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Tribological properties, corrosion resistance and biocompatibility of magnetron sputtered titanium-amorphous carbon coatings

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ABSTRACT

Amorphous carbon incorporated with titanium (a-C:Ti) was coated on 316L stainless steel (SS) by magnetron sputtering technique to attain superior tribological properties, corrosion resistance and biocompatibility. The morphology, topography and functional groups of the nanostructured a-C:Ti coatings in various concentrations were analyzed using atomic force microscopy (AFM), Raman, X-Ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Raman and XPS analyses confirmed the increase in sp^2 bonds with increasing titanium content in the a-C matrix. TEM analysis confirmed the composite nature of the coating and the presence of nanostructured TiC for Ti content of 2.33 at.%. This coating showed superior tribological properties compared to the other a-C:Ti coatings. Furthermore, electrochemical corrosion studies were performed against stimulated body fluid medium in which all the a-C:Ti coatings showed improved corrosion resistance than the pure a-C coating. Preosteoblasts proliferation and viability on the specimens were tested and the results showed that a-C:Ti coatings with relatively high Ti (3.77 at.%) content had better biocompatibility. Based on the results of this work, highly durable coatings with good biocompatibility could be achieved by incorporation of optimum amount of Ti in a-C coatings deposited on SS by magnetron sputtering technique.

1. Introduction

316L stainless steel (SS) is one of the most commonly used structural alloys and has received considerable attention in orthopedic applications due its versatile properties. For example, it has been widely used in orthopedic surgeries particularly as fixatives to support the fractured bones and also in various other applications [1–4]. However, release of ions such as nickel, chromate, and molybdenum in the serum after implantation and associated allergic reactions have become a critical problem for long-term implantation of 316L SS [5]. In order to overcome this problem, surface modification of SS by coatings has been explored to enhance and control the corrosion resistance and biocompatibility of the material. Various research groups have investigated the effect of different surface coatings on the improvement of material properties and biocompatibility using various cell types [3–9]. Furthermore, several types of coatings on SS have been investigated for the enhancement of biocompatibility [10–13]. Sharifnabi et al. deposited Mg-substituted fluorapatite coating on 316L SS and found that corrosion resistance increased in normal saline and Ringer's solution [14]. They also found that it reduced the amount of metal ion released from 316L SS. Enhanced corrosion resistance against SBF solution and hydroxyapatite layer growth on metal surface were observed on porous titanium dioxide [15] and porous zirconium dioxide [16] coated 316LL SS by Nagarajan

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et al. Improved mechanical properties were observed by Arifvianto et al., on surface mechanical attrition treated (SMAT) 316L SS [17] and Feng et al. showed that Ti ion implanted 316L SS increased the corrosion resistance and a very high implantation voltage led to the decrease in corrosion resistance [18]. Though these studies have shown some benefits of the coatings, further work is needed to develop a coating that can provide superior tribological properties [19–25], in addition to corrosion resistance and biocompatibility.

Bordji et al. have reported that the biocompatibility of osteoblast and fibroblast cells could be improved on nitrogen and carbon treated 316L SS substrates [3]. The carbon treated substrates also exhibited good wear resistance and anti-corrosion property [3]. In this regard, amorphous carbon (a-C) based coatings may be used as protective coatings not only for their biocompatibility and anti-corrosion property but also for their high wear resistance. Also, it has been shown that incorporation of metals in a-C coatings aided in further improvement of the material properties [10]. Randeniya et al. reported the enhancement in long term osteoblast proliferation using a-C coatings with relatively low titanium (Ti) content which resulted in low residual stress in the coating deposited by direct-current plasma enhanced chemical vapor deposition (PECVD) [11]. Furthermore, direct current magnetron sputtered titanium incorporated amorphous carbon nitride film on Ti alloy showed an enhanced biocompatibility and corrosion resistance [12]. In another work, Ti was identified as a good biomaterial which enhanced cell adhesion and improved the tribological properties of a-C by reducing the internal stress and increasing the sp^2 bonds in the coating [26]. However, a comprehensive study addressing the biocompatibility of the coatings as well as their tribological properties is needed to develop this into commercially viable technology that assures high durability and reliability of the implanted parts.

In this work the effects of Ti content in a-C coatings deposited on 316 LL SS by magnetron sputtering technique was investigated with respect to corrosion resistance, biocompatibility, and tribological properties of the coatings. Pure a-C and Ti incorporated a-C (a-C:Ti) were coated on 316L SS substrates using RF magnetron sputtering technique. The coatings were characterized using Raman spectroscopy, atomic force microscope (AFM), contact angle measurement apparatus, transmission electron microscope (TEM), and X-Ray photoelectron spectroscopy (XPS). Also, the mechanical properties such as hardness and Young's modulus were obtained. The friction and wear properties of the coatings were assessed using a reciprocating type of a tribo-tester. The effects of a-C:Ti coating on 316L SS substrate on the improvement of cell viability, proliferation and cell adhesion were investigated using preosteoblast cell lines. The following sections describe the details of the experimental work.

2. Experimental methods

2.1. Material synthesis

Pure a-C and a-C:Ti nanocomposite coatings were deposited on 10 × 10 cm and 10 × 20 cm 316L SS substrates using Radio Frequency [(RF) Plasmochemical reactor (ν = 13.56 MHz)] magnetron sputtering using graphite and Ti targets. The power used for graphite was kept constant at 400 W and the Ti target power was varied as 20 W, 30 W, 40 W and 50 W. The coating specimens prepared with Ti target power of 20 W, 30 W, 40 W, and 50 W were named as S1, S2, S3, and S4, respectively. The deposition parameters used for preparation of the specimens are given in Table 1. Polishing and cleaning procedures for the 316L SS substrates were carried out as described in the previous work [6].

Table 1
The coating parameters for Ti incorporated a-C coatings.

Parameters	Coating condition of a-C:Ti
Technique adopted	RF magnetron sputtering
Target material	Graphite and titanium
Substrate	316L SS
Substrate temperature	Room temperature
Graphite target power	400 W
Metal target power	20, 30, 40 & 50 W
Base pressure	0.003 Pa
Argon flow rate	50 sccm
Working pressure	0.75 Pa
Film thickness	200 nm ± 5

2.2. Specimen characterization

Raman spectroscopy measurements were carried out under backscattering geometry with a liquid-nitrogen-cooled CCD detector. The Raman spectra were collected under ambient conditions using an argon-ion laser with a 514.5 nm wavelength. The surface topography and surface roughness of the pure a-C and a-C:Ti nanocomposite coatings were measured using an AFM (Seiko SPA400). The contact angles of the coatings were measured using a contact angle measurement apparatus (Kriuss DSA 20E). TEM (JEOL TEM 2100) analysis was performed using a power of 200 KV. Chemical bonds were analyzed by XPS using an angular resolved electron analyzer with a monochromated Al Kα source (Theta Probe, Thermo Fisher Scientific).

2.3. Tribological tests

The friction and wear properties of the coating were investigated using a commercial reciprocating type of a tribo-tester. An Al_2O_3 sphere with a diameter of 1 mm was used as the counter surface after a standard cleaning procedure. All tests were conducted under the following conditions: dry sliding condition, room temperature, relative humidity of ~40%, applied load of 10 mN, and sliding speed of 2 mm/s with a 4 mm stroke. Dry sliding condition was selected as a means to accelerate the wear process. Since the purpose was to assess the relative wear resistance of the coating specimens, dry sliding was considered to be sufficient for the purpose of this work. The coefficient of friction (COF) and number of sliding cycles were recorded automatically during the sliding test through a data acquisition system. The tests were repeated five times for each specimen to assure repeatability of the data. The mechanical properties of the coatings were assessed using a commercial ultra-nano-hardness tester (CSM UNHT). A standard diamond Berkovich tip was used in the indentation tests.

The wear equation proposed by Archard [27] was used as a basis to obtain the wear rate using the following equation:

$$\text{Wear Rate} = V/W \times L \quad (1)$$

where V is the wear volume, W is the applied load, and L is the sliding distance. The wear volume was estimated from the cross-sectional area of the wear track below the horizontal line of the specimen surface, which was obtained using a surface profiler.

2.4. Electrochemical corrosion analysis in simulated body fluid solution

Electrochemical studies of uncoated and a-C:Ti coated 316L SS (S1, S2, S3 and S4) substrates were performed in stimulated body fluid (SBF) solution by cyclic polarization and electrochemical impedance spectroscopy (EIS) measurements. The SBF solution was selected for corrosion analysis of a-C:Ti nanocomposite coatings owing to its wide usage in implantation of orthopedic surgery.