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Mechanical properties of TiN ceramic coating on a heat treated Ti-13Zr-13Nb alloy

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ABSTRACT

In this paper, mechanical properties of TiN coatings deposited on Ti–13Zr–13Nb alloys prepared by filtered arc deposition were analyzed. The influences of different heat treatment on the abrasion resistance of the substrate were studied, with regards to the coating properties, microstructural features, mechanical properties and the deformation mechanism using wear test and depth-sensing nano-indentation. According to the analysis, the microstructure and enhanced mechanical properties of the alloy substrate play a vital part in affecting the tribological properties of coatings. Parallel scars with patches of surface deformation in TiN coatings on air cooled and water quenched specimens after tribological test are obviously different from those of furnace cooled and aged water—quenched samples. Transformation of β phase into α" phase was triggered by the aging heat treatment, and it was found to be the inducement resulting in the increase of hardness in the substrate. The results show that the aging of the substrate can effectually inhibit the fault activities of the TiN coating and improve the absorption of deformation energy at the surface of the sample, which enhances the coating ductility.

1. Introduction

Act as hard tissue replacements, titanium and its alloys are extensively applied in applications of biomaterials, human implants and other aspects, owing to their high strength to low Young's modulus, weight ratio, superior corrosion resistance and biocompatibility. As the population is aging in most countries, accidents and sports-related injuries are increasing, and hence, the demand for orthopedic implants is ever-increasing. Titanium alloys are categorized as α, near-α, metastable β, stable β, or α+β relying on the microstructure at the room temperature [1]. Among all the beta alloys, the Ti-13Zr-13Nb near beta alloy manifest mechanical properties similar to that of the natural bone with its low modulus of elasticity (about 100 GPa) coming with nontoxic alloy elements and are considered to be promising materials in the future for bone implants [2]. Nevertheless, poor wear resistance of titanium alloys is a dominating limiting factor restricting its application for load bearing sidling surfaces like know and hip joints at present. Therefore, to further research and develop this biomedical metal material, considerable research have been studied focusing on improving the wear resistance by strengthening the matrix and by precipitation [3]. Chi-Wai Chan [4] studied the beta titanium alloy and found that the wear and corrosion resistance of beta titanium alloy can be enhanced by laser gas alloying with nitrogen. Y.S. Zhang [5] fabricated a core-shell Ti-O alloy by oxidation of Ti powders and spark plasma sintering, this microstructural design has brought outstanding combinations of improved strength and wear resistance. P. Majumdar and S.B. Singh [6] researched the wear properties of Ti-13Zr-13Nb in dry condition and simulated body fluid to understand the effect of different medium on wear behavior of the TZNB alloy. Furthermore, Pallab Majumdar [7,8] also reported that the effect of heat treatment methods on microscopic structure and mechanical properties of Ti-13Zr-13Nb alloys. Chan Hee Park et al. [9] reported improved mechanical compatibility of submicron crystalline titanium alloy.

On the other hand, as the release of ions from the implant into the surrounding tissue may cause the biocompatibility problems, the corrosion behavior of alloys must be checked to verify the applicability of a material used for body implants. Viswanathan S. Saji. et al. [10] and T.C. Niemeyer et al. [11] researched corrosion behavior of Ti-13Zr-13Nb alloy and Ivana Dimić et al. [12] studied microstructure and metallic ion release of pure titanium and Ti-

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13Zr-13Nb alloy. It has been found that enhancing corrosion resistance of biomedical alloys served as orthopedic implants is extremely crucial, because it determines the service life of device and affects the perniciousness during corrosion process occurs in the living organism.

To enhance the biocompatibility of Ti-13Zr-13Nb alloys, the surfaces treatment to obtain protective coating were often considered using chemical, laser surface modification, ion implantation, plasma spraying, etc. [13]. The other added advantage of the treated Ti-13Zr-13Nb alloy is favorable wear resistance and corrosion resistance, in comparison with that of the Ti-13Zr-13Nb alloy strengthened by precipitates. Currently, ceramic coatings such as ZrO_2/Al_2O_3, Si_3N_4/TiO_2 and ZrO_2/SiO_2 are considered to be alternatives for metal–polyethylene based implants or metal–metal articulating devices due to their unique features of high hardness and superior tribological performance along with the excellent biocompatibility. Furthermore, the recent works in this area reveals that, the wear rates are reduced significantly when ceramic femoral head is made to slide over either polyethylene or ceramic cup. Though many previous works have reported that Al_2O_3 and ZrO_2 ceramic materials have withstood the harsh environment in the human body, brittleness and low fracture toughness of pure alumina and hydrothermal instability of zirconia implants limit their usage for biomaterial implants. In the literature, however, the influence of TiN coating on wear resistance of Ti-13Zr-13Nb has not received any attention. Owing to the outstanding abrasion resistance, favorable hardness and higher corrosion resistance, TiN coatings on titanium alloys have been widely used in practical applications to achieve surface protection of metal materials [14]. Therefore, this work is to explore the wear behavior of cathodic-arc deposited TiN coatings on Ti-13Nb-13Zr substrates under different heat treatment status. The substrates display very different microstructures and mechanical properties after 5 different heat treatment routines: β solution (as received), furnace cooled, air cooled, water quenched, and water-quenched followed by aging. These differences in the substrates resulted in very different wear behavior in the TiN coated surfaces and the possible underlying mechanism is discussed.

2. Experimental methods

TiN coatings were deposited on Ti-13Zr-13Nb disks of a diameter of 25 mm. Two types of the alloys status were conducted: a) through different ways of heat treatment; b) as received (β solution handled by manufacturer)—set as sample NO.3. The specific treatment is as follows:

25°C —25min→ 550°C —10min→ 760°C —60min→ 760°C —20min→ 500°C ⟶

- Furnace cooling to room temperature—sample NO.1
- Air cooled to room temperature—sample NO.2
- Water quench—sample NO.4
- Water quench→Ageing at 500℃ for 1h→Water quench—sample NO.5

The alloy phase composition and surface observation were carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

To ensure a uniform deposition surface for the TiN coatings, all the Ti-13Zr-13Nb substrates were polished by the same process before the deposition. Disk samples were polished with a 320 mesh carborundum sandpaper for 4 min, and then the samples were milled using a 15 μm petroleum-based lubricant diamond abrasive for 10 min. The samples were polished for 5 min with an abrasive of a 0.05 μm particle size and a chemical reagent which consists of 25 ml OP-S containing 1.5 ml hydrogen peroxide and 2.5 ml ammonia. Before coating these samples in a Filtered Arc Deposition System (FADS System), all the specimens were submerged in ethanol for a few minutes of ultrasonic cleaning and then dried. After that the FADS system was used to deposite the TiN coating on the polished disk substrates. The pressure of deposition chamber was adjusted to a base vacuum of 6.67×10^{-4} Pa. The substrates were preheated to 300 °C in vacuum, and then the samples were dry etched in-situ using pure titanium ion beam at −850 V high substrate bias. The bias voltage was decreased to −100 V at the beginning of the coating process. During the experiment, a pure titanium buffer layer was deposited on the Ti-13Zr-13Nb substrate, and the working gas of nitrogen was then introduced into the chamber through a mass flow controller with gradual flow rate increase and a final flow rate of 40 sccm to decrease residual stress and enhance adhesion between the substrate and the film. During the deposition process, to avoid the influence of the coating process parameters on the film properties and to ensure a uniform experimental conditions, five Ti-13Zr-13Nb substrates after different heat treatment were deposited on a same disc-shaped stage and the disc was kept revolving at a constant speed during the experiment. The nitrogen working gas pressure was 0.39 Pa. The coating process lasted for 2 h to achieve a film thickness of 1.4 μm.

After these, scratch testes were carried out on a scratch tester (CSM, Revetest Xpress) by using an indenter to scratch reactant films to detect the critical load at which TiN coating starts to fail (cracking or removal). The acoustic emission and friction force can be measured synchronously by the apparatus. In order to ensure the accuracy of experimental analysis, five repeated scratch tests were performed on each test specimen to obtain the result of measurements.

Tribological tests were performed by pin-on-disc tests on CETR tribometer. In the component of a pin-on-disc, the pin indicated HSS grade material and the disc represented a strip Ti alloys. The pin is designed to mushroom shaped of a radius of 8 mm hemispherical end. Technological conditions of tribological tests are shown in Table 1. The choice of Hertz pressure in test parameters was usually relatively mild and approach to the actual hot-rolling environment, which makes it easy to monitor the behavior of antagonistic oxide scales in the contact region without damaging them too quickly [15]. The disc temperature is fixed at room temperature so as to explore the original properties of films and reduce the influence of temperature. In the experiment, after set the technical conditions, the sample was placed on the tester to carry out the sliding friction test of friction pair. During the test the wear depth and abrasion resistance of samples were precisely measured and the friction coefficient was measured accurately and recorded in situ by computer control in a given friction mode. The implementation of interruption test was mainly to explore the mutual effect of TiN coatings according to the transmutation of friction coefficient curves.

After tribological tests, the profile measure of TiN coatings are determined using a Roughness tester of Surf M300 and the weight loss of wear tracks are evaluated. In addition, the weight change of samples were measured by an electric balance with a precision of 0.1 mg made in America (Seen the below Table 2).

Nanoindentation on the TiN coating was made for evaluating coating deformation using the Ultra-Micro Indentation System (UMIS). Coating hardness on Ti-13Nb-13Zr alloy was measured by a Berkovich indenter of a 200 nm radius. Restricted by thermal drift, the resolution in experiment was less than 1 nm/min. The tip was primally calibrated by fused silica as a standard material. Loading and unloading tests of incremental control were within a scale of 3–9 mN to confirm coating hardness. Fracture patterns of TiN coatings were detected through a spherical diamond indenter of a diameter of 5 μm. Since the spherical indenter can result in a more evenly stress field underneath the contact region than the