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Corrosion behavior of amorphous carbon deposit in 0.89% NaCl by electrochemical impedance spectroscopy

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ABSTRACT

Amorphous carbon films were deposited on SS316L substrates using a DC magnetron sputtering system, aiming at the application of the coated SS316L for biomedical implants. The biocompatibility and chemical stability of the carbon layers have been previously demonstrated. The films were deposited on top of sputtered titanium coatings introduced as a buffer layer to enhance film-substrate adhesion. The corrosion resistance of the a-C/Ti/SS316L systems was investigated by electrochemical techniques. The electrolyte used in this work was 0.89 wt.% NaCl at pH 7.4, which simulates body fluid ionic concentrations. The coated samples displayed corrosion resistance values in the saline solution much higher than the stainless steel substrates and the role of the Ti coating thickness was analysed in order to determine the optimal system for biological applications.

1. Introduction

In the biomedical area, implants of artificial joints are almost a routine surgical procedure [1]. The hip and the knee joints are the two most common replacements and have proven to be very effective in relieving pain. Moreover, the success rates are as high as 95% at least in the short time. Nowadays, the major problem of artificial joints concerns to the long-term durability: on the average, a total hip joint replacement lasts 10–15 years [2]. With many of the artificial joint recipients living longer and having a more active lifestyle, 10–15 years is no longer adequate. Many patients require a second implant or revision surgery, which is more difficult, has a much lower success rate, and has higher rates of complications. Even younger candidates who can benefit from total joint replacements have to wait until their arthritic condition is unbearable before being considered for a joint implant [3].

Among the different factors that influence the lifetime of orthopaedic implants (cup alignment, implant geometry, patient level of activity, etc.,) there are two which are specifically materials related: one is the wear of the moving parts, which leads to wear debris induced osteolysis [4]; the other is the corrosion of the implant surface, which leads to metal ions release with potential adverse effects such as toxicity, hypersensitivity and carcinogenesis [5].

Both of the above mentioned problems are mainly related to the surface of the implant, therefore a possible solution might come from surface modifications of the current materials. One of the methods for modifying surface properties is through deposition of a distinctive surface layer in the form of a coating. Amorphous carbon coatings have been proposed as possible and viable surface modification for metallic implants, since their hardness, wear resistant, low friction coefficient, biocompatibility and chemical stability have been clearly identified [6–8]. The family of "Amorphous carbon-based films" include a wide range of films having different properties, such as, diamond-like carbon (DLC) films, which are very hard and under certain environmental conditions might have friction coefficients in the 10^{-2} range that makes them excellent candidates for coating the moving parts of orthopaedic implants [9]. These films have been proposed to coat the counterface of the ball in hip joints; and although very successful in the lab tests, they failed during real applications due to corrosion induced wear and delamination [6]. The possible reason for this failure is the high internal stress characteristic of these DLC films. On the other hand, the less hard, graphitic-like coatings have no applications for bearings since neither the friction coefficient or wear resistance are adequate [10]. Nevertheless, during the last years, we have been investigating the osteogenesis capabilities of the graphite-like carbon (GLC) films obtaining encouraging results, which show that GLC films might be very attractive for improving the bone-implant interface, where tribology is not an issue [11,12]. A second advantage of coating the metallic implant by this inert material might be a reduction in the release of metallic ions [9,13–15]. As mentioned above, the failure of the implants is partly due to the liberation of metallic ions since the implant is subject to the harsh environment of the human body (typically oxygenated saline solution with salt content of about 0.89% at pH of 7.4). Therefore, in this work we investigated the performance of graphite-like amorphous carbon films as a corrosion resistance barrier for stainless steel substrates immersed in NaCl solutions using the electrochemical techniques.

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One of the major drawbacks of depositing amorphous carbon on metals is that the film-substrate adhesion is not good enough for real applications. Many researchers have shown that this issue can be properly addressed by depositing metallic buffer layers, such as, chromium, tungsten, or titanium based films [16–19] previous to the a-C film growth. In order to address this issue, we deposited titanium buffer layers of different thicknesses between the substrate and the a-C film. Electrochemical evaluation of the Ti/a-C double-layer systems was done to select the thickness ratio (Ti/a-C) that gives a better performance.

Both, polarization curves and electrochemical impedance spectroscopy (EIS) as a function of the immersion time were used to evaluate the corrosion barrier properties of the Ti/a-C double-layer systems. Some issues concerning the corrosion properties of physical vapor deposited (PVD) coatings are the degree of porosity and the interdiffusion and adhesion of the coating-substrate interface [20]. Porosity of PVD coatings cannot be assessed by direct methods, such as, H_2 diffusion, optical or SEM microscopy, since the pores are usually in the nanometer scale. However, electrochemical methods can indirectly determine the presence of pores or pinholes from measurements of the through-pores in the coatings [19,20]. The presence of these through-pores can be detected since they provide a passage for the electrolyte to reach the substrate, reacting chemically or electrochemically and giving rise to measurable current signals. Moreover, the film-substrate adhesion can be qualitatively evaluated by simple observation of the no-delamination of the films after long immersion times in the electrolyte.

In this paper, we presented the electrochemical impedance analysis of a series of a-C coatings deposited on medical grade 316 L stainless steel (SS) substrates using titanium layers of different thickness as buffer layers.

2. Experimental

2.1. Substrate preparation

Stainless steel sheets (AISI 316 L) were cut into square pieces of 1×1 cm size. These 1 cm^2 stainless steel (SS) pieces were used as substrates. Firstly, they were polished using SiC grit up to grade 600 and then cleaned using acetone, isopropanol and deionized (DI) water in an ultrasonic bath.

2.2. Preparation of Ti and a-C coatings by magnetron sputtering

The titanium films were deposited directly on the SS substrate from a pure titanium target (10 cm in diameter, 99.99% pure Ti) using a magnetron sputtering system. The Argon plasma was excited by a dc-pulse source working at 250 kHz and 250 W rms-power. The deposition pressure was 4 mTorr and the Ar flux was 10 sccm, while the deposition time was changed to obtain three different thicknesses for the Ti films, as shown in Table 1. Then, the samples were transferred to another chamber, where a 240 nm carbon film was deposited using a hollow cathode (10 cm in diameter graphite target, 99.99% pure C) magnetron sputtering system under dc current conditions. The deposition conditions of the carbon film were: 250 W, 20 mTorr, 10 sccm of Ar and 450 s. For both systems the substrate holder was not cooled, therefore the substrate temperature increased according to the deposition time, reaching maximum values around 120 °C. The thicknesses of the Ti films were chosen to represent different percentages of the a-C thickness; less than 10%, half-half and more than 100%.

Table 1
Samples obtained by MS deposition.

Sample Name	Thickness (nm)
SS	–
Ti1	16
Ti2	100
Ti3	530
aCTi1	240 [16] + 16 (Ti)
aCTi2	240 [16] + 100 (Ti)
aCTi3	240 [16] + 530 (Ti)

2.3. Electrochemical experiments

Electrochemical experiments were carried out using a standard three-electrode system where a saturated calomel electrode (SCE) was used as the reference electrode and a platinum counter electrode. The working electrodes were the a-C/Ti/SS system and Ti/SS films were evaluated in order to gain some understanding of the electrochemical process. The samples were sealed to a wall of the electrochemical cell using a Viton O'ring leaving an area of 0.15 cm^2 exposed to the solution.

The corrosion resistance was examined in an electrolyte of 0.89% NaCl at pH 7.4, which simulates body fluid conditions. The electrochemical impedance experiments were carried out as a function of the

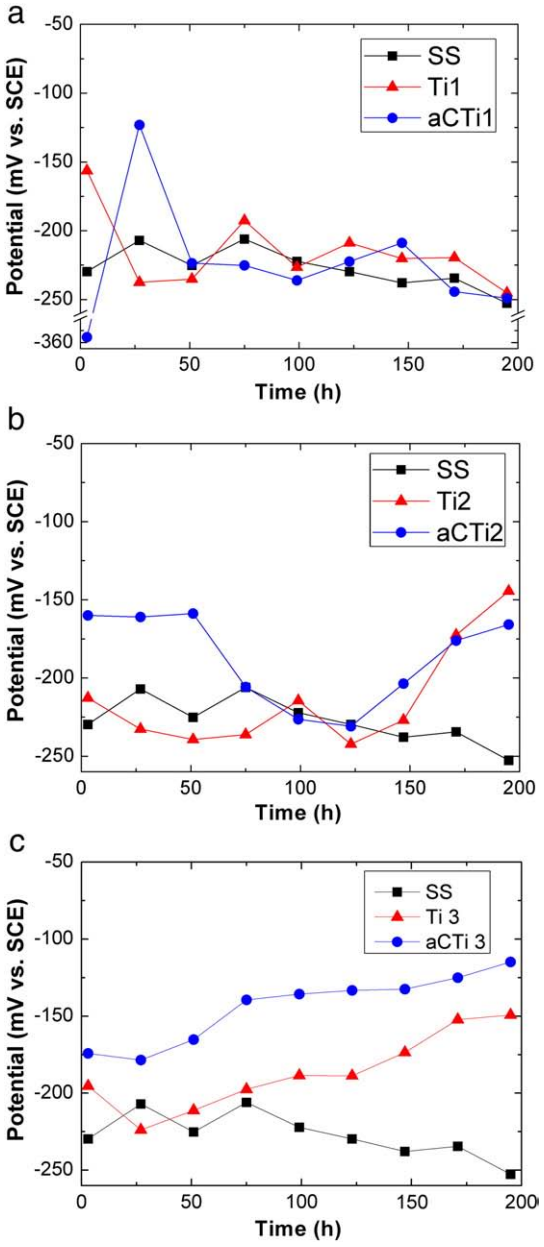

Fig. 1. Open circuit potential of the bare stainless steel substrate, the Ti coatings and the double-layer aCTi systems. a — OCP values of Ti1 and aCTi1 samples, b — OCP values of Ti2 and aCTi2 samples, c — OCP values of Ti3 and aCTi3 samples.