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Research paper

Mechanical properties of low modulus β titanium alloys designed from the electronic approach

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ABSTRACT

Titanium alloys dedicated to biomedical applications may display both clinical and mechanical biocompatibility. Based on nontoxic elements such as Ti, Zr, Nb, Ta, they should combine high mechanical resistance with a low elastic modulus close to the bone elasticity ($E = 20$ GPa) to significantly improve bone remodelling and osseointegration processes. These elastic properties can be reached using both lowering of the intrinsic modulus by specific chemical alloying and superelasticity effects associated with a stress-induced phase transformation from the BCC metastable beta phase to the orthorhombic α'' martensite. It is shown that the stability of the beta phase can be triggered using a chemical formulation strategy based on the electronic design method initially developed by Morinaga. This method is based on the calculation of two electronic parameters respectively called the bond order (B_o) and the d orbital level (M_d) for each alloy. By this method, two titanium alloys with various tantalum contents, Ti–29Nb–11Ta–5Zr and Ti–29Nb–6Ta–5Zr (wt%) were prepared. In this paper, the effect of the tantalum content on the elastic modulus/yield strength balance has been investigated and discussed regarding the deformation modes. The martensitic transformation $\beta \rightarrow \alpha''$ has been observed on Ti–29Nb–6Ta–5Zr in contrast to Ti–29Nb–11Ta–5Zr highlighting the chemical influence of the Ta element on the initial beta phase stability. A formulation strategy is discussed regarding the as-mentioned electronic parameters. Respective influence of cold rolling and flash thermal treatments (in the isothermal omega phase precipitation domain) on the tensile properties has been investigated.

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1. Introduction

Metallic implants and osseointegrated prostheses are currently made from Cr–Co alloys, stainless steels or conventional ($\alpha + \beta$) titanium alloys such as TA6V ELI alloy. The titanium alloys are mainly used in the biomedical field thanks to their unique combination of mechanical properties and their superior biocompatibility. However, the potential toxic effect of some chemical elements such as vanadium or aluminium has been pointed out for a long time. Therefore, this is a strong driving force for the development of a next generation of alloys with improved compositions with respect to the general biocompatibility criterion. One of the major keys for successful applications is connected to the use of materials with reduced modulus since long-term clinical investigations indicate that insufficient load transfer from artificial implants to adjacent remodelling bone may result in bone resorption and potential loosening of the prosthetic device. This effect called "stress shielding" effect is a direct result of the stiffness mismatch between implant material and surrounding natural bone (Meunier et al., 1990; Niinomi, 2008). With respect to this concept called isoelasticity, the beta titanium alloys display superior properties compared to stainless steels and Co–Cr alloys with elastic modulus approaching the 60–80 GPa range. However, these values are still 3 or 4 times higher than the cortical elastic modulus (20 GPa). Additional decrease of the apparent elastic modulus can be achieved from the ability of these metastable β titanium alloys to undergo a stress-induced martensitic transformation during deformation. This transformation, from the parent β phase retained in a metastable state after water quench and the orthorhombic α'' martensite, results in an extrinsic low pseudo-modulus that can be modulated through microstructural control.

The ideal material should possess good strength, high fatigue resistance, and a low elastic modulus matching the bone elasticity. Considerable efforts have been devoted by materials engineers to enhance the yield strength and to reduce the modulus. However, for a long time, all these compositions have been formulated principally by trial and error methods, with no physical background representing the optimum choices. Therefore, to reduce the intrinsic modulus of Ti alloys, Morinaga et al. (1988) developed an innovative approach based on electronic design of alloys (called "the d-electron alloy design method"). They showed a relationship between some elastic properties of titanium alloys and the value of two electronic parameters respectively called the average bond order $\overline{B_o}$ which is a measure of the covalent bond strength between titanium and alloying elements and $\overline{M_d}$, the average d orbital energy level of formulated titanium alloys, correlating with the average electronegativity and the radius of elements. The $\overline{B_o}$ and $\overline{M_d}$ values calculated on conventional titanium alloys give a $\overline{B_o}$–$\overline{M_d}$ map (Fig. 1), where α, $\alpha + \beta$ and β-type titanium regions are clearly defined (Abdel-Hady et al., 2006; Kurada et al., 1998). Calculations were made for alloying chemical element, using a "cluster based" method called DVXα (Morinaga et al., 1988). Based on this formulation strategy and considering only bio-inert alloying elements such as Nb, Ta or Zr, they finally developed an optimized quaternary beta titanium alloy called TNTZ (Titanium–Niobium–Tantalum–Zirconium) with the nominal composition (wt%) of Ti–29Nb–13Ta–4.6Zr (Niinomi et al., 2007). Improvements were obvious both from the biocompatibility and from the mechanical point of view since elastic moduli of around 60 GPa were found. The "electronic design" approach allows the comparison of titanium alloys with very different chemical compositions. The interest of this electronic approach is undeniable, showing reliable and consistent experimental results for binary titanium systems such as Ti–Nb or Ti–Ta (Abdel-Hady et al., 2006; Kurada et al., 1998). However, we presently think that extension to multielementary alloys actually rises open questions since electronic interactions between alloying elements are not taken into account into the DVX-α model (using a "composite approach"). As a result, the respective influence of each alloying element on the mechanical behaviour remains unclear with regard to multielementary (ternary or quaternary) systems. On this basis, starting from the well-known TNTZ system (Ti–29Nb–13Ta–4.6Zr) (referred as TN13TZ in this paper), we formulated modified TNTZ compositions Ti–29Nb–11Ta–5Zr (TN11TZ) and Ti–29Nb–6Ta–5Zr (TN6TZ) with various tantalum contents to investigate and compare mechanical properties such as elastic modulus, yield strength and stress-induced martensitic transformation ability. The results are discussed in relation to their respective position in the $\overline{B_o}$–$\overline{M_d}$ electronic diagram and remaining questions are highlighted.

2. Experimental methods

Chemical formulation of the titanium alloys were performed following the Morinaga model based on the cluster DVXα method. Electronic parameters $\overline{B_o}$ and $\overline{M_d}$ for each alloy were calculated from the following expressions: $\overline{M_d} = \sum X_i (M_d)_i$ et $\overline{B_o} = \sum X_i (B_o)_i$ where X_i is the molar fraction of the i element and $(M_d)_i$, $(B_o)_i$ the numerical values of M_d and B_o for each alloying element. The Ti–29Nb–11Ta–5Zr (TN11TZ) and Ti–29Nb–6Ta–5Zr (TN6TZ) (wt%) alloys were prepared using cold crucible levitation melting technique (CCLM). The ingots were subsequently homogenized at 1223 K for 12 h under inert argon atmosphere and then cold rolled with controlled reduction in thickness of 1.90 (true deformation). For thermal treatments, the specimens were encapsulated in quartz tubes under a partial pressure of high-purity argon. The specimens were quenched into water by breaking the quartz tubes. After the solution treatment (1173 K, 2 h), XRD measurements were conducted at room temperature with Cu Ka radiation. Tensile tests were carried out at a strain rate of 2.7×10^{-3} s^{-1}. The gage length of specimens was 30 mm and an extensometer was used for all the mechanical testing. For each tensile cycle, the recovered deformation, the apparent elastic modulus, the incipient modulus and the critical phase transformation stresses are measured (Fig. 2). Specimens for TEM observation were prepared by a conventional twin-jet polishing technique. TEM observations were conducted using a JEOL 2000F instrument operated at 200 kV.