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Superelastic properties of biomedical (Ti–Zr)–Mo–Sn alloys

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ABSTRACT

A new class of Ti–50Zr base biomedical superelastic alloys was developed in this study. The (Ti–Zr)–Mo–Sn alloys exhibited a shape memory effect and superelastic property by adjusting Mo and Sn contents. The (Ti–Zr)–1.5Mo–3Sn alloy revealed the most stable superelasticity among (Ti–Zr)–(1–2)Mo–(2–4)Sn alloys. The superelastic recovery strain showed a strong dependence on heat treatment temperature after cold working in the (Ti–Zr)–1.5Mo–3Sn alloy. The superelastic recovery strain increased as the heat treatment temperature increased although the critical stress for slip decreased. The (Ti–Zr)–1.5Mo–3Sn alloy heat treated at 1073 K exhibited excellent superelastic properties with a large recovery strain as large as 7% which is due to the strong $\{001\}_\beta\langle 110\rangle_\beta$ recrystallization texture.

1. Introduction

In the past decade, β-type Ti–Nb base alloys have received increased attention as biomedical superelastic materials owing to a concern regarding the release of Ni in conventional Ti–Ni base superelastic alloys [1–19]. Some examples of typical clinical applications of biomaterials possessing superior superelastic properties are cardiovascular stents, catheters, intravascular guidewires, embolization coils and orthodontic arch wires [20–27]. Many kinds of alloys have been developed to date; however the superelastic properties of Ti–Nb base alloys reported so far are inferior to those of Ti–Ni base superelastic alloys [28]. Superelasticity in β-type Ti base alloys is attributed to the stress induced martensitic transformation from a body centered cubic β phase to an orthorhombic α″ phase, thus a critical amount of β phase stabilizing element is required to reveal superelasticity at room temperature [1,4–6,29,30]. For the Ti–Nb binary alloys, superelasticity was reported to occur when the Nb content is 26–27 at.% [4]. However, the transformation strain decreases with increasing Nb content and the maximum transformation strain of a Ti–27Nb alloy is only 2.5% [4]. Therefore, for the Ti–Nb-base superelastic alloys, the small recovery strain is one of the important issues to be improved. The effect of alloying elements such as Ta [1,30–32], Zr [1,8,14,16,18,33–37], Mo [13,30], Sn [2,10,38,39], Al [40,41] and O [1,42] on the superelastic properties was extensively investigated. Among them Zr was found to be an effective alloying element to increase the superelastic recovery strain because the addition of Zr as a substitute of Nb while keeping the martensitic transformation start temperature (M_s) similar increases the transformation strain [1]. However, most studies have been carried out in the alloys with a low content of Zr [1,8,14,16,23,33–37]. A reversible martensitic transformation between the β phase and α′ phase with a hexagonal structure was reported to occur in Ti–Zr binary alloys by Li et al. [43]. They also reported a shape memory effect in Ti–30Zr and Ti–50Zr alloys; however, the superelastic behavior was not achieved because the martensitic transformation temperatures of these alloys are as high as 813 and 913 K, respectively. In this study, we designed (Ti–Zr)–Mo–Sn alloys where the atomic ratio of Ti/Zr is fixed at 1 because the martensitic transformation start temperature shows minimum value when the Zr content is 50 at.% in Ti–Zr binary alloys [44–47]. Mo was selected as a β phase stabilizing element for reducing the martensitic transformation start temperature below room temperature to obtain superelasticity at room temperature [13,30,48,49]. Sn was added to suppress the formation of the ω phase [5,39,50]. The effects of Mo and Sn contents on microstructure and mechanical properties were investigated. The effects of heat treatment temperatures on texture and superelastic properties were also investigated. It was found that a (Ti–Zr)–Mo–Sn alloy exhibits excellent superelastic properties with a large recovery strain as large as 7% by adjusting the composition and optimization of microstructure.

2. Materials and methods

2.1. Alloys preparations

Quaternary (Ti–Zr)–(1–2) at.% Mo-(2–4) at.% Sn ingots (all compositions are hereafter referred in atomic percent) were prepared by an Ar arc-melting method using high-purity (99.9%) raw materials. The ingots

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were melted six times and flipped over after each melting for better homogeneity. The mass loss after the melting procedure was negligible, so the actual composition was considered the same as the nominal composition. The melted ingots were sealed in a vacuum in a quartz tube and homogenized at 1273 K for 7.2 ks and then air cooled. Then the ingots were cold-rolled up to 98.5% in thickness reduction without intermediate annealing. Specimens for tensile tests, X-ray diffraction (XRD) measurements, and scanning electron microscopy (SEM) observation were cut using an electro-discharge machine. The damaged surface was removed by chemical etching in a solution of fluorinated acid/nitric acid/water = 1:4:5 (v/v/v). All the cold rolled specimens were encapsulated in quartz tubes in an Ar atmosphere and heat treated at 873, 923, 973 and 1073 K for 3.6 ks respectively, followed by quenching into water at RT without breaking the quartz tubes to mitigate oxidation.

2.2. Measurement of superelastic properties

In order to investigate superelastic properties tensile tests were carried out at a strain rate of $3 \times 10^{-4}\ s^{-1}$ at room temperature (RT) by a tensile testing machine (AG-X, Shimadzu). The dimensions of the rectangular shaped tensile specimens were 0.15 mm in thickness and 1.5 mm in width, with a length of 40 mm. Each tensile specimen was tested along the rolling direction, such that the tensile direction of the specimen was parallel to the rolling direction. Both ends of the tensile specimens were fixed with two chucks so that gage length becomes 20 mm and the strain of the specimens was determined by measuring the distance between the chucks using an extensometer. It is important to mention that in the case of (Ti–Zr)–1Mo–2Sn, (Ti–Zr)–1Mo–3Sn and (Ti–Zr)–1Mo–4Sn alloys, the specimens for tensile tests could not be prepared, mainly due to their poor cold workability.

2.3. Microstructural analysis and characterization

Specimens for microstructural investigations were prepared by mechanical and electro-polishing. The annealed specimens were mechanically ground with a SiC emery paper (grades from #400 to #3000), followed by polishing with alumina suspension paste (5, 1, 0.3 μm) on a polishing cloth to obtain a mirror surface. Some specimens were electro-polished using a solution of per-chloric acid/butanol/methanol = 1:6:10 (v/v/v) at 233 K.

The phase constitutions and textures in annealed specimens were investigated at room temperature using an XRD apparatus (RINT-2000, Rigaku) with Cu $K\alpha$ radiation operated at 40 kV and 40 mA. Lattice parameters of the β and α″ phases for (Ti–Zr)–Mo–Sn alloys were also measured by XRD using Si powder as a standard material. The incomplete pole figures were obtained from the diffraction intensities of three major crystal planes, i.e. {110}, {200} and {211} of the β phase. Orientation distribution functions (ODFs) were also derived while using the corresponding pole figures. The microstructural investigations were conducted by electron probe microanalysis (EPMA) JEOL JXA 8530F instrument with an accelerating voltage of 20 kV and a beam current of 1×10^{-8} A.

Differential scanning calorimetry (DSC) equipped with a nitrogen cooling system (DSC-60, Shimadzu) was used to evaluate the phase transformation temperatures with a heating and a cooling rate of $10\ K\ min^{-1}$ in the temperature range of −373 and 323 K.

3. Results and discussion

3.1. Effect of Mo and Sn contents on phase constitution and mechanical properties

Fig. 1 shows XRD profiles of (Ti–Zr)–(1–2)Mo–(2–4)Sn alloys heat treated at 1073 K for 3.6 ks. The phase constitution was changed by both Mo and Sn contents. For the alloys containing 1Mo (Fig. 1a), the (Ti–Zr)–1Mo–2Sn alloy consists of only single α″ phase. The (Ti–Zr)–1Mo–3Sn alloy exhibits a strong peak from the β phase with small peaks from the α″ phase and the (Ti–Zr)–1Mo–4Sn alloy exhibits only peaks from the β phase. These results imply that the addition of Sn decreases the martensitic transformation start temperature which is consistent with previous reports [2,5,12,38,39]. For the alloys containing 1.5Mo (Fig. 1b), the (Ti–Zr)–1.5Mo–2Sn alloy consists mainly the α″ phase while the (Ti–Zr)–1.5Mo–(3,4)Sn alloys consist of only β phase. For the alloys containing 2Mo (Fig. 1c), all (Ti–Zr)–2Mo–(2,3,4)Sn alloys exhibit only peaks from the β phase, indicating that the martensitic transformation start temperatures of these alloys are below room temperature. It is also clear, by comparing the XRD profiles of (Ti–Zr)–(1,1.5,2)Mo–2Sn alloys, that the increase in Mo also decreases the martensitic transformation start temperature. These results imply that both Mo and Sn decrease M_s of Ti–Zr base alloys remarkably which is consistent with the previous studies on Ti base alloys. The effect of Mo and Sn on the martensitic transformation temperature has been investigated mainly in Ti–Nb alloys. It was reported that an increase in 1 at.% Sn leads to a decrease in M_s of about 150 K in Ti–Nb–Sn alloys [2] although Sn has been considered as a neutral element for α/β

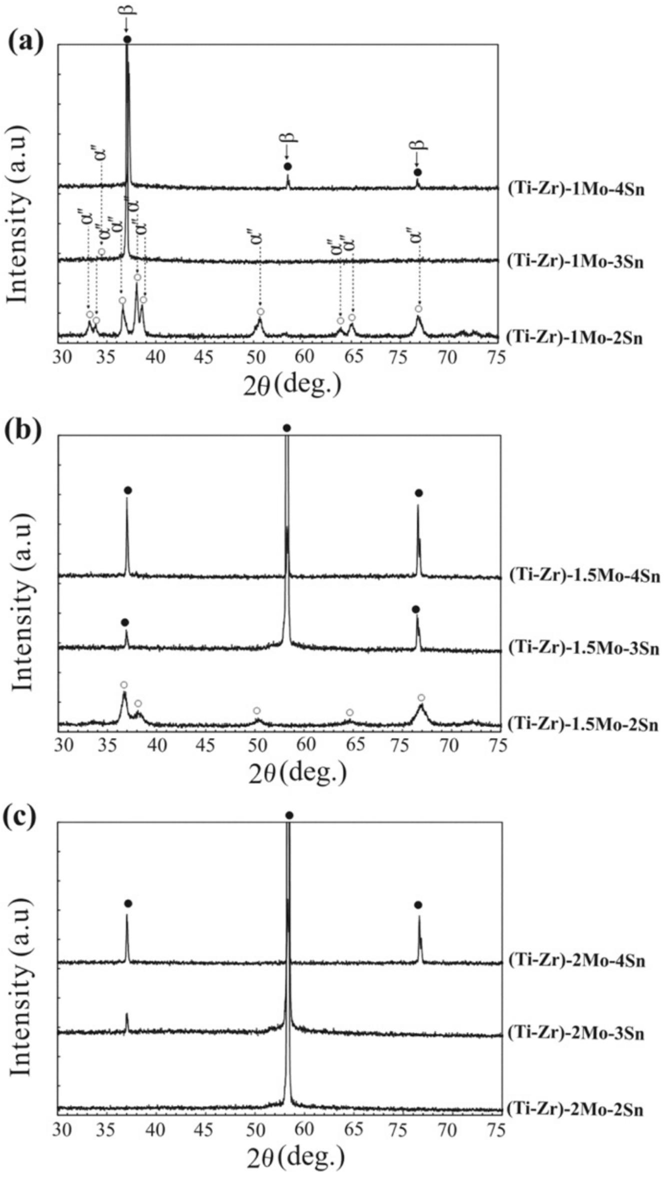

Fig. 1. XRD profiles of (a) (Ti–Zr)–1Mo–(2–4)Sn, (b) (Ti–Zr)–1.5Mo–(2–4)Sn and (c) (Ti–Zr)–2Mo–(2–4)Sn alloys.