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Research Paper

Effect of Sn addition on the microstructure and superelasticity in Ti–Nb–Mo–Sn Alloys

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ABSTRACT

Ti–7.5 Nb–4Mo–xSn ($x=0$–4 at%) alloys were developed as the biomedical materials. The effect of the Sn content on the microstructure and superelasticity of the alloys was investigated. It is found that Sn is a strong stabilizer of the β phase, which is effective in suppressing the formation of α″ and ω phases in the alloys. Moreover, the Sn addition has a significant impact on the mechanical properties of the alloys. With the increase of Sn addition, the yield stress of the alloys increase, but their elastic modulus, the fracture strength and the ductility decrease, and the deformation mode of the alloys changes from (322) twining to α″ transformation and then to slip. The Ti–7.5 Nb–4Mo–1Sn and Ti–7.5 Nb–4Mo–3Sn alloys exhibit a good superelasticity with a high σ_{SIM} due to the relatively high athermal ω phases containing or the solution hardening at room temperature. Under the maximum strain of 5%, Ti–7.5 Nb–4Mo–3Sn (at%) alloy exhibits higher super elastic stability than that of Ti–7.5 Nb–4Mo–1Sn alloy.

1. Introduction

Nickel–titanium alloys have been found to be the most useful of all the titanium-based shape memory alloys (SMAs) as biomedical materials due to their large recoverable strain value, low elastic modulus, and high corrosion resistance (Barras and Myers, 2000; Frick et al., 2006). However, it has been found that pure nickel may exhibit hypersensitivity and carcinogenicity to human body (Wang et al., 1996). There is a prohibition tendency for nickel–titanium alloy system in the biomedical field in European countries in recent years due to the problem of human nickel allergy. Therefore it is preferable to develop absolutely safe nickel-free titanium-based shape memory alloys for biomedical applications.

Recently, some Ni-free Ti alloys such as Ti–Nb (Souza et al., 2010; Brailovski et al., 2011; Laheurte et al., 2010; Sun et al., 2011; Chai et al., 2008; Wang et al., 2009; Miura et al., 2011; Al-Zain et al., 2010; Nozoe et al., 2007), Ti–Mo (Al-Zain et al., 2010; Lin et al., 2007; Oliveira et al., 2007; Oliveira et al., 2009a,b; Sutou et al., 2006; Zhang et al., 2005;) and Ti–Zr (Brailovski et al., 2011; Wang et al., 2009) have been extensively investigated as SMA due to their low elastic modulus, high biocompatibility and non-toxicity. It is well known that the SME of Ti–Nb alloys is attributed to the reversible martensitic transformation between α″ martensite and parent phase (Ozaki et al., 2004), and the martensitic transformation temperatures (M_s) and the shape memory behavior of Ti–Nb alloys are strongly dependent on their compositions. It has been reported that Ms of Ti–Nb alloys decreases from the melting point of Ti to −90 °C with the increase of the Nb content (Kim et al., 2004). A SME of 3% has

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been obtained in Ti–(22–29 at%) Nb alloys. Moreover, for Ti–Nb alloys, their superelasticity (SE) strain can be improved up to 3.3% by cyclic loading–unloading training but their SME are not prone to be improved due to their low martensitic transformation stress (σ_{SIM} is about 200 MPa) (Kim et al., 2006). By contrast, Ti–Mo based alloys exhibit a relatively small superelasticity recovered strain (about 2.5%), but a high σ_{SIM} (about 450 MPa) (Zhang et al., 2005). Thus, in order to enhance the SE, and its stability, Miyazaki et al. added Mo to Ti–Nb alloys to develop the Ti–15Nb–4Mo alloy, which σ_{SIM} and a total recovery strain reached about 420 MPa and 3.5%, respectively (Al-Zain et al., 2010). In addition, Sn addition has an important influence on the SME and SE behavior of Ti–Nb or Ti–Mo alloys. It has been reported that Ms of Ti–Nb–Sn alloys decreases rapidly with increasing Sn content and a large SE strain was obtained in Ti–16Nb–4.9Sn alloy (Al-Zain et al., 2010). Moreover, Ozaki et al. (Ozaki et al. 2004) found that the addition of 2.5 at% Sn to Ti-22 at% Nb could suppress the α'' martensitic transformation. While, Yang et al. (Hu et al., 2008) found that Sn is a stronger β stabilizer than Nb in the Ti–Nb–Zr–Sn system from first-principles calculations, and a certain amount of Sn addition could reduce the elastic modulus of the alloy by suppressing ω phase formation. Based on the previous work, we designed a quaternary Ti-based alloy, Ti–7.5Nb–4Mo–1Sn (in atom percent), according to the d-electron orbit theory, and the alloy exhibits stable SME and SE (Zhang et al., 2011). But how the Sn content affects the microstructure and the mechanical properties of the quaternary alloy is not reported yet. Therefore, in the present work, the Ti–7.5Nb–4Mo–xSn ($x=0$–4) alloys were fabricated by an arc melting method, and the microstructure and mechanical properties of the alloy were investigated, emphasizing on clarifying the effect of the Sn content on the SME and SE of the alloy.

2. Experimental

The ingot of the Ti alloy was fabricated by an arc melting method using pure Ti, Nb, Mo and Sn as raw materials. To ensure the composition homogeneity, the ingot was flipped and remelted five times. The nominal composition of the ingot is Ti–7.5Nb–4Mo–xSn ($x=0$–4), and the ingots were hot-pressed by 50% at the temperature of about 1073 K. The samples for X-ray diffraction (XRD) measurement and tensile tests were cut from the ingot by an electro-discharge machine, and vacuum sealed in quartz tubes with Ar atmosphere. The samples were solution-treated at 1273 K for 1.8 ks followed by quenching them into ice water. After that, the specimens were acid etched to remove the oxidized skin. The phase structures present in the microstructure were identified at room temperature by XRD using a Rigaku D/Max 2500PC diffractometer operated at 50 kV and 100 mA with a Cu Kα radiation ($\lambda=1.5406$ nm). To evaluate the SE of the alloy, tensile tests were carried out on an Instron 5569 universal testing machine, using the tensile specimens with a gage section of 1 mm × 2.5 mm × 8 mm, and the geometry of the samples is schematically shown in Fig. 1. The transmission electron microscopy (TEM) observations were conducted using a JEM-2100 operated at 160 kV. Samples for TEM were prepared by an electro-polishing in a solution of 200 vol% methanol, 20 vol% glycol and 10 vol% HNO_3 at 15 V–20 V under −30°C. Microhardness was obtained using a Vickers hardness tester (HVS-30Z) with a load of 10 kgf. Elastic moduli were determined by a Tribo Indenter from monotonic load tests to a depth of 7000 nm using a Berkovich tip with a measured radius of 5000 nm. The data were analyzed using the Oliver and Pharr method (Pharr, 1998).

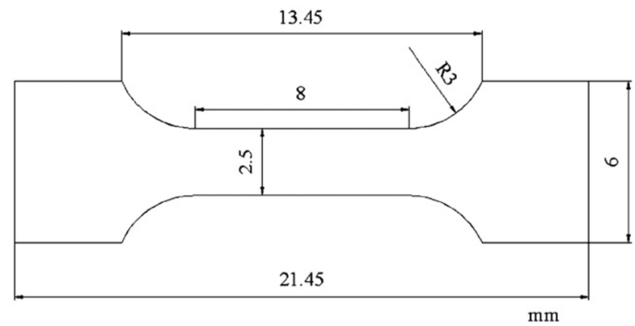

Fig. 1 – Schematic geometry of the tensile test specimen.

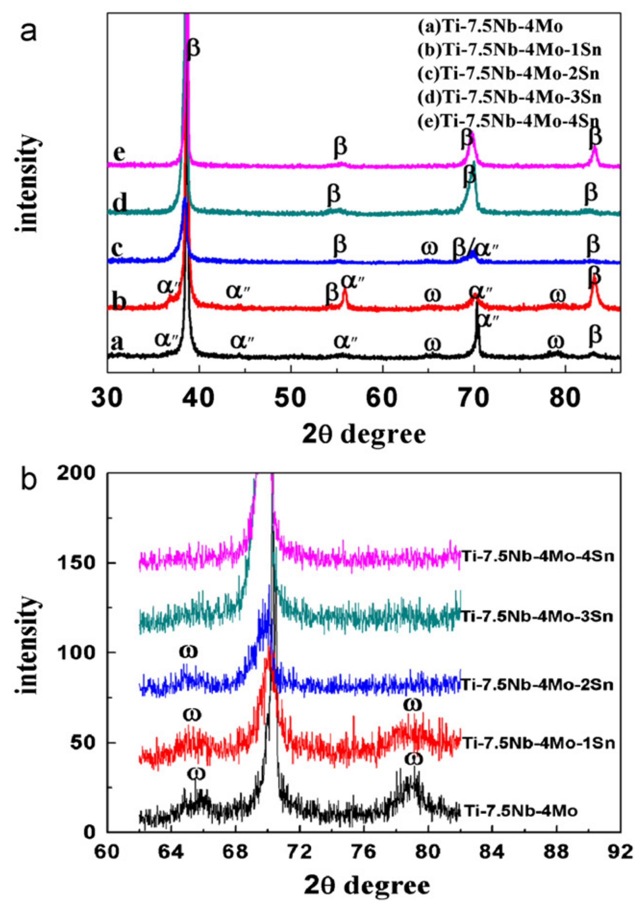

Fig. 2 – XRD spectra of the solution-treated Ti–7.5Nb–4Mo–xSn alloys.

3. Results and discussion

3.1. Microstructure

Fig. 2 shows the XRD spectra of solution-treated Ti–7.5Nb–4Mo–xSn ($x=0$–4) alloys. The alloy without Sn content (Ti–7.5Nb–4Mo)