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A metastable β-type Zr-4Mo-4Sn alloy with low cost, low Young's modulus and low magnetic susceptibility for biomedical applications

Shun Guo [a, b], Yao Shang [a], Jinming Zhang [a], Junsong Zhang [a, **], Qingkun Meng [c, ***], Xiaonong Cheng [a], Xinqing Zhao [b, *]

[a] School of Materials Science and Engineering, Jiangsu University, Zhenjiang, 212013, China
[b] School of Materials Science and Engineering, Beihang University, Beijing, 100191, China
[c] School of Materials Science and Engineering, China University of Mining and Technology, Xuzhou, 221116, China

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By alloying and thermo-mechanical treatment, a novel low-cost metastable β-type Zr-4Mo-4Sn alloy was designed and fabricated for biomedical applications. Upon solution treatment plus quenching, the β-type Zr-4Mo-4Sn alloy exhibits a combination of low Young's modulus (48 GPa) and low magnetic susceptibility (1.22×10^{-6} cm^3 g^{-1}). This low magnetic susceptibility (χ) is reasonably attributed to the choice of alloying components with low χ, i.e., Zr ($\chi_{Zr} = 1.32 \times 10^{-6}$ cm^3 g^{-1}), Mo ($\chi_{Mo} = 0.75 \times 10^{-6}$ cm^3 g^{-1}) and Sn ($\chi_{Sn} = 0.03 \times 10^{-6}$ cm^3 g^{-1}). An analysis of single-crystal elastic constants and Hill approximation indicated that in comparison to binary β-type Ti-based alloys, the present β-type Zr-4Mo-4Sn alloy possesses lower bcc-structural (β-phase) stability represented by its lower C' and much lower C_{44}, resulting in the ultralow Young's modulus of Zr-4Mo-4Sn alloy.

1. Introduction

Magnetic resonance imaging (MRI) has distinct advantage over X-ray computed tomography (CT) in medical diagnosis, since the former is more convenient for imaging soft tissue and has no any side-effects originating from ionizing radiation of X-ray [1]. However, exact MRI is unrealizable when metallic implants exist in human body. This is because that the metallic implants possess much higher magnetic susceptibility than that of human body, which can lead to artifacts in MRI images [2,3]. Additionally, the current metallic implant materials also possess much higher Young's modulus (55–120 GPa for Ti and its alloys, 210 GPa for 316 L stainless steel and 240 GPa for Co-Cr-Mo alloy) than natural human bone (10–30 GPa), giving rise to so-called "stress shielding effect" and eventual implant failure [4–8]. Therefore, the design and fabrication of novel metallic materials with a combination of low Young's modulus and low magnetic susceptibility has become an ever more research hotspot in the field of advanced biomedical materials.

As is well known, zirconium (Zr) has lower magnetic susceptibility ($\chi_{Zr} = 1.32 \times 10^{-6}$ cm^3 g^{-1}) than Ti ($\chi_{Ti} = 3.15 \times 10^{-6}$ cm^3 g^{-1}), while retaining no cytotoxicity, good biocompatibility and excellent corrosion resistance [9–11]. Therefore, quite recently, some antecedent investigations have begun to focus on design and fabrication of Zr alloys, in an attempt to achieve a combination of low Young's modulus and low magnetic susceptibility for biomedical applications. For instance, it has been found by Nomura et al. that by the doping of β-stabilizers (e.g., Nb and Mo, etc.), β-type Zr alloys with body cubic (bcc) structure can be obtained, with the similar Young's moduli with Ti alloys but lower magnetic susceptibility than Ti alloys [12–14]. Up to now, the tensile Young's moduli of β-type Zr alloys are within the range of 60–90 GPa, which are still not compatible enough to match with that of human bone (10–30 GPa) [4,13,14]. More importantly, the underlying mechanism of low Young's modulus for β-type Zr alloys with low magnetic susceptibility has yet to be addressed clearly, which is obviously adverse to developing novel β-type Zr alloys with a bone-compatible Young's modulus.

Quite recently, our research group reported that by alloying and thermo-mechanical treatment, a combination of low Young's modulus (44 GPa) and low magnetic susceptibility

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: zhangjunsong7397@163.com (J. Zhang), qkmeng@cumt.edu.cn (Q. Meng), xinqing@buaa.edu.cn (X. Zhao).

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(1.42×10^{-6} cm^3 g^{-1}) can be achieved in a metastable β-type Zr-12Nb-4Sn alloy [15]. However, the magnetic susceptibility of Zr-12Nb-4Sn alloy, 1.42×10^{-6} cm^3 g^{-1}, is still not low enough to match with human bone, though being much lower than Ti-based alloys (about 4–8 × 10^{-6} cm^3 g^{-1}) [15]. In the present study, Zr with low magnetic susceptibility ($\chi_{Zr} = 1.32 \times 10^{-6}$ cm^3 g^{-1}), rather than Ti ($\chi_{Ti} = 3.15 \times 10^{-6}$ cm^3 g^{-1}), was still selected as host element in order to achieve low magnetic susceptibility. The difference is that, here, molybdenum (Mo) was chosen as β-stabilizer instead of Nb, since it possesses lower magnetic susceptibility ($\chi_{Mo} = 0.75 \times 10^{-6}$ cm^3 g^{-1}) than Nb ($\chi_{Nb} = 2.24 \times 10^{-6}$ cm^3 g^{-1}). Moreover, compared with expensive Nb, lower-cost Mo is more beneficial for material cost control and future extensive applications. Additionally, stannum (Sn, $\chi_{Sn} = 0.03 \times 10^{-6}$ cm^3 g^{-1}) was also added as trace alloying element, since it can effectively suppress the formation of high-modulus ω phase in β-type Ti and/or Zr alloys [15,16]. Thus, here, an attempt was made to prepare a novel metastable β-type Zr-Mo-Sn alloy with a combination of low cost, low magnetic susceptibility and low Young's modulus. What is more, the physical mechanism of low Young's modulus in the present Zr-Mo-Sn alloy was discussed, which might shed some light on design and development of novel β-type Zr alloys with lower Young's modulus comparable with that of human bone.

2. Experimental procedure

A button ingot with a nominal composition of Zr-4Mo-4Sn in wt.% was fabricated from nontoxic Zr (99.9%), Mo (99.9%) and Sn (99.9%) under an Ar atmosphere by an arc-melting furnace. The button ingot was melted repeatedly 6 times with inversion to acquire composition homogenization. The re-melted ingot was subjected to a homogenization treatment at 1223 K for 4 h in vacuum, followed by forging at 1073 K and cold rolling into a plate with a thickness of ~1 mm. The cold rolled plate was solution treated at 1023 K for 1 h in a vacuum quartz tube and quenched by water (abbreviated as STQ).

Microstructure was characterized by X-ray diffractometer (XRD) with a Cu Kα X-ray radiation, optical microscope (OM) and FEI Quanta 200 F transmission electron microscope (TEM). Tensile tests were performed by an Instron-8801 testing system, using an extensometer for precise strain measurement, at a strain rate of 1×10^{-3} s^{-1}. The in-situ synchrotron X-ray diffraction (SXRD) experiments were conducted on the 11-ID-C beam-line of Advanced Photon Source (APS), at Argonne National Laboratory (ANL). A detailed description of in-situ SXRD experiments can be seen in a previous reference [17]. The two-dimensional SXRD Debye-Scherrer rings during loading were calibrated, using Fit2d software and a standard CeO_2 calibration specimen, and output one-dimensional patterns, which can provide the information of d-spacing for different crystallographic planes through a further Gauss function fitting. The magnetic susceptibility (χ) of Zr-4Mo-4Sn alloy, together with commercially available Co-Cr-Mo alloy, pure Ti, Ti-6Al-4V alloy, Ti-6Al-7Nb alloy and a recently developed β-type Ti-33Nb-4Sn alloy, was measured at room temperature using a magnetic susceptibility balance, with a magnetic field strength of 0.35 T.

3. Results

Fig. 1a shows the XRD pattern of STQ Zr-4Mo-4Sn alloy. In this

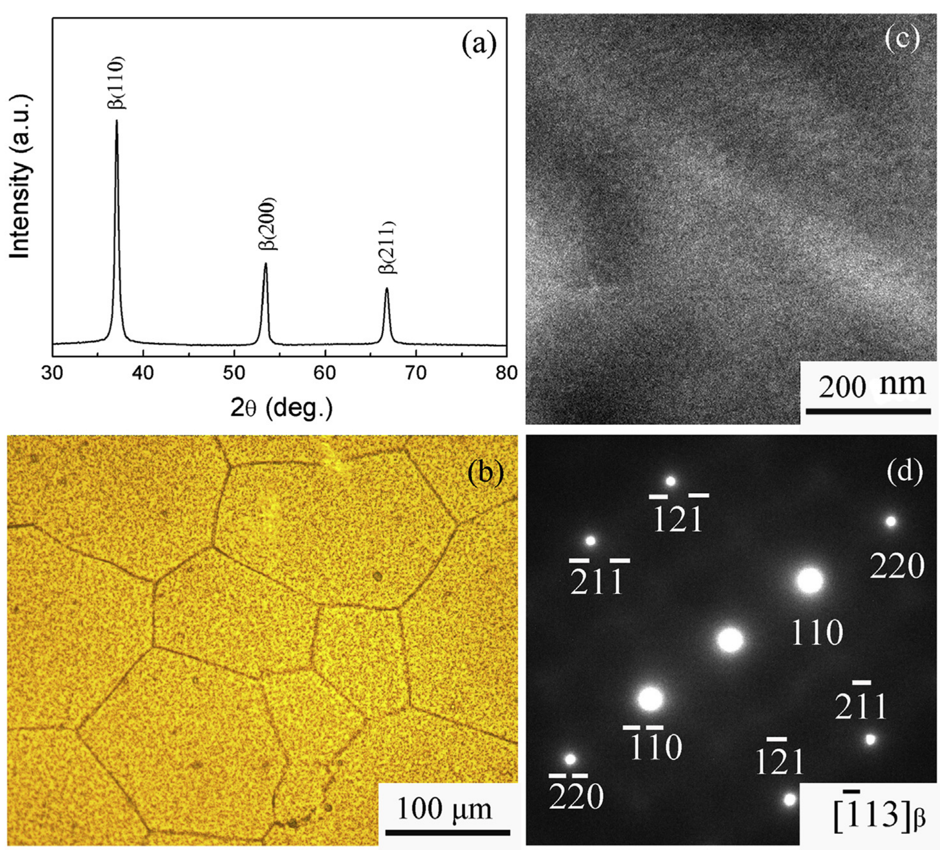

Fig. 1. Microstructure of STQ Zr-4Mo-4Sn alloy: (a) XRD pattern, (b) OM image, (c)TEM bright field image and (d) the corresponding $[1(—)13]_\beta$ zone axis selected area electron diffraction (SAED) pattern. Notice that the Zr-4Mo-4Sn alloy exhibits single β phase.