in the coupled $\theta - 2\theta$ peak integration mode, and the predominant growth directions (texture) were determined by pole figure measurements (Siemens D5000 diffractometer, $Cu(K_{\alpha})$ radiation). The angle 2θ corresponds to the diffraction angle, where θ is the angle of the incident beam relative to the sample surface. In the pole figure measurements, φ describes the sample rotation around the surface normal, while χ refers to the diffraction plane tilt relative to the surface normal. Scans were carried out with the following parameters: φ angle steps every 4°, χ angle steps every 2°, and integration time 100 s/point.

3. Results and discussion

The θ -2 θ scans of polycrystalline diamond films grown on an untreated and on a sandblasted titanium substrate are compared in Fig. 1. The diffraction peaks of α -titanium (the low-temperature phase of the hcp structure), titanium carbide, and diamond crystalline phases are easily identified. The split of the Ti(101), and Ti(103) diffraction peaks might be a consequence of residual bi-axial stress within the cold-rolled



Fig. 1. The XRD patterns of diamond films on, respectively, sandblasted (upper), and mechanically untreated (lower) titanium substrates are indicative of α -titanium, titanium carbide, and diamond crystalline phases. The four diffraction peaks labelled as '?' remain unidentified (see text).

titanium substrates, although the overlapping of the titanium lines with their nearest neighbours could be taken into consideration as well.

As far as characteristic features of non-diamond phases seen in the XRD spectra are concerned, the diamond coatings are almost identical regardless of the pre-treatment procedure that has been carried out to increase the nucleation density (sandblasting). However, apart from the easily recognized Ti, TiC and diamond peaks, there are still four unidentified diffraction lines in Fig. 1. Unfortunately, their identification is unresolved because the diffraction patterns of structures that could be considered here, such as graphite or β -titanium (the high-temperature phase with bcc symmetry), are substantially different. Moreover, the formation of titanium hydrides by the in-diffusion of interstitial hydrogen [6], as well as the presence of titanium oxide in the rutile structure, formed under plasma oxidation [7], can be excluded. The peaks are neither related with sand particles that are expected to remain on the substrate after sandblasting, even though this procedure is found to speed up the growth process by a factor of 1.33, as indicated by weight measurements. This issue needs to be addressed in more detail.

In order to determine the structural dependencies between the titanium substrate, the interfacial carbide layer and the diamond coating, Ti(101), TiC(200), and D(111) pole figures were measured; comparative results taken from untreated and sandblasted samples are given in Fig. 2.

The results show that the preferred growth directions depend on the substrate pre-treatment. In fact, even if each titanium substrate is found to be textured, the diamond grains in sandblasted samples seem to be oriented solely along the scratches, whereas in untreated samples considerable mosaicity is present. Furthermore, untreated samples exhibit (h00) texture when considering both TiC(200) and D(111) pole figures, with the latter being somewhat asymmetric due to bi-axial stress in the layer. On the other hand, diamond films grown on sandblasted substrates feature an intermediate texture somewhere S. Kulesza et al. / Surface & Coatings Technology 201 (2006) 203-207



Fig. 2. The pole figures of the Ti(101), TiC(200), and D(111) diffraction peaks taken from a sandblasted sample (upper row), and an untreated one (lower row).

between (h00) and (hhh); the TiC structure is no longer (h00)textured. In such a case, both TiC and diamond grains are oriented parallel to the scratches as demonstrated by the resemblance of the TiC(200) and D(111) pole figures relative to the Ti(101) one. This suggests that the deposited structures are strongly disordered due to substrate abrasion.

In order to investigate the diamond structure as a function of deposition temperature, Raman spectra of three samples grown at 630, 730, and 800 °C are shown in Fig. 3. Apart from Raman peaks characteristic of sp³- and sp²-bonded carbon, tiny peaks around 1140 and 1490 cm⁻¹ are noticeable as well. For years, the 1140 cm⁻¹ line has been attributed to nanocrystalline diamond [8], although more recently a connection with carbon– hydrogen bonds in the grain boundaries was proposed [9]. In turn, the 1490 cm⁻¹ peak is suggested to correspond to curved graphene sheets, i.e. spⁿ-hybridized structures equivalent to open carbon nanocages (2 < n < 3) [9]. On that account, the obtained diamond coatings seem to be comprised of diamond grains of different size containing hydrogen atoms in the C–H form inside, and with graphitic inclusions filling the empty space between the grains.



Fig. 3. The Raman spectra of diamond coatings deposited onto untreated Ti substrates at three different temperatures. In spite of additional spectral features pointing towards the presence of chemical and phase impurities within the obtained films, the optimal deposition temperature appears to be around 730 $^{\circ}$ C.



Fig. 4. Raman spectra of diamond coatings onto Ti substrates with and without a spontaneously formed native oxide layer.

According to the analysis presented in [10], the volume fraction of non-diamond phase impurities is estimated at 42%, 12%, and 18%, respectively, which suggests 730 °C as an optimal deposition temperature. Below that range thermodynamic equilibrium abruptly moves towards formation of diamond-like carbon (DLC), while at higher temperatures a gradual increase of the volume fraction of non-diamond components is observed. At the same time, the growth rates calculated from weight difference measurements prior and after growth equal to 1.4, 3.4, and 7.6 μ m/h, respectively. As mentioned earlier, in search of optimal deposition conditions one has to find a compromise between acceptable coating quality and required growth rate.

The natural chemical reactivity of titanium results in the presence of a thin native oxide layer protecting this material against atmospheric conditions. On the other hand, titanium oxide is known to enhance diamond nucleation on substrates that do not form stable carbides, such as quartz [11]. A



Fig. 5. Comparison of Raman spectra of diamond coatings onto untreated titanium substrates deposited with an under- and oversaturated methane concentration in the gas mixture. The insets show a magnification of the region around the 1330 cm⁻¹ Raman diamond peak (sp³—diamond phase, dis—disordered sp² phase).

spontaneously nucleated oxide allows polycrystalline diamond to grow onto titanium substrates as well. To verify this oxide effect, untreated although otherwise spontaneously oxidised titanium substrates were half coated with an additional pure titanium layer prior to diamond deposition ($\sim 1 \mu m$ thick, magnetron sputtering). According to the Raman spectra in Fig. 4, such a pre-treatment gave rise to selective diamond growth. In fact, a dark diamond overlayer was grown on the Ti-masked part of the substrate, which got covered with native titanium oxide during prolonged exposure to the air, whereas almost no diamond film was formed on the clean titanium surface that remained metallic white and shiny despite identical deposition conditions.

This oxide effect has not been recognized before, since it was believed that the in-diffusion of carbon followed by carbide formation is a sufficient prerequisite for diamond nucleation in CVD processes [12]. Interestingly, formation of non-diamond phases onto the clean titanium surface is suppressed as well, which would imply that carbon atoms cannot stick to a clean titanium surface or that they at least encounter a substantial diffusion barrier. This effect has not been explained so far.

In Fig. 5 Raman spectra of diamond films grown at different hydrocarbon concentrations are compared. The upper curve is taken from a sample deposited at a constant ratio of $CH_4/H_2=5\%$, while the lower one comes from a sample deposited in a two-step process providing initial carbon oversaturation using 15% of CH_4 for the first 15 min followed by 5% for the rest of the deposition. The saturation aims at forming a thick interfacial carbide layer, which should improve the adhesion between the substrate and the diamond coating.

Both spectra do not differ substantially as far as Raman peaks and their positions are concerned, although detailed analysis reveals the splitting of the ~ 1338 cm⁻¹ peak in the Coversaturated sample (left inset in Fig. 5) in contrast to the unsaturated one (right inset in Fig. 5). The observed feature can be associated with abundant graphitic carbon formation under high hydrocarbon content as indicated by the Raman intensity ratio of sp³- to sp²-bonded carbon in Fig. 5. In fact, perfectly flat graphene sheets (in highly-oriented pyrolytic graphite (HOPG), for example) contribute solely to the 1580 cm⁻¹ Raman peak (Gline ascribed to E2g symmetry vibrations), although at their edges carbon atoms re-hybridize into the sp³-configuration due to their enormous distortion out of the graphene sheets, which gives rise to the substantial 1340 cm^{-1} line as well [13]. Therefore, the low-frequency component of the $\sim 1338 \text{ cm}^{-1}$ line is attributed to the ordered diamond phase, whereas the highfrequency one is attributed to the disordered sp³-bonded carbon atoms.

In general, SEM images, as shown in Fig. 6, proved that none of the investigated coatings was found to undergo delamination regardless of the deposition conditions as well as pre-treatment procedures used throughout in this study. However, the deformation of the investigated samples was observed after the deposition as a result of the strain-relief behaviour in the titanium subjected to high temperature. On that account, residual stress in the substrates would be the



Fig. 6. Cross-sectional SEM image of the diamond film (D) grown on the untreated titanium substrate (Ti) with an interfacial titanium carbide layer (TiC). Despite significant roughness, the diamond coating adheres firmly to the substrate.

most important factor limiting the use of titanium and its alloys for diamond deposition.

4. Conclusions

To summarize, structural properties of diamond coatings grown on pure titanium substrates are investigated in this paper. Surface abrasion due to sandblasting is found to have a positive effect on the diamond growth rate, although it removes the structural dependencies between Ti and the predominant TiC and diamond growth directions. In contrast, both TiC and diamond films grown on an untreated titanium substrate exhibit (h00) texture. The presence of a spontaneously formed native titanium oxide layer is found to have a beneficial effect on the diamond layer formation as compared by diamond deposition on clean and oxidised titanium substrates. We also studied the effect of a saturated hydrocarbon plasma on the coating adhesion. On the whole, none of the investigated coatings was found to undergo delamination, pointing to appropriate deposition conditions. Nevertheless, residual stress in cold-rolled titanium plates may limit the use of such substrates for diamond deposition.

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