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# Studies on corrosion and wear behavior of submicrometric diamond coated Ti alloys

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ABSTRACT

Implants made out of Ti alloys often fail due to their lower wear and corrosion resistance. In order to obviate this problem, submicrometric diamond films were grown on Ti–13Nb–13Zr and Ti–23Nb–0.7Ta–2Zr–O (Gum metal) using hot filament chemical vapor deposition technique. Deposited films were characterized using XRD, Raman, SEM, AFM and nanointender. The electrochemical corrosion and reciprocatory wear behavior of the coated samples were evaluated in simulated body fluid. The results demonstrate that corrosion and wear properties of the diamond coated Gum metal are far superior than Ti–13Nb–13Zr alloy, due to the presence of beta phase in the former alloy.



## 1. Introduction

Titanium and its alloys are extensively used for various applications ranging from aircraft structures to artificial human implants because of their high-strength to weight ratio, excellent corrosion resistance and biocompatibility [1]. In the field of biomaterials, titanium and its alloys are commonly used in artificial joints, dental implants, and surgical equipment owing to their immunity to corrosion by all body fluids and tissues and its innate ability to join with human bone [2]. In addition, the non-ferromagnetic property of Ti alloys allows patients with titanium implants to be safely examined using magnetic resonance imaging (MRI). However, titanium and its alloys suffer from several limitations like low wear resistance, erosion and fretting fatigue failure [3]. The low frictional wear resistance of Ti implants led to the release of fine metallic and polymer particles to the body. As the body attempts to eliminate these wear particles, it triggers an autoimmune reaction, which causes resorption of living bone tissues, causing joint failure.

Submicrometric diamond coatings on titanium and its alloys can overcome all these drawbacks by virtue of their extreme hardness and wear resistance, low friction coefficient, stable chemical properties, non-ferromagnetic nature, and biocompatibility [4,5]. Besides, submicrometric diamond coating provides a suitable surface for cell attachment spreading and proliferation as assessed by the behavior of human fibroblast cells [4]. The excellent wear resistance and the low friction coefficient of submicrometric diamond could drastically reduce the amount of wear debris generated during the joint functioning and increase the life of the prosthesis [6]. Even in the extreme case of small wear of the coatings, the residues (diamond particles) are completely harmless as they withstand initially little or no adverse reaction from human monocytes and polymorphous nucleo leukocytes [7]. In fact, it has been demonstrated that diamond particles appear to possess high bioactivity at the molecular level, presenting antioxidant and anticarciogenic properties [8]. Hence, submicrometric diamond coatings on surgical and dental instruments, such as scalpels and dental burrs, may improve the performance and lifetime of tools as well as their biocompatibility. Submicrometric diamond coated burrs can work with no sign of deterioration even in more than 1000 operations, while, the conventional burrs are ineffective after 30–60 operations [9]. This wide range of biomedical applications has incited a great interest in submicrometric diamond coated Ti alloys and a number of papers were published in this field [4–9]. However, to the best of our knowledge, there are no reports on wear and corrosion behavior of submicrometric diamond coated Ti–13Nb–13Zr (Ti1313) and Ti–23Nb–0.7Ta–2Zr–1O (Gum metal).

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The Ti1313 is a near $\beta$ phase alloy with a combination of h.c.p ($\alpha$) and b.c.c ($\beta$) structures. It is a well established low modulus biocompatible alloy and has been approved by FDA. Similarly Gum metal, an upcoming $\beta$ phase Ti alloy, exhibits high strength ($>1$ GPa), low Young's modulus ($\sim$60 GPa), high yield strain ($\sim$2.5%) and excellent cold workability. Diamond films were deposited on Ti1313 and Gum metal substrates using hot filament chemical vapor deposition (HFCVD) system. This technique has several advantages like uniformity over large area, relatively simple set-up, ease of operation and adaptability to product geometries [10]. In this study, we discuss in detail on the wear and corrosion behavior of submicrometric diamond coated Ti1313 and Gum metal.

## 2. Experimental details

As received hot rolled Ti1313 (20 mm $\times$ 20 mm) and forged Gum metal (20 mm $\times$ 20 mm) substrates were polished using silicon carbide (SiC) (220–1600 grits) and cleaned with distilled water. Further polishing by diamond paste (1 μm) provided a mirror polished finish to the substrates surface. The substrates were then ultrasonically cleaned in acetone for 30 min and dried using a hot air dryer. Prior to the deposition, the substrates were seeded with diamond nano particles ($\sim$4 nm diameter), dispersed in dimethyl sulfoxide (DMSO), using a low power ultrasonicator for 15 min. The substrates were again cleaned with ethanol in an ultrasonicator for 1 min and placed inside the cold walled aluminum chamber of HFCVD system (sp3 Diamond Technologies Inc, USA). A parallel array of tungsten (0.12 mm diameter) filaments, with 12 mm wire to wire spacing, was placed above the substrates. The HFCVD chamber was continually pumped using a rotary pump, while the process gases, methane (45 sccm) diluted in excess of hydrogen (2250 sccm), were metered in at carefully controlled rates. The gas distribution assembly allowed the control of the gas flow patterns in and around both the filament assembly and the substrate to ensure uniformity in the coating. The set chamber pressure during the deposition was 10 Torr, maintained precisely by a throttle valve connected to the rotary pump. Temperature of the electrically heated tungsten filament assembly was $\sim$2200 °C, as monitored by a two-color pyrometer. The substrate temperature was measured using a K-type thermocouple, located directly underneath the substrate indicated 800 °C. The whole growth process was performed for 2 h and the thickness of the resulting film was estimated to be $\sim$1 μm.

Phase analysis of the deposited films was carried out using X-ray diffraction (X'pert Pro, PANalytical) with Cu K$\alpha$ radiation. Raman spectra of the deposited films were recorded using a confocal Raman microscope (Alpha 300, Witec) with an excitation radiation of 532 nm of a Nd:YAG laser operated at less than 20 mW. The surface roughness and microstructure were observed using an atomic force microscopy (easyScan 2, Nanosurf) and a field emission SEM (Quanta 3D, FEI) respectively. The mechanical property of the deposited films was analyzed using a nanoindenter (Hysitron).

A three-electrode cell arrangement was used for the electrochemical measurements, with a saturated calomel reference electrode (SCE) as a reference electrode and a platinum wire as an auxiliary electrode (ASTM G5-94). The electrolyte used for simulating human body fluid conditions was Hank's solution (ASTM F2129-08), prepared using laboratory grade chemicals and double distilled water. The pH of the solution was precisely maintained at 7.4. Freshly prepared solution was used for each experiment. Nitrogen gas, with a flow rate of 150 ml min$^{-1}$, was purged through the electrolyte to attain a de-aerated atmosphere, and the temperature was maintained at 37 °C (human body temperature). The open circuit potential (OCP) and the electrochemical polarization were measured using a potentiostat (Gill AC, ACM Instruments), controlled by the sequencer software. The OCP was registered during 60 min and the potentiodynamic polarization was determined in a range of $-750$ mV to 2500 mV (vs. SCE) at a scan rate of 0.166 m Vs$^{-1}$. Linear polarization tests were carried out in a potential range of $\pm$20 mV with respect to the SCE at a scan rate of 0.166 mV s$^{-1}$. The resistance to polarization was calculated by measuring the slope of the linear portion of the curve at zero current density. The impedance spectra were measured with a frequency sweep from $10^4$ Hz to $10^{-1}$ kHz on a logarithmic increment. A total number of 200 data points were recorded for each experiment. The best fit circuit was identified based on the subsequent analysis of Nyquist, Bode phase and Bode magnitude plots. Zman (V2.0) software (ZAHNER-Elektrik, Germany) was used for further assistance in circuit fitting.

Wear test study was performed using a reciprocating wear test machine (Ducom, ASTM G133). This system applied a vertical load to the contact surfaces, along the longitudinal axis of the pin and perpendicular to the sliding direction. Hank's balanced salt solution (HBSS) was used as lubricant in these studies. The wear tests were carried out at a constant load of 10 N for a testing duration of 10,000 cycles, at constant frequency of 2 Hz. These were applied during a 15 mm stroke at a sinusoidal frequency of 2 Hz. Ultra-high-molecular-weight polyethylene (UHMWPE) polymer ball of 5 mm diameter was used as the counter body. Before and after wear tests, both the diamond coated specimen and the balls were ultrasonically cleaned in acetone for 15 min. Freshly prepared Hank's solution was used for each experiment and the pH of the solution was precisely maintained at 7.4. The temperature during wear tests was maintained at 37 $\pm$ 2 °C.

## 3. Results and discussions

### 3.1. X-ray diffraction

X-ray diffraction (XRD) patterns of the diamond films deposited on Gum metal and Ti1313 substrates are shown in Fig. 1. The XRD pattern exhibited two peaks at 43.91° and 75.29°, indexed to the diffraction from (111) and (220) crystal planes of diamond respectively. The peaks at 35.93°, 41.73°, 60.49° and 72.41° confirmed the presence of TiC crystal planes at (111), (200), (220) and (311) respectively [11]. All other peaks, the $\beta$ phase

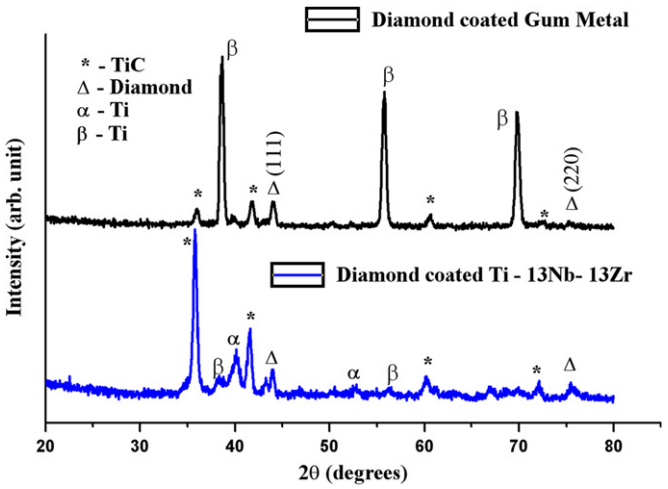


**Fig. 1.** XRD patterns of diamond thin films deposited on Gum metal (Ti–23Nb–0.7Ta–2Zr–O) and Ti–13Nb–13Zr substrates.