Design of a novel superelastic Ti-23Hf-3Mo-4Sn biomedical alloy combining low modulus, high strength and large recovery strain

Muhammad Farzik Ijaz*, Denis Laillé, Lorène Héraud, Doina-Margareta Gordin, Philippe Castany, Thierry Gloriant**

INSA Rennes, UMR CNRS 6226 Institut des Sciences Chimiques de Rennes, 20 avenue de Buttes de Coëmes, 35708 Rennes cedex 07, France

*Corresponding author. farzik98@gmail.com (M. F. Ijaz)

**Corresponding author. Prof. T. Gloriant. INSA Rennes, France. Tel: +33 223238241.
e-mail: Thierry.Gloriant@insa-rennes.fr

Abstract

In this study, a new Ti-23Hf-3Mo-4Sn superelastic alloy for biomedical applications was elaborated and characterized. Outstanding combination of high strength (~1GPa), low Young's modulus (55 GPa) and large recovery strain of about 4% were achieved. These mechanical properties make this newly developed Ti-23Hf-3Mo-4Sn alloy very promising for biomedical applications.

Keywords: titanium alloy; superelasticity, microstructure; tensile tests.

1. Introduction

Multifunctional β Ti-based alloys elaborated with biocompatible alloying elements have become an important field of investigation for biomedical applications due to their advantageous characteristics, such as low modulus and high elastic recovery [1-8]. Over the years, due to distinct compositional modifications and/or targeted alloy design, several new kinds of metastable β Ti-based alloys with superior superelastic properties have been introduced. For example, metastable β Ti-Nb and Ti-Zr based alloys have been found to exhibit large superelastic recovery strain at room temperature through reversible stress-induced martensitic transformation between parent β phase (body centered cubic structure) and martensite α" phase (orthorhombic structure) [5,6,9-15]. On the other hand, "the d-electron criteria" including Bo/Md map have been used iteratively to predict and evaluate the mechanical stability of β-phase at room temperature [16-18]. Although the different studied systems showed very interesting properties, high mechanical strength still remains a key objective for this kind of alloys [8]. Indeed, for multiple biomedical applications it is necessary to explore new kind of alloying systems that combine low elastic modulus, high mechanical strength and large recovery strain. It is worth noting that these properties are strongly influenced by the chemical composition [16-18]. In some previous study, it has been shown that the binary Ti-Hf based system may offer good opportunity to replace conventional biomaterials due to its high strength and low elastic modulus [19]. However, alloys elaborated from this system did not revealed any superelasticity at room temperature until now. In this study a novel superelastic β-type Ti-23Hf-3Mo-4Sn alloy was designed by coupling d-electron criteria with the phase transformation temperature. For this alloy composition, the Hf content was fixed at 23 at.%, which corresponds to the lowest β-transus temperature point in the binary Ti-Hf phase diagram [20]. In this study, 3 at.% Mo was added in order to retain the β phase at room temperature on quenching. At the same time, the solid solution strengthening effect of Mo content was also exploited [8,11,15]. On the other hand, 4 at.% of Sn was also added due to its well-known significant influence on the superelastic properties of β Ti-alloys by suppressing the harmful ω phase formation [4,12]. For the Ti-23Hf-3Mo-4Sn (at.%) alloy composition, the average value of Bo and Md are calculated to be 2.851 and 2.539 respectively. With such values it can be predicted that the metastable β phase will be retained at room temperature during quenching after solution treatment [16-18] and a superelastic behavior associated to the stress induced martensitic transformation will be elicited at room temperature.

2. Material and methods

The Ti-23Hf-3Mo-4Sn (at.%) ingot was elaborated by cold crucible levitation melting (CCLM) under vacuum, by using a high frequency magnetic induction generator heating system. After melting, a homogenization annealing was performed in the β-phase domain at 1223 K for 72 ks under high vacuum (~10^{-7} mbar) and then quenched in water. After the homogenization step, the ingot was cold rolled up to a reduction level larger than 95% of the initial thickness without intermediate annealing. The final thickness of the cold rolled sheet was about 0.5 mm. Then, from the cold rolled sheet, specimens for tensile tests were machined along the rolling direction. The dimensions of the tensile specimens were 0.5 mm in thickness, 3mm in width and a gage length of 20 mm. The cold rolled tensile specimens were then solution treated under high vacuum (~10^{-7} mbar) at high temperature for 1.8 ks followed by water quenching at room temperature. The aim of this final heat treatment is to restore a fully recrystallized β-phase microstructure from the cold rolled state with a reduced β-grain size. In this study, two different solution treatment temperatures were selected: 1073 K and 1173 K.

Microstructures were characterized and observed by X-ray diffraction (XRD, CuKα radiation) and by optical microscopy (OM). For the optical microscopy observations, samples were mechanically "mirror" polished and etched in a 5 % HF, 5 % HNO_3, 90 % H_2O solution.

The mechanical properties of the different heat treated Ti-23Hf-3Mo-4Sn alloy specimens were evaluated by tensile tests with a strain rate of 10^{-4} s^{-1}. An extensometer was used to evaluate the strain. The superelasticity was more precisely characterized by cyclic loading-unloading tensile tests. With this kind of tests, the strain was incremented by steps of 0.5% and each step was followed by a total release of the stress.

3. Results and discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of cold rolled specimens heat treated at 1173 K (a) and at 1073 K (b) for 1.8 ks, respectively and then quenched in water. On these XRD profiles, it can be observed that both specimens only exhibited the peaks related to the β phase.

Figure 2 shows the typical optical micrographs for the Ti-23Hf-3Mo-4Sn alloy specimens heat treated at 1173 K (a) and at 1073 K (b), respectively. These optical microscopy images clearly show that both solution treated alloys possess an equiaxed β-phase grain microstructure, which are in the good agreement with XRD observations. The average grain sizes of the specimens heat treated at 1073 K and 1173 K were estimated to be about 45 and 70 μm, respectively.

In order to evaluate the mechanical and superelastic properties, cyclic loading-unloading tensile tests until rupture were carried out. Figure 3 shows the cyclic loading-unloading curves obtained for the Ti-23Hf-3Mo-4Sn alloy specimens heat treated at 1173 K (a) and at 1073 K (b) for 1.8 ks, respectively. It can be observed that both specimens revealed a perfect superelastic behavior at room temperature. The presence of the strain-plateau confirms the occurrence of stress induced martensitic transformation ($\sigma_{\beta\rightarrow\alpha''}$) as shown in Fig. 3 (a) and (b). As mentioned above, the superelastic property is attributed to the reversible stress-induced martensitic transformation between the parent β phase (body centered cubic) and the martensite α'' phase (orthorhombic structure) as widely observed in various metastable β Ti-based alloys such as Ti-Nb [4-6,9-11] and Ti-Zr based alloys [13,15]. However, according to our knowledge, no work has claimed the superelastic behavior in Ti-Hf based alloys.

The values of maximum recovery strain, ε_r^{max}, and the critical stress for slip, σ_{CSS}, obtained after cyclic tests were measured for each heat treatment and are listed in Table. 1. In addition, for the sake of comparison, the mechanical characteristics of commercially pure CP-Ti (grade 2), Ti-6Al-4V (grade 5 ELI) and binary Ti-Nb alloys [7,10] are also presented in Table. 1. In the present study, the critical stress for slip, σ_{CSS}, is defined as the stress at which 0.5% of plastic deformation, ε_p, is induced during the cycling tensile test. For better understanding, an illustration is also shown in Fig. 3a. Some points of notice should be mentioned here: firstly, it can be seen that the specimens heat treated at 1173 K and 1073 K exhibited a large recovery strain, ε_r^{max}, of 4.2% and 3.8% respectively as shown in Table. 1. This value of recovery strain revealed in our newly developed Ti-23Hf-3Mo-4Sn alloy is larger than that commonly observed values in binary solution treated Ti-Nb alloys [5,7,10]. Mechanical characteristics listed in Table. 1 also show that the specimen heat treated at 1073 K and 1173 K exhibited a σ_{CSS} of about 620 and 640 MPa, respectively. These values of σ_{CSS} are also much higher than that observed in the classic Ti-Nb based superelastic alloys [5-7,10-12,18].

Consequently, it is supposed that the superior superelastic property of the Ti-23Hf-3Mo-4Sn alloy is due to its higher σ_{CSS}. Thus, according to current understanding, it is believed that the higher value of σ_{CSS} can be attributed to the addition of Mo because the solid solution strengthening effect of Mo is widely reported in literature [11]. Other secondary factor for the improvement of recovery strain could be due to the suppression of ω phase by Sn addition that is also reported in literature [4,12]. Nevertheless, confirmation of these assumptions would require an extensive study and will be the subject of future investigations.

With the present Ti-23Hf-3Mo-4Sn alloy, it can be clearly observed that the ultimate tensile strength, σ_{UTS}, is very high when compared with the previously studied alloys [7,8,10,14,18]. Indeed, 920 MPa for the specimen heat treated at 1173 K and 1010 MPa for the specimen heat treated at 1073 K were reached. Consequently, from tensile test results, it can be concluded that the Ti-23Hf-3Mo-4Sn alloy composition exhibits a unique combination of multifunctional mechanical properties such as and low Young's modulus (~55 GPa), large superelastic recovery strain of ~4% and higher ultimate tensile strength (~1000 MPa) when compared to the other traditional Ti-based implant materials. Based on this comparison, the Ti-23Hf-3Mo-4Sn alloy can be highly considered for advanced biomedical applications due to its biocompatible composition and its good combination of mechanical properties adapted for medical devices.

4. Conclusion

In summary, a new family of biocompatible metastable β-type Ti-Hf based superelastic alloy was introduced in this work. The phase constitution, mechanical and superelastic properties were investigated. After solution treatment and quench, the alloy clearly showed a large recovery strain of about 4% due to reversible stress induced martensitic transformation and high value of critical stress for slip at around 620-640 MPa was observed. Tensile tests have also revealed a very high ultimate tensile strength close to 1 GPa. Thus, the Ti-23Hf-3Mo-4Sn alloy exhibits a novel combination of high strength, low elastic modulus and large recovery strain which was not yet simultaneously reported with other biomedical β Ti-based superelastic alloys.

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Figure and table captions.

Figure 1. XRD profiles from the cold rolled specimens heat treated at: (a) 1173 K and (b) 1073 K for 1.8 ks.

Figure 2. Optical micrographs of the cold rolled specimens solution treated at: (a) 1173 K and (b) 1073 K for 1.8 ks followed by water quenching.

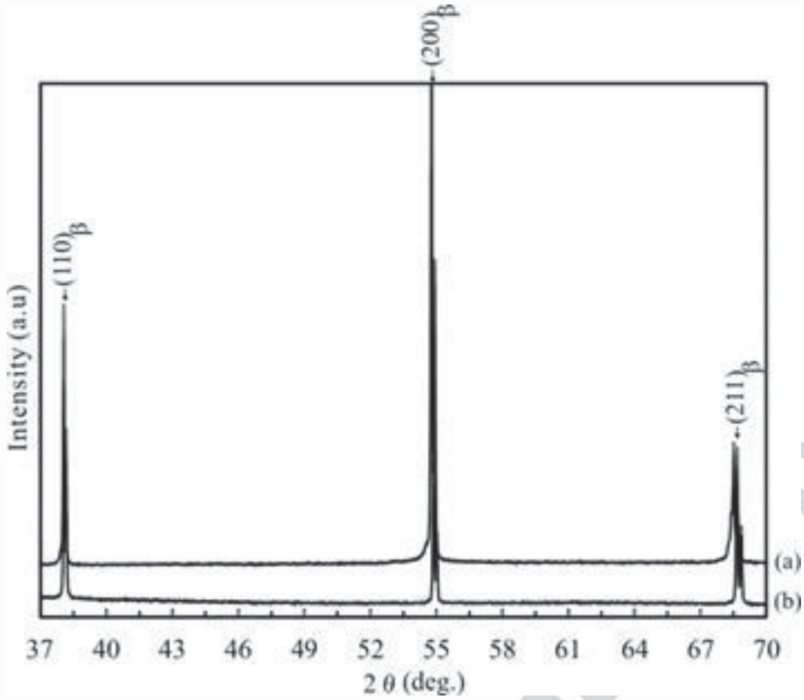
Figure 3. Stress-strain curves obtained by cyclic tensile tests for the specimens solution treated at: (a) 1173 K, and (b) 1073 K for 1.8 ks and quenched in water.

Table 1. Comparison of mechanical and superelastic properties of the studied Ti-23Hf-3Mo-4Sn alloy with some traditional Ti-based implant materials.

Alloy	ε_r^{max} (%)	σ_{CSS} (MPa)	E (GPa)	σ_{UTS} (MPa)
Ti-23Hf-3Mo-4Sn (1173K/1.8ks)	4.2	640	55	920
Ti-23Hf-3Mo-4Sn (1073K/1.8ks)	3.8	620	55	1010
Ti-26Nb	2	360	50	420
Ti-6Al-4V (grade 5 ELI)	0.7	-	110	860
CP-Ti (grade 2)	0.3	-	105	360

Highlights

- A new biomedical metastable β-type Ti-Hf-Mo-Sn superelastic alloy was elaborated.
- The phase constitution, mechanical and superelastic properties were investigated.
- High strength, low Young's modulus and large recovery strain were achieved.



(200)$_\beta$
(110)$_\beta$
(211)$_\beta$
Intensity (a.u)
(a)
(b)
37
40
43
46
49
52
55
58
61
64
67
70
2 θ (deg.)

Figure 1

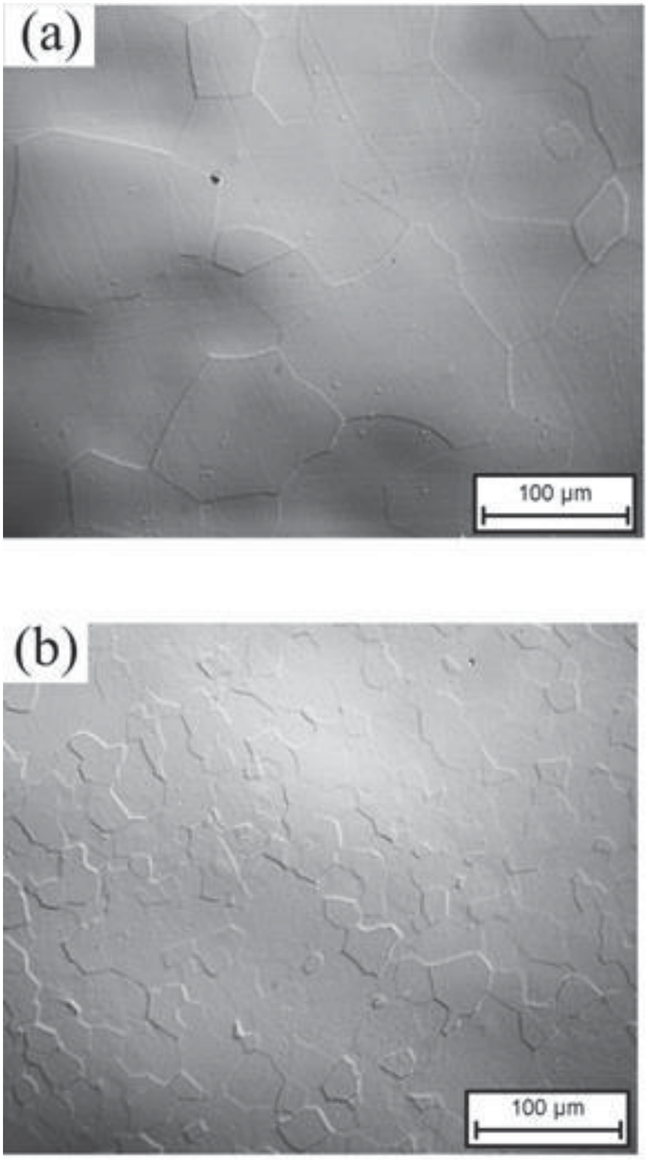


figure 2

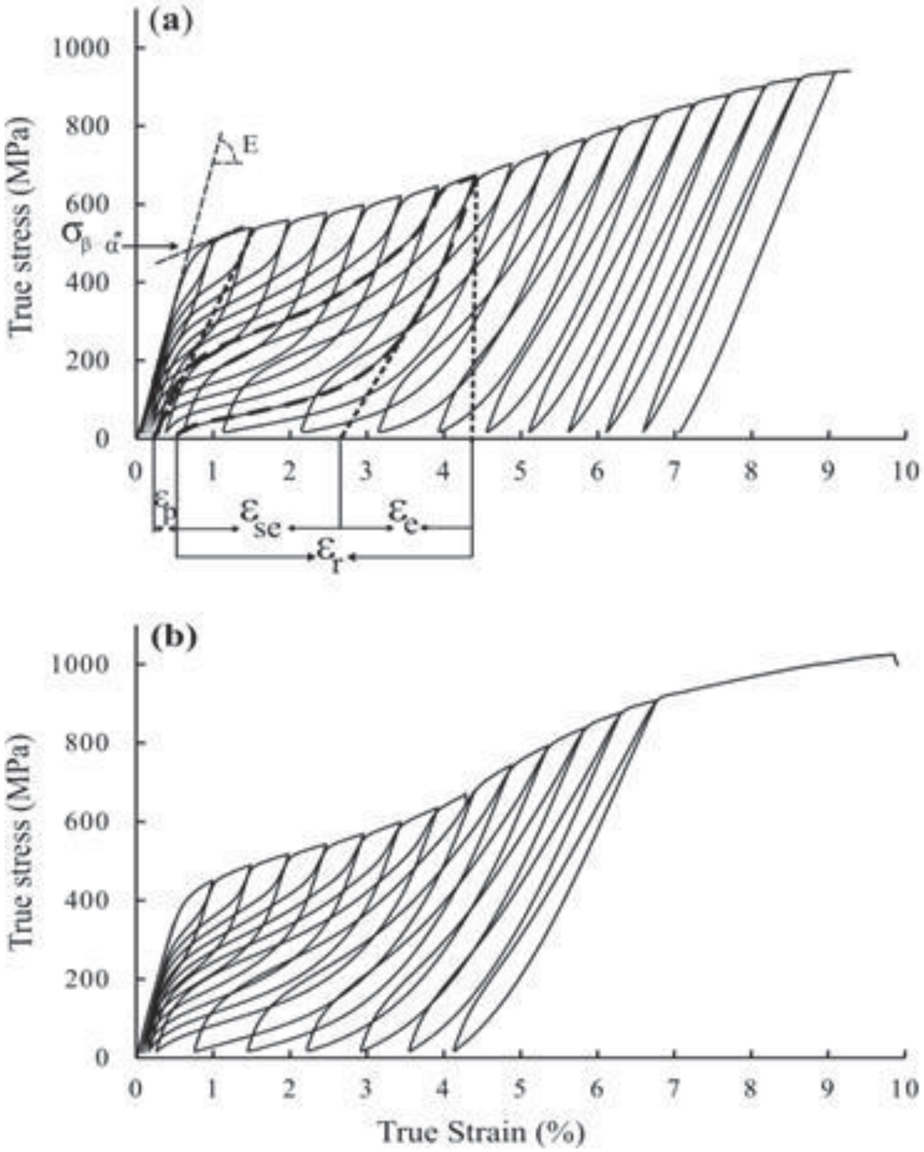

(a)
True stress (MPa)
1000
800
600
400
200
0
E
0
1
2
3
4
5
6
7
8
9
10
(b)
True Strain (%)

figure 3