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Surface morphologies, tribological properties, and formation mechanism of the Ni–CeO_2 nanocrystalline coatings on the modified surface of TA2 substrate

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ABSTRACT

In order to remedy the poor tribological properties and low micro-hardness for pure titanium (TA2) materials, the Ni–CeO_2 nanocrystalline coating was deposited from a Watts–Nickel electrolyte on the modified surface of TA2 substrate. In the present study, an available method of chemical activation was innovatively employed to make surface modification for TA2 substrate, in which the modified surface was characteristic of a rough surface and fully covered by the Ce-rich conducting phase for better electrodeposition. In order to study the effect of surface pretreatments on the modified TA2 surface, the surface roughness profiles and average roughness values were carried out using optical profilometry on the measured surfaces. A predictive modeling of TA2 surfaces before and after surface pretreatments was compared and successfully validated for better understanding of the formation mechanisms of electrodeposited Ni coatings reinforced with CeO_2 nanoparticles. To clarify the beneficial effects of CeO_2 addition on surface morphologies, phase composition, and textural evolution, the as-received nanocrystalline coatings were evaluated using various analytical techniques such as XRD, FE-SEM/EDX, and TEM. In addition, the scratch tests performed with an acoustic emission (AE) detector were conducted for the determination of interfacial adhesion between the as-deposited coating and the modified surface of TA2 substrate. Tribological properties and micro-hardness of investigated specimens were also examined. Experimental results revealed that this innovatively chemical activation was more favorable for increasing interfacial adhesion. The existence of well-distributed CeO_2 phase that precipitated along the defective grain boundaries in the coating was contributed to make particulate reinforcement, thereby achieving better structural densification for Ni–CeO_2 coatings. Meanwhile it exhibited superior tribological properties of the Ni–CeO_2 coatings as compared to those of pure nickel and TA2 substrate, which was mainly attributed to the Ce-rich abrasive products that acted as a self-lubricating phase to make the effect of solid lubricants on worn surfaces.

1. Introduction

Titanium and titanium alloys have attracted significant interest in recent years for industrial applications in aerospace engineering, marine equipment and biomedical materials, due to their higher modulus of elasticity and exclusive properties including superior corrosion resistance, perfect biocompatibility and high strength-to-weight ratio [1,2]. However, because of inevitable defects like low micro-hardness, inferior tribological properties, and poor thermal conductivity, it will not meet the ever-increasing demands for rapid developments of the applications upon the subjections to the harsh conditions at an elevated temperature [3]. For a durability and reliability prospective of the Ti-based components, many progresses in the field of surface modification for pure titanium and its alloys have been extensively carried out over the last decades. According to an extensive survey from literature review, it has exhibited the great improvements of oxidation resistance, surface structure, and biological properties for Ti-based materials by means of using appropriate surface techniques such as mechanical alloying [4], thermal spraying [5], plasma sputtering [6], laser-induced surface cladding [7], anodizing/micro-arc oxidation [8], ion-beam assisted implantation [9], electrolytic deposition of hydroxyl-apatite (HA) coatings [10], etc. These techniques mainly focus on the modification of surface features of pure titanium and its alloys in order to achieve a high degree of bioactivity and biocompatibility. Recent developments in manufacturing of the man-made biological materials of Ti-based alloys like dental devices and artificial bones, have driven these surface modification techniques to develop rapidly and extend their application possibilities. Nevertheless, the above-mentioned methods have put forward a large amount of strict requirements in areas, for instance, the exact demands of experimental conditions, the strict compositions for substrate materials, and the expensive procedures of subsequent surface treatments. From a practical viewpoint, such limitations

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resulting from the above methods have restricted surface modification of Ti-based materials, as well as further limited their potential applications in the aerospace engineering and biomedical devices.

It is well documented that pure titanium and its alloys are characteristic of high chemical activity, which will result in the formation of a very stable and passive oxide scale to fully cover on its surface when exposed to air. Worse still, it will be difficult for traditional techniques to remove this passive oxide scale (mainly composed of TiO_2 and TiO ceramic phases) once it serves as a barrier layer formed on the surface. As a result, this passive oxide scale that fully covered on the activated surface of Ti-based alloys has seriously restricted the improvements of surface properties even with the use of surface modification techniques. To cope with this problem, a large amount of survey research has been reviewed for searching an effective approach to solve the aforementioned limitations of surface modification for Ti-based materials. According to the results from our studies, the influence of interfacial adhesion between the different modification techniques and processing conditions has not been fully understood, despite the fact that many attempts in the field of surface modification for Ti-based materials have been extensively carried out for tailoring an advanced coating formed on the modified surface. For instance, a novel approach of laser-induced cladding with a high energy density was employed for fabricating a HfB_2-containing Ni-based composite coating on the TA2 surface, hence leading into the significant increase of wear resistance and denser structure of the as-received coating attached with strong metallurgical bonding towards TA2 substrate [11]. The laser-induced surface cladding with a wide variety of design parameters was evaluated by Chen et al. [12], as a result of improved properties of micro-hardness, tribological properties, and oxidation resistance for pure Ti substrate coated with Fe coatings relative to that of un-coated samples. An experimental study of nano-crystalline growth of electrodeposited hydroxyapatite (HA) coatings on pure Ti plates was investigated by Yousefpour et al. [13], which revealed that this novel method of a hydrothermal–electrochemical deposition in an electrolyte containing calcium and phosphate ions was favorable for achieving better cell proliferation and biocompatibility with bone cells and human blood as compared to those of bare samples. Recently, a research study of Ti–6Al–4V substrate covered with and without the hydroxyapatite–polysulfone coating by an electrospinning method was compared by Santhosh et al. [14], in which it pointed out that the improved bioactivity and superior corrosion resistance were obtained for the coated samples as immersed in a simulated body fluid (SBF) solution. In addition, it was also reported that, in the case of ion-beam assisted implantation, the low-energy high-current pulsed electron beam treatment was applied to make surface modification for TA2 materials, indicative of great contributions to the structural integrity and dislocations strengthening on the modified surfaces [15]. Recognizing that beneficial effects of both the work hardening and grain refinement by surface nanocrystallization, a systematic research of individual contributions to tribological properties and hardness for titanium alloys (TC4) was proposed and evaluated by Amanov et al. [16], which involved in the study of plastic deformations and surface features by means of measuring the coefficient of friction and the worn surfaces for the specimens.

According to the results from an extensive survey, previous studies of surface modification for Ti-based materials mainly focused on the aforementioned conventional methods and namely, the pretreatment method of chemical activation for surface modification of TA2 materials was not clearly studied till now. Hence this work proposed an effective and simple method for surface modifications of TA2 substrate. In the present study, a novel surface pretreatment of chemical activation was expected to obtain multiple purposes including the dissolution of the stable passive oxide layer on the surface of TA2 substrate and a rough/activating surface for better electrodeposition. The main objective of this paper was to explore an available and simple surface pretreatment method for tailoring a fully denser structure of electrodeposited Ni–CeO_2 coatings on the modified surfaces of TA2 substrate, as well as achieve the superior interfacial adhesion. The as-received Ni–CeO_2 nanocrystalline coatings, which processed denser microstructure, high micro-hardness, and excellent tribological properties, would become an attractive candidate for surface protection and modification of Ti-based components against the severely operating conditions like high temperature oxidation and tribological attacks.

2. Experimental procedures

2.1. Specimen surface pretreatments

Polished pure titanium plate (commercially Pure Grade 2, TA2) having dimensions of 100 mm × 20 mm × 2 mm was used as substrate in the present work. Prior to the coating preparation, surface pretreatments for TA2 substrates were included: mechanical polishing using $800^{\#}$ SiC waterproof abrasive paper and the ~5 nm Al_2O_3 polishing paste, followed by chemical activation of surface pretreatments in an acid aqueous solution at room temperature (detailed compositions of this activating solution and its processing parameters are summarized in Table 1). Unlike the traditional activating solution (only contained 5 wt.% HF and 10 wt.% HF agents), the modified activating solution used in this study for surface pretreatments of TA2 substrate was composed of the additives of 1.5 wt.% $TiCl_3$ and 0.5 wt.% $Ce(NO_3)_3$ agents into the above traditional activating solution. In particular, the introduction of above additives into the HF-containing activating solution could not serve as corrosion inhibitors for etching reactions to reduce the process of hydrogen adsorption, but also act as an active agent for complexing with the Ce-rich phase to fully cover the surface of TA2 substrate. As a result, the well-distributed Ce-rich phase, which was characteristic of strong chemical adsorption onto the modified A2 surface, would make great contributions to the bonding interactions with electrodeposited Ni coatings.

Following the pretreatments with chemical activation, the as-treated specimens were washed with distilled water and then quickly placed in a modified Watts–Nickel electrolyte to fabricate the Ni–CeO_2 coatings using a novel method of ultrasonic-assisted double pulsed electrodeposition. The bath compositions consisted of analytical reagents were as follows: 350 g L^{-1} nickel sulfate, 40 g L^{-1} nickel chloride, 50 g L^{-1} boric acid, etc. The bath temperature was maintained at 35 ± 2 °C and its pH value was adjusted to ~3.5 by adding a dilute H_2SO_4 solution. For uniform, homogeneous distribution of the CeO_2 nanoparticles in electrolyte, agitation mechanism such as bath circulation, magnetic stirring, and ultrasonic field was employed for the as-prepared emulsion within a certain range of 10–12 g L^{-1} CeO_2 addition. In case of ultrafine particles, some appropriate surfactants (e.g., sodium dodecyl benzene sulfonate, polyoxyethylene octyl phenyl-10, and saccharin sodium) were used to prevent the as-pretreated CeO_2 nanoparticles from agglomeration. Prior to each electrodeposition procedure, the electrolyte was subjected to the ultrasonic field and continuously oscillated using mechanical stirring at a rotational speed of 150 rpm. With respect to the introduction of ultrasonic field (80 kHz/100 W) into the process of electrodeposition, such nano-

Table 1
Chemical compositions of the modified activating solution and its operating conditions of surface pretreatments for TA2 substrates.

Compositions of the modified activating solution and its operating conditions used for surface pretreatments	
Hydrofluoric acid, HF	5 wt.%
Hydrochloric acid, HCl	10 wt.%
Titanium trichloride solution, $TiCl_3$	1.5 wt.%
Nitrite cerium, $Ce(NO_3)_3$	~0.5 wt.%
Surface active agents	~0.1 wt.%
Mechanical stirring rate	80 rpm
Temperature	30 ± 5 °C
pH value	~3.6