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Biotribological properties of Ti/TiB_2 multilayers in simulated body solution

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ABSTRACT

Ti/TiB_2 multilayers with various modulation ratios were prepared by magnetron sputtering on biomedical titanium alloy Ti6Al4V. The tribological properties of the multilayers sliding against ultra-high molecular weight polyethylene under lubrication with Hank's solution were also investigated. The results demonstrated that the tribological properties strongly depended on the modulation ratios of multilayers. The coefficient of friction of multilayers with a modulation ratio of 1:5 was 0.1, a reduction by 28.6%; the wear volume loss of UHMWPE decreased by almost one order of magnitude compared to that of Ti6Al4V alloy, exhibiting excellent anti-friction and anti-wear properties. The oxidation wear of Ti6Al4V alloy could be restrained effectively and converted to abrasion wear and/or adhesive wear by the laminate structures in the multilayers, suggesting that this material may serve as a potential candidate for the surface modification of artificial joints.

1. Introduction

Titanium and titanium alloys are often used as biomedical materials due to their biocompatibility, corrosion resistance, workability, low toxicity, and high specific strength [1–3]. However, debris from these materials may cause inflammation and even implant failure because of the poor wear resistance [4]. Therefore, surface modification is necessary for improving tribological properties. With the rapid advancement of surface modification technology in recent years, new biofilms or coatings with desired properties have been developed, such as, bioceramic coating (HA) [5], DLC [6], and cermet coatings (TiN, TiC, TiNC) [7–9]. These films may improve biocompatibility and wear resistance but still fail to meet the overall functional requirements. For example, HA coating, which is highly biocompatible, has poor mechanical properties and weak adhesion strength between the coating and substrate. In addition, a well-defined cermet coating with good tribological properties may be limited by poor plasticity and toughness, high residual stress, and an uncontrollable thickness during application.

Titanium diboride (TiB_2) is an important ceramic material owing to its good mechanical properties like high hardness and modulus, chemical stability in harsh environments and good oxidation resistance [10]. These properties make TiB_2 an excellent choice for applications in thin films as protective coatings against wear, erosion, corrosion, abrasion, etc. Recently, magnetron sputtering has been used increasingly to prepare TiB_2 coatings because of its fast deposition rate, strong adhesion to the substrate, and controllable composition [11,12]. Because the composite properties of different materials can be both combined and modulated, the mechanical properties of coatings, such as hardness and toughness, may be improved by altering the composition and/or structures of the sublayers in a multilayer structure [13]. For example, the structure of nacre consisted of inorganic and organic constituents. Many researchers reported that the soft organic layer of nacre could erase the stress derived from the hard inorganic layer [14]. Especially for multilayers with alternating soft and hard sublayers, the laminated structure may deflect crack propagation in the interfaces, such that the wear resistance may be improved by releasing the stress in the interfaces [15]. The wear resistance of TiN and AlN were greatly enhanced owing to the fabrication of Ti/TiN and Al/AlN [16,17].

In this study, Ti/TiB_2 multilayered films were prepared by magnetron sputtering on biomedical titanium alloy Ti6Al4V (TC4). During this process, Ti was abstracted into a soft layer, and TiB_2 was abstracted into a hard layer. The biotribological properties of Ti/TiB_2 multilayers with various modulation ratios (the ratio of Ti to TiB_2 thickness is denoted t_{Ti}:t_{TiB2}) were also investigated in Hank's solution.

2. Experimental

Ti/TiB_2 multilayers were prepared on TC4 alloy using a JSD560-V high vacuum magnetron sputtering system. The chemical composition of the TC4 alloy is shown in Table 1. The test

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specimen was in a rectangular shape of 10 mm × 15 mm and a thickness of 2 mm. After abrasion with SiC paper (600, 1000, and 2000 grit), the specimen was polished to a mirror surface. The specimen was then cleaned ultrasonically in deionized water, acetone, and ethanol for 10 min and dried using compressed nitrogen after each cleaning cycle.

The substrates were sputter-cleaned for 10 min in a sample chamber and transferred to the sputtering chamber. The thickness of each sublayer was set by controlling the sputtering time of the Ti and TiB_2 targets (both 99.5% purity) via a built-in computer system. Using this method, a periodic modulation structure was formed. Table 2 shows the design parameters of Ti/TiB_2 multilayers with various modulation ratios. A TiB_2 monolayer with a thickness of 600 nm was prepared for the comparative study.

The biotribological properties of the multilayers were investigated on a universal multifunctional tester (UMT-2). The schematic diagram of the friction pair is shown in Fig. 1. An artificial joint material, ultra-high molecular weight polyethylene (UHMWPE), was selected as the match tribopair and processed into a pin specimen with a diameter of 4 mm and length of 25 mm. Each specimen was polished to an average surface roughness of $R_a = 0.8 \pm 0.05$ μm. The average surface roughness of multilayer was of $R_a = 0.01 \pm 0.005$ μm according to the measurement of 3D non-contact microcopy. Prior to each wear test, the multilayer and UHMWPE pin were ultrasonicically cleaned in ethanol for 10 min and then air-dired. All wear experiments were performed using a pin-on-flat reciprocal tribometer at 37 °C in Hank's lubrication solution for 30 min. Parameters such as reciprocating amplitude, frequency, and normal load were set to 1.6 mm, 10 Hz, and 30 N, respectively. The coefficients of friction were recorded automatically during the tests, and each wear test was repeated three times to obtain average values. The volume loss ΔV (mm^3) of the UHMWPE pin was calculated by using the equation,

$$\Delta V = \Delta m / \rho$$

where Δm corresponds to the mass loss of each UHMWPE pin; ρ is the specific weight of the UHMWPE pin which is about 0.94 g/cm^3.

The structure of the films was investigated using ARL/XTAR X-ray diffraction with Cu $K\alpha$ radiation ($\lambda = 0.154056$ nm), a tube voltage of 45 kV, and a tube current of 40 mA. The XRD patterns were collected using angular step sizes of 0.02° from 20° to 80°. The sectional structures and worn surfaces of the multilayers were observed using a Quanta 250 FEG field emission scanning electron microscope (FESEM). The X-ray photoelectron spectrometer (XPS) analysis was performed on a Thermal VG K-Alpha system. The core level spectra for Ti, B, and O were recorded using a monochromatic Al $K\alpha$ source ($h\nu = 1486.6$ eV) at 12 kV acceleration voltage.

3. Results and discussion

3.1. Microstructure of Ti/TiB_2 multilayers

Fig. 2 shows a cross-sectional SEM image of the multilayer with a modulation ratio of 1:1. The multilayer consists of a well-defined layered nanostructure with planar interfaces, and the interface between each sublayer is clearly distinguished. The Ti appears as bright stripes, while dark stripes correspond to TiB_2. The multilayer consists of six layers and has a total thickness of approximately 600 nm. Both the Ti and TiB_2 sublayers are about 100 nm, suggesting that the design modulation ratio of 1:1 was achieved. These results indicate that a multilayer with uniform composition, clear interface, and controllable sublayer thickness may be prepared by magnetron sputtering.

Fig. 3(a) shows the XPS survey spectrum obtained from the Ti/TiB_2 multilayer. Features originating from Ti, B, O, and C are evident. The presence of oxygen is not surprising since the sample had been exposed to ambient conditions, resulting in a thin oxide layer on the surface. Moreover, features corresponding to carbon indicate that either a volatile substance that rapidly evaporated or an area of local rather than uniform contamination. The primary chemical state of the Ti and B is shown in Fig. 3(b) and (c). According to standard icon of TiB_2 (NIST X-ray photoelectron spectroscopy database), the peaks at binding energy of 454.3 eV correspond to the $2p_{3/2}$ peak of Ti, and 186.3 eV correspond to 1s peak of B, which indicates that the surface of the multilayer mainly consisted of TiB_2.

Table 1
Chemical composition of the TC4 alloy (wt%).

Al	V	H	O	N	C	Fe	Ti
6.25	4.21	0.0073	0.19	0.0045	0.018	0.22	Bal.

Table 2
Design parameters of Ti/TiB_2 multilayers with various modulation ratios.

Samples no.	Modulation ratio	Periodic thickness/nm	Ti thickness/nm	TiB_2 thickness/nm	Total thickness/nm
1	1:1	200	100	100	600
2	1:3	200	50	150	600
3	1:5	200	33	167	600
4	1:7	200	25	175	600
5	1:9	200	20	180	600
6	TiB_2	–	–	600	600

*Note that the modulation period is of 3.

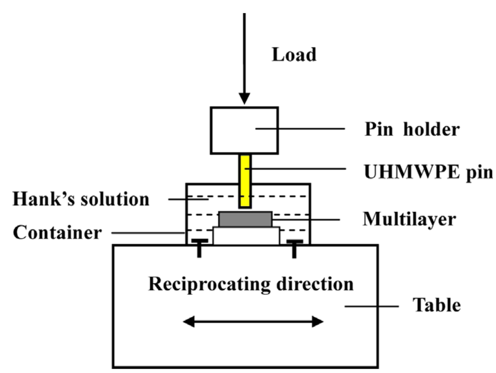

Fig. 1. Schematic diagram of the friction pair.

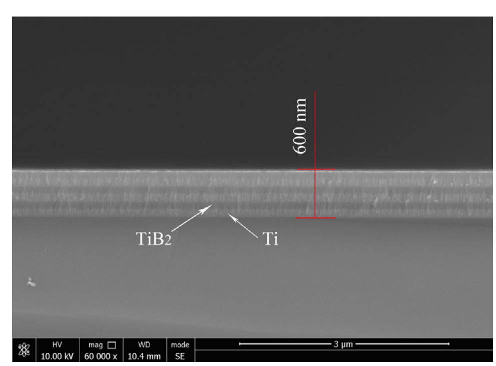

Fig. 2. Cross-sectional SEM image of Ti/TiB_2 multilayer with modulation ratios of 1:1.