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Comparison of structural, mechanical and corrosion properties of thin TiO_2/graphene hybrid systems formed on Ti–Al–V alloys in biomedical applications

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A B S T R A C T

In this paper, comparative studies on the mechanical and corrosion properties of hybrid coating systems based on titanium dioxide thin films (200 nm) and graphene monolayers have been investigated. The pure titanium dioxide layers were deposited on a Ti6Al4V alloy surface using the conventional magnetron sputtering process and the so-called "magnetron sputtering with modulated plasma" process. A graphene monolayer was transferred to a titanium alloy substrate using the "PMMA-mediated" method. The structural characteristics of the obtained thin films were examined by using Raman spectroscopy, X-ray diffraction (XRD), a scanning electron microscope (SEM) and atomic force microscopy (AFM) measurement. The mechanical properties, i.e. hardness, were tested by using a nanoindenter test. The corrosion properties of the coatings were determined by analysis of the voltammetric curves.

The deposited TiO_2 thin film prepared by the conventional magnetron sputtering process consisted of visible grains with the size of ca. 50–100 nm and had a nanocrystalline anatase phase (TiO_2(a)). The TiO_2 thin film deposited by plasma-modulated sputtering had a nanocrystalline rutile structure TiO_2(r) and its surface consisted of big, irregular grains and was not as homogeneous as the coating prepared by the conventional method.

The hardness of TiO_2(a) and TiO_2(r) thin films was equal: 7.59 GPa and 14.2 GPa, respectively.

Graphene transferred to a titanium dioxide thin film surface was a single layer without defects. Unfortunately, the nanoindentation method, used to measure the hardness of the titanium dioxide/graphene coating systems, is not sensitive to one or few atomic layers of graphene deposited on the top of the coating structures. Therefore, the measurement did not reveal changes of titanium dioxide thin film hardness after graphene deposition, in comparison with uncoated TiO_2 thin films such as TiO_2(a) and TiO_2(r) thin films. Futhermore, the graphene monolayer can be very easily removed from the titanium dioxide thin film surface (e.g. by scratching).

The best corrosion properties (the lower value of corrosion current density) were obtained for sample Ti6Al4V coated with a TiO_2(a) thin film. A deposition graphene monolayer on the top of all tested thin films improves the corrosion potential (E_{corr}) value, which is much more positive than E_{corr} registered for the other samples. A positive value of the corrosion potential is characteristic of materials with low electrochemical activity and thereby very good corrosion resistance. Moreover, these coatings systems maintain stability of the mechanical properties during the corrosion process.

1. Introduction

Metallic biomaterials like Ti and Ti alloys are widely used in artificial hip joints, bone plates and dental implants due to their excellent mechanical properties and endurance [1]. However, the long-term performance of surgical implants is directly dependent on their surface properties. Most implanted metallic biomaterials have a tendency to lose electrons in solution and, as a result, they show a high potential to corrode in biological environments, which usually cause inflammations and loosening of the implants [2]. Corrosion is an unwanted chemical reaction, which can result in the degradation of metal implants to oxides, hydroxides, or other compounds. These degradation products may cause a local inflammatory response, leading to the cessation of bone formation, synovitis, and loosening of artificial joint implants [2]. Additionally, their low surface hardness, high friction coefficient and poor wear resistance also limit their application as metallic biomaterials [3,4]. Low wear resistance can lead to the formation of wear debris

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