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Wettability and corrosion tests of diamond films grown on Ti6Al4V alloy

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Abstract

Diamond thin films were successfully deposited on both sides of jetted substrates Ti6Al4V alloy, without intermediate layers deposition, by using an enhanced 2.45 GHz microwave-assisted technique. This system is based on discharge surface-wave guide, Surfatron system. It was used as a bias-enhanced nucleation (BEN) applied between the plasma shell and the substrate, reaching a nucleation density around 5×10^9 parts cm^{-2} in just 5 min. These films showed a good quality and a total residual stress around -2.4 GPa that was evaluated by Raman scattering spectroscopy. In spite of the high residual stress, the films adhesion on substrate was excellent, even when a load of 250 kgf was applied.

Wettability of these films designed a small hydrophobicity that is very similar to those of other carbon structures used as biological implants. The surface energy value of 50.5 mJ m^{-2} indicated that is possible to get a good tissue adhesion on diamond films. These films were also exposed to various biological fluids, including isotonic NaCl and Ringer's solution for 1 month and acid–water solution for 2 months. Diamond surface chemical stability was analyzed from films micrographs by scanning electron microscopy (SEM). The results revealed that the diamond films surfaces were not degraded by environmental agents.

Keywords: Wettability; Diamond film; Nucleation; Titanium alloy; Adhesion

1. Introduction

Titanium alloys have demonstrated physical, mechanical and chemical properties for many structural applications [1]. For these applications, CVD diamond coatings become a goal for solving their low wear resistance and high fatigue [2,3]. The main disadvantage of this system, diamond on titanium alloys, is its poor film adhesion that occurs partially due to the thermal expansion mismatch between diamond and substrate [2–4]. The adhesion study has already been explored in previous works [5,6] and specific results for such a films are shown elsewhere [7], where the indentation tests showed that diamond films can support a load of 250 kgf without delamination.

Diamond films on Ti6Al4V alloy have interesting properties for many applications, mainly the biological applications [8,9]. In agreement with the recent literature and other authors [10,11], the biomaterials for human body should satisfy the following requirements: wettability, biostability and chemical stability. Besides, implant system must present excellent adhesion and very good mechanical characteristics.

Pinzari et al. [12] and Djemia et al. [13] investigated the wettability of diamond films grown on silicon and Ti6Al4V alloy in different growth conditions, respectively. The water contact angles (θ) varied from 75° to 96° for films deposited on silicon substrate and from 59° to 64° for films deposited on Ti6Al4V alloy. Both of them observed that wettability change is due to the surface contaminant removal, graphitic sp^2 carbon and hydrogen inclusions, which depends on the

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deposition conditions and surface topography (roughness, morphology, etc.).

In a more detailed study, Ostrovskaya et al. [14], based on the wettability data of auto-sustained diamond films, studied the variation in diamond films surface tension induced by different methods of surface treatment (hydrogenation and oxidation). They concluded that hydrogenation of the diamond films surface increases the wettability angle to 93° as compared with diamond surface oxidized by air.

However, it was, in a recent work, that Kaibara et al. [11] showed the importance of the wettability control for biological applications. They analyzed, in terms of wettability on the nanoscale, the hydrogen-terminated and oxidized diamond surfaces. They concluded that the difference in wettability between diamond surfaces could be applied in the fields of medicine and biotechnology, i.e. for the fabrication of DNA or protein tips.

All these studies indicated the importance of wettability and its relationship with the studies that it comes being developed for biological application.

The purpose of this study was to evaluate if CVD diamond thin films deposited on jetted Ti6Al4V substrates, by using BEN during 5 min with a deposition time of 5 h, could be used for biological application. There are no reports in the literature with similar results by using these experimental conditions, substrate pretreatments and film growth, for biological application. Besides, these films are very adherent to substrate which is one of the conditions demanded to be able use them as biomaterial.

2. Experimental procedure

Films were grown by using the Surfatron system that has been described elsewhere [6,15]. Basically, the surfaguide set is composed of the launcher and two coaxial dielectric tubes. The inner tube is made of quartz and used as a discharge tube. This tube has an abrupt transition that is essential to finish the surface-wave (SW) propagation and create expanded hemispherical plasma shell slightly bellow the transition. The plasma shell is uniform with a thickness of few millimeters, and has high energy density. The substrate is placed close to this plasma shell, 0.5 mm approximately.

Depositions were carried out on both sides of Ti6Al4V 1×1 cm^2 and 1.2 mm thick substrate. We have taken 10 samples that were mechanically pretreated by glass microspheres jet in order to improve the film adhesion. This treatment resulted in a substrate surface roughness lower than 0.3 μm, obtained by Surface Perfilometer, model Alpha-Step 500 of TERCOR Instruments. For all experiments, the samples were cleaned with ethanol and prepared by ultrasonic hexane bath with 0.25 μm diamond powder during 60 min.

Substrate temperature, T_{dep}, was kept at 700 °C with a gas flow rate of 100 sccm and a pressure inside the reactor of 27 Torr by setting the microwave power at 2.5 kW for all experiments. Negative bias of −400 V was applied during 5 min (t_b) by using a gas mixture of 8.0% methane in hydrogen. Then, the films were grown from a gas mixture of 0.7% methane in hydrogen for a deposition time, t_{dep}, of 150 min, separately, in each side of the substrate. After the deposition on the first side of samples, the microwave power supply started to be decreased and the mass flow controllers were turned off. So, the substrate temperature was decreased around 40 min. After 1 h inside of the reactor turned off completely, the substrate reaches the environment temperature and the sample is placed in its backside for the second deposition. It was not necessary to do a new cleaning in the sample because the growth atmosphere is very clean.

All diamond films showed the same characteristics, such as high density nucleation, good adhesion on Ti6Al4V alloy and growth rate around 0.7 μm h^{-1}. These films grow in the format of agglomerates grains due to substrates superficial roughness and growth temperature. They presented a roughness (R_a) of 0.5 μm that it was measured by nanoscope atomic force microscopy (AFM) system. The nucleation density as a function of BEN parameters, deposition time and sample preparation are subjects of another submitted work [16].

3. Results and discussions

3.1. Raman spectrum

The film quality was evaluated by Renishaw Raman spectrometer with a 514.5 nm Ar-ion laser. In order to improve the Raman data statistics, a large number of spectra were recorded from each sample. Five points in a sample area were chosen and the spectra were scanned five times on each point of such area.

The Raman spectra of diamond coatings grown on Ti6Al4V alloy are very similar for both sample sides and one of them is depicted in Fig. 1. The diamond films peaks values were around 1339±2 cm^{-1}. By considering the natural diamond of 1332 cm^{-1}, this Raman shift corresponds to a total residual stress around −2.4±0.7 GPa [3,4,6]. Although this stress value seems to be significant, it is lower when compared with the thermal stress of −6.0 GPa for this growth temperature. Raman band centered at 1550 cm^{-1} is attributed mainly to amorphous sp^2-bond. As the film is very thin and a high methane concentration was used during BEN step, the very wide Raman band is due to incorporation of non-diamond carbon phase in the interface.

3.2. Contact angle and surface tension measurements

The contact angle (θ) measurements have been performed in order to evaluate films surface tension (γ) in liquids whose surface tension components are known [12]. The films surface tension components were calculated by