Available online at www.sciencedirect.com

SciVerse ScienceDirect

Scripta Materialia 67 (2012) 57–60

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

A study of low Young's modulus Ti–Nb–Zr alloys using *d* electrons alloy theory

Li You and Xiping Song*

State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China

Received 6 March 2012; revised 18 March 2012; accepted 19 March 2012
Available online 24 March 2012

Six kinds of alloys in Ti–Nb–Zr alloy system were designed using *d* electrons alloy theory, and the relations between their Young's modulus and electron parameters were investigated. The results show that the Young's moduli of the designed alloys are low, with a minimum of 38.8 GPa. A formula was proposed to represent the interatomic bonding force of these alloys, which showed good agreement with the Young's modulus. Low Young's modulus β-Ti alloys can be designed by evaluating their interatomic bonding force.

Keywords: Titanium alloys; Elastic behavior; *d* electrons alloy theory; X-ray diffraction; Tension test

Titanium alloys are now the most widely used biomaterials for implant applications because of their excellent biocompatibility and high corrosion resistance [1,2]. However, the fact that the Young's moduli of the titanium alloys currently used are much larger than those of human bones [3] causes stress shielding in the vicinity of the implant area, which is harmful to human health. Therefore, recent research of biomedical titanium alloys has focused on the design of low Young's modulus titanium alloys [4–7].

A new theory proposed by Morinaga et al. [8], named *d* electrons alloy theory, has proved to be an effective method of designing titanium alloys with low Young's modulus. For example, Ti–29Nb–13Ta–4Mo (wt.%), Ti–29Nb–13Ta–2Sn (wt.%) [9] and Ti–23Nb–0.7Ta–2Zr–1.2O (at.%) [10] alloys designed using the theory have low Young's moduli, ranging from 45 to 55 GPa. The theory involves two parameters, *Bo* and *Md* [8]. The former is a measure of the covalent bond strength between Ti and an alloying element M, and the latter correlates well with the electronegativity and the metallic radius of elements. Each element has a specific *Bo* value and a specific *Md* value for the body-centered cubic (bcc) cluster and separately for the hexagonal close-packed (hcp) cluster, based on calculations using the DV-Xα molecular orbital method (see Table 1). A titanium alloy can be shown as a point in the binary $\overline{Bo}$–$\overline{Md}$ diagram [8] by taking the compositional average of the *Bo* and *Md* values of each element in the titanium alloy, which are denoted as $\overline{Bo}$ and $\overline{Md}$.

In the $\overline{Bo}$–$\overline{Md}$ diagram of the bcc-Ti cluster, all the titanium alloys can be distributed into three regions (α, α + β and β). Around the α + β/β boundary the β-phase is metastable, and will probably transfer into non-equilibrium-phases (ω, α′ and α″) under the condition of water quenching. It has been reported that the metastable β-phase has the lowest modulus among these-phases, and that the Young's modulus of the titanium alloys decreases as the $\overline{Bo}$ and $\overline{Md}$ increase along the metastable β-phase boundary [11–13], so the low Young's modulus of the titanium alloys can be achieved if we can obtain metastable β-phase with high $\overline{Bo}$ and $\overline{Md}$.

The Ti–Nb–Zr alloy system has proved to be a good substitute for developing absolutely safe Ni-free biomedical Ti alloys because Ti, Nb and Zr are non-toxic elements and do not cause any adverse reaction in the human body. However, the Young's moduli of the Ti–Nb–Zr alloys reported so far are not low enough [4,14], and there has been little research into the Young's moduli of metastable β-phase Ti–Nb–Zr alloys with high $\overline{Bo}$ and $\overline{Md}$. Moreover, the quantitative relationship between the Young's modulus and the $\overline{Bo}$ and $\overline{Md}$ has

* Corresponding author. Tel.: +86 10 62333213; fax: +86 10 62333447; e-mail: xpsong@skl.ustb.edu.cn

1359-6462/$ - see front matter
http://dx.doi.org/10.1016/j.scriptamat.2012.03.020

Table 1. List of *Bo* and *Md* values for various alloying elements in hcp-Ti and bcc-Ti clusters.

Element	*Bo* hcp-Ti	*Bo* bcc-Ti	*Md* (eV)
Ti	3.513	2.790	2.447
V	3.482	2.805	1.872
Cr	3.485	2.779	1.478
Mn	3.462	2.723	1.194
Fe	3.428	2.651	0.969
Co	3.368	2.529	0.807
Ni	3.280	2.412	0.724
Cu	3.049	2.114	0.567
Zr	3.696	3.086	2.934
Nb	3.767	3.099	2.424
Mo	3.759	3.063	1.961
Hf	3.664	3.110	2.975
Ta	3.720	3.144	2.531
W	3.677	3.125	2.072
Al	3.297	2.426	2.200
Si	3.254	2.561	2.200
Sn	2.782	2.283	2.100

not yet been clarified. Therefore, the purpose of this paper is to design low Young's modulus Ti–Nb–Zr alloys by using *d* electrons alloy theory and to propose a formula to represent the quantitative relation of the Young's modulus and the $\overline{Bo}$ and $\overline{Md}$ that could provide a theoretical guide to the design of low Young's modulus biomedical Ti alloys.

The $\overline{Bo}$ and $\overline{Md}$ values of single β-phase and non-single β-phase Ti–Nb–Zr ternary alloys [15,16] were first calculated; these are shown in Figure 1. It was found that the boundary between the single β-phase and the non-single β-phase was almost a straight line (the solid straight blue line in Fig. 1). We could thus assume that the straight line was the metastable β-phase boundary of the Ti–Nb–Zr alloy system. It can be seen in Figure 1 that the metastable β-phase boundary of the Ti–Nb–Zr alloy system has an offset from that proposed by Morinaga et al. [8] and Abdel-Hady et al. [13] for alloys without Zr. This difference can be explained by the shift effect of the element Zr [13,17]. Six kinds of alloys in the Ti–Nb–Zr alloy system were then designed along the metastable β-phase boundary in order to obtain a low Young's modulus, and to investigate the corresponding relation of the Young's modulus and the $\overline{Bo}$ and $\overline{Md}$, as indicated by the numbers 1–6 in Figure 1. The corresponding compositions were calculated to be Ti24Nb, Ti20Nb12Zr, Ti17Nb21Zr, Ti11Nb38Zr, Ti6Nb53Zr and Ti70Zr by definition of the $\overline{Bo}$ and $\overline{Md}$. Here, the alloy compositions are expressed in atomic percent.

The alloys in this study were prepared by arc-melting from pure metals of Ti, Nb and Zr, with a purity of more than 99 mass% under argon atmosphere. They were re-melted three times to ensure a homogeneous composition, then suction cast into a copper mould. This suction casting is similar to water quenching: it cools the alloy rapidly and is conducive to obtaining a single β-phase in the alloy. Tension samples were cut from the as-cast alloys. The dimensions of the tension samples are shown in Figure 3. The Young's moduli of these alloys were measured from the stress–strain curve in tensile tests with a strain gauge. For each alloy, three samples were tested for each experimental Young's modulus. The phase structures were also determined by X-ray diffraction with Cu K_α radiation.

Figure 2 shows the XRD profiles of the six kinds of alloys in the Ti–Nb–Zr alloy system. It can be seen that Ti24Nb, Ti20Nb12Zr, Ti17Nb21Zr and Ti11Nb38Zr are composed only of β-phase (bcc), while Ti6Nb53Zr is composed of both β- and α′-phases (hcp), and Ti70Zr is composed only of α′-phase. From Ti24Nb to Ti6Nb53Zr, the β-phase diffraction peaks move toward smaller angles, indicating that the β-phase lattice constant becomes larger.

The dimensions of the tension samples and the Young's modulus with error bars are shown in Figure 3. For alloy Nos. 1–6, the Young's moduli are 66.7, 54.8, 52.4, 38.8, 48.0 and 74.7 GPa, respectively. These results indicate that the Young's moduli of the Ti–Nb–Zr alloys designed near the metastable β-phase boundary are indeed very low. The minimum Young's modulus is 38.8 GPa, which is lower than that of any β-Ti alloy so far reported. It can also be seen that, as the $\overline{Bo}$ and $\overline{Md}$

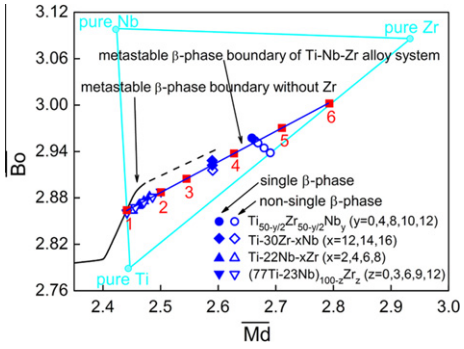

Figure 1. $\overline{Bo}$–$\overline{Md}$ diagram of the bcc-Ti cluster. The six selected alloy locations are numbered 1–6 along the deduced metastable β-phase boundary of the Ti–Nb–Zr alloy system.

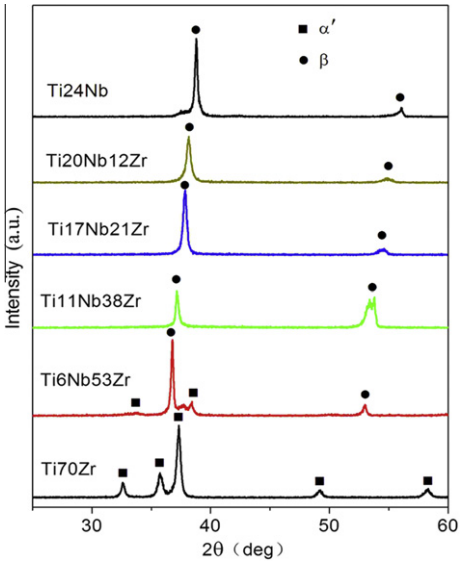

Figure 2. XRD profiles of the six kinds of alloys in the Ti–Nb–Zr alloy system. The-phase structures of the Ti–Nb–Zr alloys change from β-phase to α′-phase as the number of alloys increases.