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Original Article

Protective nature of nano-TiN coatings shaped by EPD on Ti substrates

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ABSTRACT

The hardness and corrosion resistance of TiN coatings, processed by Electrophoretic Deposition (EPD) to cover polished and unpolished Ti substrates, have been evaluated. A deposition time of 5 min has been enough to obtain a cohesive layer of 7–8 μm in thickness. The coatings were thermally treated in vacuum atmosphere at 1200 °C for 1 h with heating and cooling rates of 5 °C min^{-1}. The surfaces have been covered homogeneously optimizing the properties of the Ti substrates. Uniform and dense TiN coatings have been obtained onto polished substrates, while on unpolished Ti the nitrogen diffuses toward the substrate, moderately dissolving TiN coating. The nanohardness values of the polished samples have been increased from 2.8–4.8 GPa up to 6.5–8.5 GPa. Besides, the corrosion current density has been reduced more than one order of magnitude obtaining a protective efficiency of 82%. These values have been compared with other works in literature where authors used complex and costly processing techniques, demonstrating the strong impact of the colloidal processing over the specific properties of the material.

1. Introduction

Ti and Ti alloys have attractive properties such as high specific strength, biocompatibility, low density and corrosion resistance, being key compositions in aerospace, marine, biomedicine and industrial engineering applications [1,2]. Ti-based materials are bio-inert and they are frequently used in biomedical devices to replace heart valves, joints and bones. In this application the most relevant limitation of Ti and Ti alloys is their low bioactivity and poor tribological properties, such as poor fretting behavior, wear resistance and high coefficient of friction [3]. In biomedicine as well as in other applications, the surface microstructure modification and/or coating have been assessed as strategies to improve the surface properties of Ti alloys. Physical and chemical vapor deposition (PVD and CVD) have been explored as coating processes to produce ultra-hard films on Ti alloys [4–6], but also recently other processes as DC reactive magnetron sputtering [7,8], electrodeposition [9], nitriding [10], laser surface treatment [11], solid state diffusion [12] and ion implanting [13], have been also proposed. Most of those techniques are limited by requirements of “atmosphere” or “pre-placement”, complexity or high cost, making these processes difficult to implement in practice. In this sense, the look for non-expensive methods to shape hard coatings is still challenging.

Colloidal processing includes promising techniques for coating comparatively cheaper and based on a safe and healthy living environment technology. Those techniques are widely employed in ceramics since they have been probed to provide a high control over the resulting microstructures [14,15] throughout the manipulation of the particles dispersion maintaining the interparticle repulsion networks and then the suspension stability. Among the different colloidal processes, the Electrophoretic Deposition (EPD) is the most suitable one especially when we are dealing with the coverage of 3D and complex shapes. It consists in the electrophoretic movement of charged particles in a stable suspension and their deposition onto a conducting substrate. EPD has been widely implemented in both the academic and the industrial sector due to the simplicity of the apparatus and the short shaping times needed to complete the coating process. Moreover, EPD allows nanostructures tailoring and strengthening the control over the microstructure of 3D coatings [16]. The films thickness and the amount of the deposited mass can be easily tuned and controlled varying the concentration of the suspension, the applied potential or the deposition time [17].

Among ultra-hard ceramics, Cr and Ti-based nitrides (CrN, CrAlN, TiN, TiAlN, etc.) and borides (TiB) [18] as well as TiN mixtures with different alloys (NiTi, FeNi) [9] are extensively considered in the literature as Ti coatings, as monolayer or even in multilayer systems (i.e. TiN/AlN, TiN/TiCN) [5,19,20], to improve the surface toughness and corrosion properties. Results show that surface texturing of the Ti-based substrates plays an important role to prepare anti-wear coating with

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good adhesion, high toughness, hardness or low coefficient of friction. The mechanical response of TiN coatings yielded the decrease of the coefficient of friction while nanohardness ranges 7–18 GPa for surface nitriding, PVD and sputtered coatings [7,10,21] and Vickers hardness measured for laser cladding coatings achieved 500–1000HV1.0 where its variation depends on the amount of deposited TiN [22].

On the other hand, corrosion studies of TiN coatings on Ti-based substrates are not frequently found in the literature. In 2013, Pohrelyak et al. [10] reported the relationship of the sample roughness with the corrosion resistance in a Ringer solution for the modified surface of a Ti alloy by nitriding. In recent published works, corrosion results in different test solutions (HCl or NaCl) shows that the resistance of nitrides (TiN, TiAlN, CrN, CrAlN) depends on the coating composition and the number of layers, increasing the resistance efficiency in NaCl up to the 86.11% for CVD coatings in stainless steel [8,23].

Thereby, the objective of this work is to evaluate the hardness and corrosion resistance of TiN coatings processed by EPD to cover Ti substrates, considering that it is a simple shaping process to obtain coatings with good adhesion properties [24,25]. In previous works[24], the preparation of TiN nanoparticle (~30 nm) suspension and its further electrophoretic deposition on stainless steel and Ti substrates were reported. The advantage of the use of nanoparticles to shape those coatings is their lower sintering temperature, which allows the consolidation of dense gold-like TiN films of 10–20 μm on stainless steel substrates and 5 μm coatings on Ti specimens after a thermal treatment of 1200 °C in vacuum atmosphere. In the present manuscript, the crystallographic and microstructural characterization of optimized EPD coatings of TiN was firstly discussed, and further improvements on the mechanical response and the corrosion resistance of TiN/Ti materials compared to that of Ti bare-surface were determined.

2. Materials and methods

2.1. TiN suspensions and EPD process

As-received commercial TiN nanopowder (Hefei Kaier Nanometer Energy & Technology, China) with a mean particle size of 30 nm was used to prepare the suspensions following a previously reported process [26]. A TiN suspension (0.1 gL^{-1}) was prepared using isopropyl alcohol (99.7%, Panreac, Spain) as solvent and 1.5 wt.% of polyethylenimine (PEI, Sigma–Aldrich, Germany) as stabilizer. Mechanical stirring and sonication (Ultrasonication Probe, UP 400S, Hielscher, Germany) were used as dispersing methods to break the soft agglomerates of TiN nanoparticles.

Ti substrates of 15 mm of diameter and 0.5 mm of height were processed by uniaxial pressing at 600 MPa, and then sintered in vacuum atmosphere at 10^{-5} mbar at 1050 °C for 2 h with heating and cooling rates of 5 °C min^{-1} [26]. The sintered Ti substrates were polished using alumina suspensions (9, 1 and 0.3 μm).

TiN films were shaped from nanoparticle stabilized suspensions by EPD on as-prepared and polished sintered Ti substrates. The counter electrode in the electrophoretic cell was a Pt foil of 2 × 2 cm, separated from the work electrode by a distance of 2 cm. EPD was optimized and studied specimens was performed under galvanostatic conditions using a high voltage power source (2611 System SourceMeter, Keithley Instruments Inc., USA) applying current densities of 0.2 mA cm^{-2} (voltage up to 90 V). TiN coatings of 0.8–1 mg cm^{-2} were shaped on Ti substrates. After EPD, coatings were dried at room conditions and thermally treated in vacuum atmosphere at 1200 °C for 1 h with heating and cooling rates of 5 °C min^{-1}. Fig. 1 shows a scheme of the coating process.

2.2. Characterization of the coatings

The microstructure of the polished and unpolished Ti substrates and the resulting TiN coatings was investigated by Scanning electron microscopy (SEM) using a S-4700 microscope (Hitachi, Japan). The roughness of the coatings was measured using a profilometer (Surtronic 3+ instrument, Taylor Hobson) and each profile was recorded five times per samples. The crystallographic composition of the coatings was analyzed by X-ray diffraction (XRD, Bruker D8 Advance) using a Cu Kα radiation, where the scanning angular (2θ) was varied from 20° to 70° and the scanning speed was 2° min^{-1}. The characterization of the composition of the coating after sintering was completed by using confocal Raman microscopy coupled with an atomic force microscopy (AFM) instrument (WiTec alpha300R) with a Nd:YAG laser excitation at 532 nm and a 100× objective.

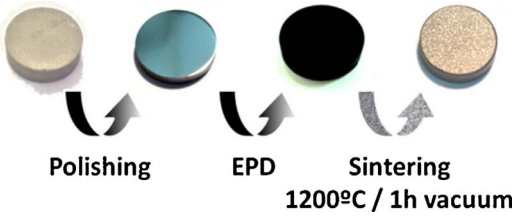

Fig. 1. Scheme based on the aspect of Ti specimens: as-prepared, polished, after TiN deposition by EPD and after sintering at 1200 °C/1 h.

The nanohardness of the new surfaces was explored using a CETR Bruker nanoindenter fitted with a Berkovich diamond tip of 100 nm radius, increasing the load from 0 to 500 mN. The hardness and elastic modulus were obtained from the curves using the Oliver-Pharr method. The hardness of the samples was also tested at the specimens along the interface Ti-TiN by Vickers method with a 200 N load. Indentations were repeated 10 times on different areas to show the evolution of the hardness from the surface to the center of the sample.

The corrosion resistance of the coated Ti specimens was tested determining polarization curves. A saturated calomel electrode (SCE) and a Pt wire was used as the reference electrode and counter electrode respectively, while the un-coated and coated Ti was the working electrode. A 3.5 wt.% NaCl solution was used as electrolyte. The polarization of the samples was carried out in the range of −100 to 1000 mV above the open-circuit potential at 0.5 mV s^{-1}.

3. Results

3.1. Microstructure of as-deposited and deposited coatings

XRD spectra of TiN coating deposited on as-prepared and polished Ti substrates after sintering at 1200 °C are shown in Fig. 2a and b, respectively. In both cases the substrate peaks are denoted as Ti. All reflections correspond to the hexagonal lattice of the Ti (JCPDS No. 00-044-1294). In the case of TiN coating on as-prepared substrate (Fig. 2a), the peaks which correspond to TiN can be slightly identified among those of the Ti indicating a low presence of TiN. The peaks positions of TiN were compared with the JCPDS file No. 00-038-1420 and the corresponding planes were indexed. Oppositely, the high intensity of the X-ray diffraction pattern of TiN in the analysis of the coating deposited on polished substrates evidences the clear existence of a TiN layer (Fig. 2b). One intense TiN (111) diffraction peak can be observed at 36.25° which suggests the presence of the phase with B1 NaCl cubic structure. Comparing the XRD pattern of the TiN coating on the polished substrate with that of the as-received powders [24], a preferential orientation of TiN (111) can be identified, similarly to the TiN layers obtained by Subramanian et al. in 2011, and Cui et al. in 2017 [7,27], both processed by magnetron sputtering. The comparative analysis of both TiN spectra suggests that TiN can moderately dissolve nitriding the Ti substrate during sintering. Unpolished substrates favor nitrogen diffusion throughout Ti probably due to their porous and rough surface, and the TiN partially vanishes. In fact, energy-dispersive X-ray spectroscopy analysis (not shown here) of the TiN coated as-