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TiZrNbTaMo high-entropy alloy designed for orthopedic implants: As-cast microstructure and mechanical properties

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ABSTRACT

Combining the high-entropy alloy (HEA) concept with property requirement for orthopedic implants, we designed a $Ti_{20}Zr_{20}Nb_{20}Ta_{20}Mo_{20}$ equiatomic HEA. The arc-melted microstructures, compressive properties and potentiodynamic polarization behavior in phosphate buffer solution (PBS) were studied in detail. It was revealed that the as-cast TiZrNbTaMo HEA consisted of dual phases with bcc structure, major bcc1 and minor bcc2 phases with the lattice parameters of 0.3310 nm and 0.3379 nm, respectively. As confirmed by nanoindentation tests, the bcc1 phase is somewhat harder and stiffer than the bcc2 phase. The TiZrNbTaMo HEA exhibited Young's modulus of 153 GPa, Vickers microhardness of 4.9 GPa, compressive yield strength of $\sigma_y = 1390$ MPa and apparent plastic strain of $\varepsilon_p \approx 6\%$ prior to failure. Moreover, the TiZrNbTaMo HEA manifested excellent corrosion resistance in PBS, comparable to the Ti6Al4V alloy, and pitting resistance remarkably superior to the 316L SS and CoCrMo alloys. These preliminary advantages of the TiZrNbTaMo HEA over the current orthopedic implant metals in mechanical properties and corrosion resistance offer an opportunity to explore new orthopedic-implant alloys based on the TiZrNbTaMo concentrated composition.

1. Introduction

Metallic materials have been key materials to fabricate the orthopedic implants, due to their advantage in superior mechanical properties, including the high yield strength, ductility, fatigue strength and fracture toughness. Typically, the cobalt-chromium-molybdenum (CoCrMo) and titanium alloys are currently used for artificial joint replacement such as hip, knee, and shoulder prostheses [1–3]. In spite of the good biocompatibility, titanium alloys (e.g., Ti6Al4V) are inadequate to be used as bearing surfaces owing to their poor wear resistance, which is probably associated with the low shear strength and repassivation behavior of the surface oxide layer [1]. In contrast, CoCrMo alloys (e.g., Co28Cr6Mo, complying with the ASTM F75 for cast and the ASTM F799 for wrought alloys) are more wear-resistant, and are clinically used as bearing surfaces of the joint prostheses, such as artificial joint of metal-on-metal (MoM) bearings which was re-introduced by the early 1980s as an alternative to metal-on-polyethylene (MoP) bearings. Recently, however, it becomes a great concern that some CoCrMo bearings have shown unacceptably high failure rate [3]. Patient with CoCrMo implants may have increased metal ion levels of cobalt and chromium in the blood [4–6]. A number of in vitro and in vivo studies demonstrated that metal particulates and their byproducts may be associated with cytotoxicity, DNA damage, metal hypersensitivity reactions and pseudotumors [7–11]. In this sense, the current orthopedic materials are not perfect, and it remains of interest to develop newer, more wear resistant bearing couples that could last the lifetime of implants [12].

As suggested by Willmann [13], the ideal materials used for bearing surfaces in joint replacement should exhibit the following properties: a biocompatible chemical composition to avoid adverse tissue reactions, an excellent resistance to corrosion in the human body environment, high hardness and stiffness to maintain good wear resistance, synoviaphilicity for lubrication and low friction, and high thermal conduction coefficient to avoid proteinous synovia degeneration. In this sense, high modulus of material is required to ensure the wear resistance of bearing surfaces and avoid deformation of the articulating surfaces under peak load of eight-time body weight. It should be emphasized that such a requirement for bearing surface materials is different from some prostheses such as the femoral stems and tibial trays [14,15], where the materials with lower modulus are expected to reduce the stress-shielding effects that cause peri-prosthetic bone resorption and aseptic loosening [16].

Recently, it is of interest to note that high-entropy alloys (HEAs) with compositional features of multicomponent (five or more elements) and equiatomic or near-equiatomic concentration have attracted much attention [17–24], due to their potentially interesting properties. Meanwhile, vast opportunities for new compositions and microstructures are offered by this area, in particular for complex concentrated alloys (CCAs) [25]. Ever since Senkov et al. [26] firstly

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developed refractory HEAs with a single bcc phase in W-Nb-Mo-Ta and W-Nb-Mo-Ta-V alloy systems, several bcc HEAs based on the early transition metals were studied on phase selection and preliminary mechanical properties, including the Nb-Mo-Ta-W, V-Nb-Mo-Ta-W, Ta-Nb-Hf-Zr-Ti, Hf-Nb-Ti-Zr, Hf-Mo-Ta-Ti-Zr and Hf-Mo-Nb-Ta-Ti-Zr equiatomic alloys [27–32]. These HEAs exhibit high yield strength (σ_y = 900–1600 MPa) at ambient temperature, among which someone manifests sizable compressive plasticity. From the biocompatibility perspective, it is interesting to note that majority of these elements are biocompatible [33–38], except the toxic vanadium [39]. Even considering the situation of metal ion release from metal implant, released metal ions of zirconium, niobium and tantalum belong to titanium-type ion, and do not always combine with biomolecules to appear toxicity because active ion immediately combines with a water molecule or an anion near the ion to form an oxide, hydroxide, or inorganic salt [40].

Combining the HEAs concept with elemental biocompatibility, we initiate to design a biocompatible HEA potentially used for orthopedic implants. The Ti-Zr-Nb-Ta-Mo quinary system was selected as the base composition. Hafnium was excluded due to its less resistance to tribocorrosion in simulated body fluid [41], while molybdenum with high elastic modulus (E = 324 GPa) was introduced in the alloy, which is expected to play a role to enhance the wear resistance [38]. To this end, the purpose of this paper is three-fold. First, as-cast microstructure and phase selection of arc-melted TiZrNbTaMo alloy were characterized. Second, fundamental mechanical properties of the HEA were investigated, including the Young's modulus, Vickers microhardness and compressive properties. Third, electrochemical behavior of the HEA in phosphate buffer solution (PBS) was examined with potentiodynamic polarization tests, preliminarily to assess its corrosion resistance under physiological environment, together with a comparison with the Ti6Al4V, 316L SS and CoCrMo alloys. Finally, solid-solution strengthening mechanism in the alloy was discussed in terms of Labusch approach.

2. Material and methods

Using commercial elemental bulk materials with purity higher than 99.9% (in weight percentage) as starting materials, quinary Ti-Zr-Nb-Ta-Mo alloy ingots in equiatomic fraction were fabricated by arc melting. Arc-melted ingots in weight of about 50 g were fabricated under a Ti-gettered argon atmosphere in a water-cooled copper hearth, subjected to remelting and flipping of several runs to ensure compositional homogeneity. The final average composition of the alloy was confirmed with energy dispersive x-ray spectroscopy (EDX), as listed in Table 1.

Crystalline structure of the as-cast TiZrNbTaMo HEA was analyzed by x-ray diffraction (XRD) using a Rigaku D/max 2500 diffractometer (Rigaku, Tokyo, Japan) with monochromatic Cu K_α radiation. Lattice parameters of crystalline phases with bcc structure were determined using (321) diffraction lines. Step-scanning mode was used for scanning within a range of relevant diffraction angle (2θ) to ensure the accuracy of measured position of diffraction peaks. Microstructure of the as-cast alloy was examined under a Quanta 600 scanning electron microscope (SEM) (FEI, Eindhoven, The Netherlands). Chemical composition and elemental mapping on cross-section surfaces of the as-cast alloy were analyzed using an EDX detector attached on SEM.

Measurements of Vickers microhardness were conducted on as-polished cross-section surface of the alloy specimen using a Mitutoyo MVK-H3 hardness testing machine equipped with a 136° Vickers diamond pyramid under 200 g load dwelt for 20 s. The samples were mechanically ground with SiC abrasive papers to 2000 grits, and then polished with 2.5 μm diamond paste, followed by supersonic cleaning in ethanol and distilled water. At least fifty individual measurements were performed to ensure the reproducibility.

To characterize the hardness and Young's modulus of constituent phases, nanoindentation tests were carried out on the cross-section surface using a Nano Indenter G200 (Agilent Technologies, USA) with Berkovich indenter with tip radius of 20 nm. The sample surface was mechanically ground with SiC abrasive papers to 2000 grits, and then polished with 1 μm Al_2O_3 suspension and subsequent 0.04 μm colloidal silica. The fine-polished sample was further ion-milled to remove potential deformation layer on the surface, followed by ultrasonic cleaning in ethanol and distilled water. The final surface roughness was determined to be about 20 nm using a LEXT OLS4000 laser scanning confocal microscope (Olympus, USA). Indentation was performed in depth-control mode of depth limit of 350 nm with surface approach velocity of 10 nm/s, peak hold time of 10 s and data acquisition frequency of 5 Hz.

Cylindrical specimens machined from the as-cast alloy ingot for compression tests were 4.5 mm in diameter and 9.0 mm in height. They were taken from middle part of the cross-section of alloy ingot in order to associate with the representative microstructures. Compression tests were performed at ambient temperature with a computer-controlled AG-I mechanical testing machine (Shimadzu, Japan). A thin Teflon sheet was used between specimen loading surface and dies to reduce the friction-induced confinement. Quasistatic strain rate applied on the specimens was controlled at 10^{-3} s^{-1}. At least four specimens were tested to ensure the reproducibility. Morphology of fractured surfaces for representative failure specimens under compression were examined under SEM.

Phosphate buffer solution (PBS) was used preliminarily to assess the corrosion resistance of the alloy under simulated physiological environment [42,43]. Electrochemical behavior in PBS was examined with potentiodynamic polarization tests. Cubic specimens with dimension of 5 mm × 5 mm × 5 mm were taken from middle part of the cross-section of alloy ingot, connected to the copper wire, embedded in a polytetrafluoroethylene (PTFE) holder, mounted in epoxy resin, and then ground with emery paper to 1200 grits for the tests. The measurements were conducted on a Model 2273 electrochemical workstation (EG&G Princeton Applied Research), connected to a three electrode cell with saturated calomel as reference electrode and platinum foil as counter electrode. The PBS electrolyte with the recipe the same as in previous work [42] was deoxygenized by high-purity N_2 flow. The temperature was maintained at 37 ± 1 °C using a thermostatic bath. Prior to the measurements, the specimens were immersed in electrolyte for 1 h, in order to attain a stable state of open circuit potential (OCP). Potentiodynamic polarization was measured in a range from −0.35 V versus OCP to 1.2 V_{SCE} with a scanning rate of 0.167 mV/s. For comparison,

Table 1
Chemical composition (at.%) examined by EDX for different regions in arc-melted TiZrNbTaMo HEA.

Location in ingot	Region in microstructure	Ti	Zr	Nb	Ta	Mo
Top	DR	14 ± 1	8 ± 1	20 ± 1	33 ± 1	25 ± 1
	ID	23 ± 1	41 ± 1	13 ± 1	9 ± 1	14 ± 1
Middle	DR	16 ± 1	11 ± 1	20 ± 1	29 ± 2	24 ± 1
	ID	24 ± 1	44 ± 2	12 ± 1	7 ± 1	13 ± 1
Global	DR	15 ± 2	10 ± 2	20 ± 1	31 ± 2	24 ± 1
	ID	24 ± 1	43 ± 2	12 ± 1	8 ± 1	13 ± 1
	Average	19 ± 1	21 ± 1	19 ± 1	21 ± 1	20 ± 1