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Full Length Article

Promising Ta-Ti-Zr-Si metallic glass coating without cytotoxic elements for bio-implant applications

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ABSTRACT

Tantalum (Ta) is considered as one of the most promising metal due to its high corrosion resistance, excellent biocompatibility and cell adhesion/in-growth capabilities. Although there are some researches exploring the biomedical aspects of Ta and Ta based alloys, systematic characterizations of newly developed Ta-based metallic glasses in bio-implant applications is still lacking. This study employs sputtering approach to produced thin-film Ti-based metallic glasses due to the high melting temperature of Ta (3020 °C). Two fully amorphous Ta-based metallic glasses composed of $Ta_{57}Ti_{17}Zr_{15}Si_{11}$ and $Ta_{75}Ti_{10}Zr_8Si_7$ are produced and experimentally characterized in terms of their mechanical properties, bio-corrosion properties, surface hydrophilic characteristics, and in-vitro cell viability and cells attachment tests. Compare to conventional pure Ti and Ta metals, the developed Ta-based metallic glasses exhibit higher hardness and lower modulus which are better match to the mechanical properties of bone. MTS assay results show that Ta-based metallic glasses show comparable cell viability and cell attachment rate compared to that of pure Ti and Ta surface in a 72 h in-vitro test.

1. Introduction

The most essential factor dividing biomaterials from all the other materials is biocompatibility [1]. Upon interacting with tissues, biomaterials sometimes might induce some unacceptable reactions such as allergic, toxic reactions and the generation of carcinogen with the body. Additionally, the activations of immune cells like macrophage and neutrophil need to be prevented simultaneously. For long-time bio-implant applications, adequate mechanical properties also play an essential role. Most polymers and ceramics cannot suffer load-bearing and cyclic loading owing to poor strength, low fatigue endurance limit, and low fracture toughness [2]. By comparison, metals are more favorable for load bearing bio-implant applications and have been widely used in dental implant and joint replacement. Nowadays, Ti, Ti-alloys, Co-Cr alloys, PEEK and PMMA are most well-known bio-implant materials [1–3]. Due to the lower wear resistance, the debris releasing of Ti would take place after long-time uses. Debris releasing would give rise the effect in stimulating immune system, releasing cytokine, hormone and growth factors such as PTH (parathyroid hormone) and RANKL (receptor activator of nuclear factor kappa-B ligand), which would lead to osteoclasts cell activation and even demineralization phenomenon [4,5].

Additionally, the mismatch of Young's modulus between bone and implant might lead to the troublesome stress shielding effect. Thus, after long-time uses, bone loss could happen and bone mineral density could decrease owing to such shielding effects, reducing the strength of bone. The shielding effect is considered as a phenomenon that a preferential load applies on the implant with higher Young's modulus in lieu of surrounding bone [6,7]. In light of the above mentioned issues, an ideal bio-implant material should possess high biocompatibility, suppress debris releasing, and reduce stress shielding effects concurrently.

Recently, tantalum has attracted much attention of researchers and clinicians. Tantalum possesses promising biocompatibility, adequate mechanical properties, high corrosion resistance and good osteoconductivity simultaneously [8–16]. Matsuuo et al. [8] reported that there is no significant inflammatory response after implanting Ta in rats. Stiehler et al. [9] demonstrated that the

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number of cell adhesion on Ta is more than that on Ti, and the proliferation and differentiation of cell on Ta reveal satisfactory biocompatibility as well. According to the reports by Findlay et al. [10], Ta indeed benefits to the attachment, growth and differentiation of human osteoblasts. Miyazaki et al. [11] indicated the apatite layer can format on Ta surface via Ta-OH group on the surface in simulated body fluid. Apatite, the primary inorganic component of human tissue, can avoid simulating foreign body response system and integrate with the surrounding tissue [17].

Nonetheless, the melting point of Ta is 3017 °C, making the cast of Ta based alloys highly difficult. Besides, the Young's modulus of Ta is much higher than human bone, leading to severe stress shielding and limiting the application as bio-implant bulk materials. Consequently, Ta is usually manufactured as porous scaffolds [12,13] or deposits on substrates [14]. Levine et al. [12] integrated porous tantalum applied in total knee arthroplasty and spinal arthroplasty. Balagna et al. [14] and Kiuru et al. [18] indicated CrCoMo alloys with Ta-coating are prone to the wear resistance and corrosion resistance.

Metallic glasses or termed as amorphous alloys, different from crystalline metals, are metallic materials lack of periodical arrangements. Consequently, metallic glasses are short of structure defect, such as grain boundaries and dislocations, etc. Furthermore, amorphous alloys own some special chemical and physical properties. In contrast to their corresponding crystalline alloys, metallic glasses exhibit higher strength, higher hardness, higher corrosion resistance (owing to the absence of structure defects), but lower Young's modulus (owing to the lower bonding in random packing structure) [19–23]. The high strength can allow the high porosity foam can still bear high enough load. The high hardness can efficiently suppress debris release. The high corrosion resistance is favorable for biocompatibility testing. And the lower Young's modulus can match much better with the modulus of human bone. For these reasons, metallic glasses used as bio-implant applications have been widely investigated recently, and the Ti-based metallic glasses are basically the focus of global studies.

To fabricate bulk metallic glasses (BMGs), the glass forming ability (GFA) plays an essential role. Consequently, Ti-based metallic glasses are usually added with smaller-sized elements, such as Be, Ni and Cu, which would benefit GFA. But these elements are prone to harmful reactions in human body and cells [24,25]. In 2013, Calin et al. [26] developed Cu-free Ti-based metallic glasses, Ti-Zr-Si and Ti-Zr-Nb-Si. Additionally, in our previous studies [21,25], Ti-based metallic glasses without Cu indeed exhibited good bio-corrosion resistance and biocompatibility while the Ti-based metallic glasses with Cu content decrease cell viability and corrosion resistance. In comparison with the Ti based metallic glasses, nonetheless, very few Ta-based metallic glasses have been designed and studied for bio-implant applications. Most papers mentioning metallic glasses with limited Ta [27–30] only discussed the mechanical properties. And most Ta added BMGs also contain non-bio-friendly elements, such as Ni and Cu. Without Ni and Cu, the cast fabrication becomes highly difficult. Conversely, thin film metallic glasses (TFMGs) can be successfully manufactured for alloy systems with lower GFA, since they can be prepared by physical deposition instead of casting. It is well known that most chemical interactions between human body and bio-implant materials take place along the material surface. The TFMG coating on other metals can be considered as surface modification.

In this study, the Ta-based TFMGs, Ta-Ti-Zr-Si with no non-bio-friendly elements, were designed and systematically evaluated, in terms of in vitro electrochemical responses in simulated body fluid (SBF), cells attachment and cell viability behavior, and mechanical property exploration, etc. Note that Si is added in this system, since Si is also a small sized element playing the similar role in randomizing the atomic packing as Be, Ni or Cu. But Si is completely non-bio-toxic.

2. Materials and methods

2.1. Materials preparation

In this study, pure Ta and Ti-Zr-Si alloys metallic targets were applied to manufacture thin film metallic glasses. The purity of Ta target is 99.9% and the composition of Ti-Zr-Si alloy target is $Ti_{43}Zr_{43}Si_{14}$ in at%. And the pure Ti plates and Si plates with $5 \times 5\,mm^2$ were chosen as substrates. The Ta-based metallic glasses, Ta-Ti-Zr-Si, were deposited via co-sputtering system. Both targets were placed on DC cathodes. The base pressure of operator chamber should be achieved below 5×10^{-7} torr. And argon (Ar) is chosen as working gas introduced into the chamber after reaching the base pressure. Besides, before sputtering, a movable shuttering is used to pre-sputter targets for 5 min. A series of Ta based TFMGs have been prepared in our laboratory [28]. In this study, only two representative fully amorphous films are examined for their biocompatibility. For comparison, the pure Ti and pure Ta films are also sputtered. The thicknesses of all deposited films are about 600 nm.

2.2. Chemical compositions and structure analysis

The chemical compositions of as-deposited Ta-Ti-Zr-Si thin film metallic glasses were examined by X-ray photoelectron spectroscopy (XPS) with Mg–Ka (1253.6 eV) radiation operated at 10 kV and 5 mA under the vacuum pressure of 10^{-7} Pa. Also, the structure of as-deposited Ta-Ti-Zr-Si thin films was confirmed by X-ray diffraction (XRD) with Cu-Kα (λ = 1.5406 Å) radiation operated at 40 kV and 40 mV at room temperature. The scanning range is from 20° to 60° with every step for 5 s.

2.3. Mechanical property

MTS nanoindenter XP with Berkovich tip, a three sided pyramid, is utilized to estimate the hardness and Young's modulus under continuous stiffness measure (CSM) mode with strain rate of $1 \times 10^{-2}\,s^{-1}$. Additionally, the scratch mode was applied to estimate the wear resistance via different depths of scratch under unified stresses.

2.4. Electrochemical analysis

The electrochemical properties and bio-corrosion behaviors were characterized by electrochemical measurements. The potentiodynamic polarization measurements and AC impedance tests were conducted by the CHI 614D electrochemical work station in a three-electrode cell. The specimens with $16\,mm^2$ worked as working electrodes were immersed in simulated body fluid, Hank's solution (with a composition of 0.137 M of NaCl, 5.4 mM of KCl, 0.25 mM of Na_2HPO_4, 0.44 mM of KH_2PO_4, 1.3 mM of $CaCl_2$, 1.0 mM of $MgSO_4$, and 4.2 mM of $NaHCO_3$, pH = 7.4), at 310 K while the counter and reference were platinum plate and Ag/AgCl respectively. Not until did the value of open circuit potential (OCP) vary less than 2 mA per 5 min, the AC impedance and potentiodynamic polarization measurement carried out. The AC impedance test was carried out in the frequency from 10^{-2} to 10^{-5} Hz and the amplitude was set as 10 mV. The polarization with scanning rate of 0.33 mV per second started from the readings of OCP subtracting 0.2 V to 2 V.