INTERNATIONAL JOURNAL OF Electroactive Materials

Int. J. Electroactive Mater. **8 (2020) 63-67**
www.electroactmater.com

RECEIVED
22 July 2020

REVISED
07 August 2020

ACCEPTED FOR PUBLICATION
23 August 2020

PUBLISHED
07 September 2020

A Brief Review on the Properties of Titanium as a Metallic Biomaterials

Farrah Noor Ahmad[1,2*], Hussain Zuhailawati[2]

[1]Faculty of Mechanical Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, Jalan Permatang Pauh, 13500 Permatang Pauh, Pulau Pinang, Malaysia.
[2]Biomaterials Niche Area, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Pulau Pinang, Malaysia.
***E-mail**: farra728@uitm.edu.my

ABSTRACT: Titanium and its alloys are getting much attention due to their excellent properties particularly in biomedical applications. However, the current implant materials, i.e. cp-Ti and Ti-6Al-4V alloys exhibit higher elastic modulus than that of the human bone, thus creating a stress shielding effect which leads to implant failure. Recently, the β-type titanium offers a great potential as a future material candidate in fabricating more suitable biomaterials owing to its non-toxicity, allergy-free characteristic, and lower elastic modulus similar to that of the bone. In developing the novel β-type titanium, sufficient knowledge on the β-stabilizing elements required in producing β phase titanium is important. Therefore, the phases and properties of new titanium alloys with their β-stabilizing elements are reviewed.
Keywords: Bone implant; Titanium; Phase transformation

1. Introduction

The rapid growth in the number of older people in many countries has resulted in an increasing demand for bone implants. Currently, 70% - 80% of the clinically used implants are made of metallic materials [1]. Stainless steel, cobalt-chromium alloy, and titanium alloy are among the suitable metallic biomaterials that can be implanted in the human bodies. However, in comparison to the former biomaterials, titanium alloy often becomes the material of choice due to its low density, good biocompatibility, high corrosion resistance, high strength-to-weight ratio, and good mechanical properties [2-3].

The first generation of Ti-based bone implant material is the commercially pure titanium (cp-Ti). However, cp-Ti has a limitation of low mechanical properties. To overcome such restriction, Ti-6Al-4V alloy is used which is considered sufficient to meet the needs for high strength biomaterial applications such as in hip implants, knee implants, bone screws, and plates. This is because Ti–6Al–4V alloy demonstrates superior hardness, strength, and corrosion resistance than cp-Ti [4-5]. However, the presence of vanadium (V) and aluminium (Al) in Ti-6Al-4V alloy is of concern due to their cytotoxic effect on the human body. For long term implantation, Al could develop the risk to neurological disorder and the worst case the Alzheimer's disease while V could increase the potential to allergic reaction and toxicity in human tissues [6]. In fact, a study revealed that high Al content contributes to passive layer breakdown which delays bone integration after implantation [7]. Overall, the release of toxic metal ions in the human body becomes an issue of concern since it could increase the metallic ion content in the blood and produce an unwanted immune response, thus reducing the performance of the metallic implant.

Despite the Ti-6Al-4V alloy of α+β phase being the most commonly used implant material, its elastic modulus (110 GPa) is however still much greater than that of the human cortical bone (10-30 GPa) [8-9]. This leads to the stress shielding phenomenon which results in implant loosening and breakage of their biological contact with the neighbouring tissues. Once the implant loosening takes place, failure will occur. Consequently, a revision surgery is required, and the patient will experience an extreme pain. Therefore, to minimize the stress shielding, a mismatch in elastic modulus should be avoided as much as possible by selecting the most suitable biomaterial with acceptable properties.

The issue associated with Ti-6Al-4V alloy has initiated the idea for exploring a new class of titanium alloy which is the β-Ti alloy. This alloy could replace V and Al as well as adding β-stabilizer that functions to decrease the elastic modulus and hence minimizing the load-bearing capabilities of bone. Niobium (Nb), stannum (Sn), and tantalum (Ta) are among the non-toxic and strong β-stabilizers that have the potential to form homogenous β phase in titanium matrix. Hence, this paper aims to review the properties and phase transformation involved in developing β-type titanium alloys for biomedical applications.

2. Properties and Phase Transformation of Titanium and Its Alloys

Titanium is a transition metal and it belongs to Group IV in the periodic table. It has a high melting point (1668 °C) and exhibits a hexagonal close packed crystal structure (HCP) with an elastic modulus of 116 GPa [10-11]. The density of titanium is considered low (4.54 g/cm3) and is more comparable to the bone density (1.8-2.0 g/cm3) than other metallic biomaterials such as stainless steel (8.0 g/cm3) and cobalt-based alloys (8.5 g/cm3).

Titanium can exist in more than one crystal structure where the transformation is dependent on temperature. Below 882 °C, titanium exists in HCP crystal structure composed of alpha phase (α phase). When heated to temperatures above 882 °C, the HCP structure of titanium undergoes allotropic transformation into body centred cubic (BCC) structure of beta phase (β phase). This transition temperature is known as the transus temperature. The β-transus temperature of titanium alloys represents the minimum temperature above which the equilibrium of α phase does not exist.

In general, there are three types of alloying elements used in titanium alloys: α-stabilizers, β-stabilizers, and neutral elements. The elements that produce α phase in titanium alloys are known as α-stabilizers while the elements yielding β phase are classified as β-stabilizers. β-stabilizers can be further subdivided into β-isomorphous elements and β-eutectoid elements based on the alloying elements added to titanium, as shown in **Fig. 1**. Isomorphous elements such as niobium (Nb), vanadium (V), molybdenum (Mo), and tantalum (Ta) have high solubility in titanium. However, eutectoid elements, i.e. manganese (Mn), chromium (Cr), silicon (Si), iron (Fe), cobalt (Co), nickel (Ni), and copper (Cu) demonstrate very limited solubility in titanium and are prone to intermetallic compound formation. Meanwhile, elements such as stannum (Sn), hafnium (Hf), and zirconium (Zr) are considered as neutral elements since they have nearly no effect on the α/β phase boundary.

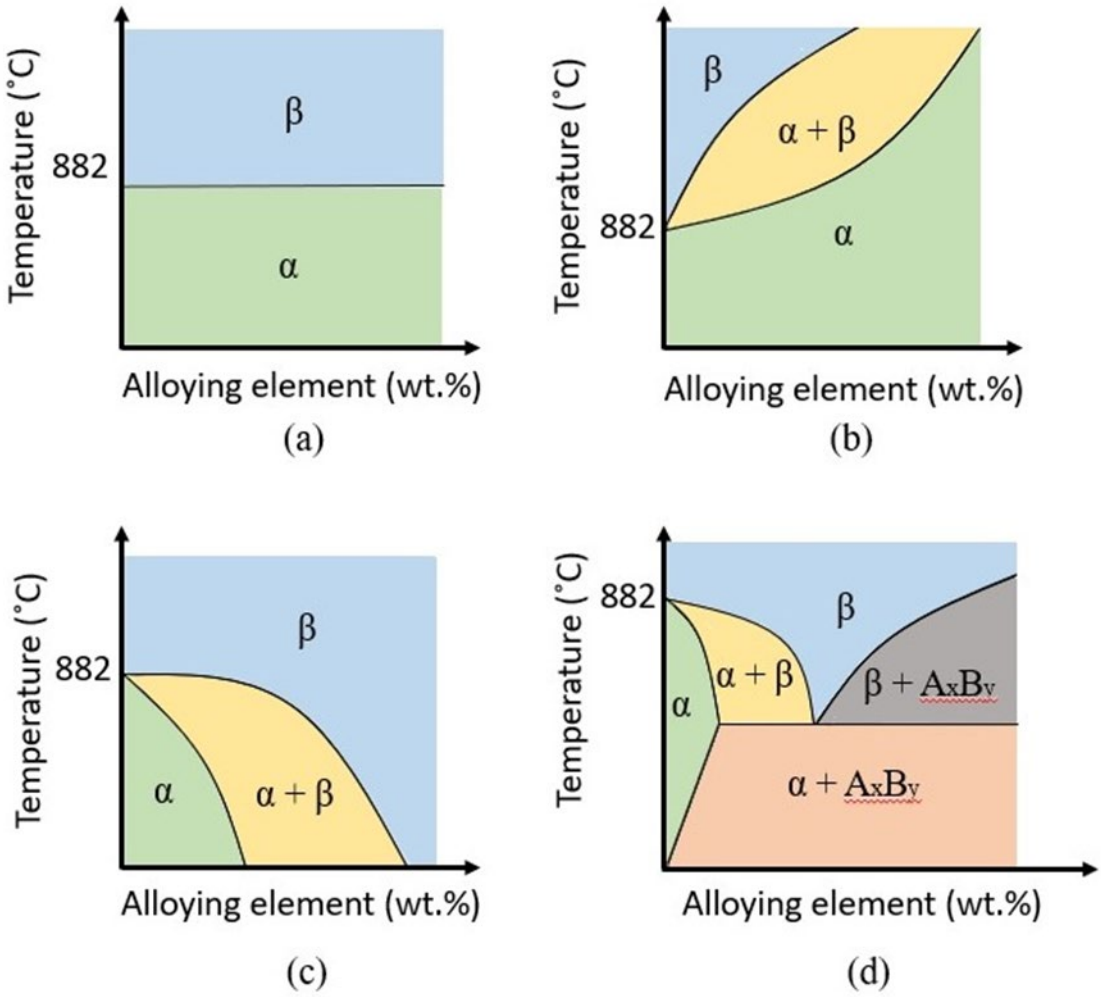


Figure 1: Different types of stabilizer in titanium alloys (a) neutral, (b) α-stabilizing, (c) β-stabilizing (isomorphous) and (d) β-stabilizing (eutectoid) [12]

The addition of alloying elements (α/β stabilizing agents) into titanium could alter the transformation temperature between α-HCP and β-BCC, hence affecting the formation of α phase and β phase. It has been reported that the stability of β phase can be increased by the addition of Zr and Sn in titanium alloys [13]. This is in line with a study reported by Hu et al. (2008) [14] on the alloying effects of Nb, Zr, and Sn on the phase stability of Ti-Nb-Zr-Sn alloy. They found that Nb and Sn could strongly stabilize β phase over the α phase and ω phase, however Zr does not improve the stability of β phase. Sutowo et al. (2019) [15] in their study on the effect of Sn content in Ti-6Mo-6Nb-xSn alloys (x = 0, 4, 8, and 12 wt.%) revealed that the β-transus temperature decreased continuously with increasing Sn content which promotes the formation of β phase. Moreover, they also reported that a higher Sn content produces a lower amount of α phase in β matrix, and the lowest elastic modulus of 88 GPa was contributed by the addition of 12 wt.% Sn. In another study, Han et al. (2015) [16] reported that the addition of Nb β-stabilizer was effective in decreasing the β-transus temperature. They found that the transus temperatures of Ti-15Nb and Ti-20Nb alloys were 777 ˚C and 734 ˚C, respectively. Ti-15Nb alloy exhibited the lowest elastic modulus value of 114 GPa in comparison to other compositions. Meanwhile, Ahmad (2020) [12] has successfully produced cp-Ti and Ti-40Nb alloy by powder metallurgy via mechanical alloying and sintering in argon gas flow at 1200 ˚C. It was found that with the addition of Nb, the intensity of the peaks corresponding to the β phase increases with some weakened α peaks were observed. This suggests that Nb has dissolved in the solvent lattice and the solid solution has been formed, as shown in **Fig. 2**. An increase in the proportion of β phase was also observed, affirming the function of Nb as a β-stabilizer, as presented in **Table 1**. The elastic modulus recorded by the Ti-40Nb alloy was 65.10 GPa.

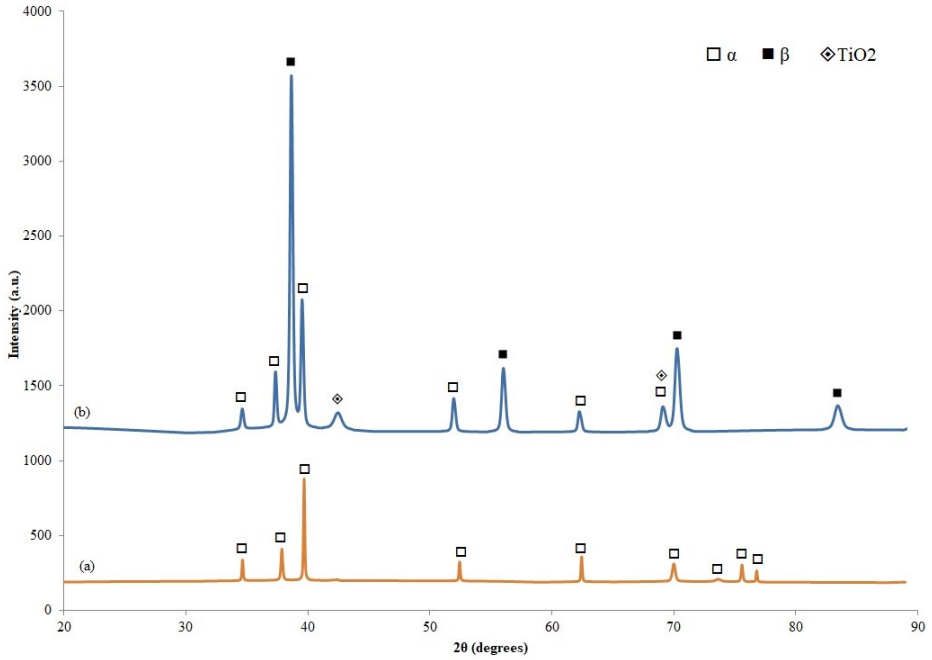


Figure 2: The different phases present in (a) Ti and (b) Ti-40Nb alloy [12]

Table 1: Phase percentage of α phase and β phase in Ti and Ti-40Nb alloy [12]

Metal alloy	Phase percentage (%)	
	α	β
Ti	100	0
Ti-40Nb	11	89

On the other hand, Lindwall et al. (2018) [17] mentioned that the β-transus temperature increases due to the increasing oxygen content in Ti-V alloy which reduces the solubility of vanadium in titanium matrix. Although β-stabilizing agent is added into titanium to enhance the formation of β phase, additional oxygen is however still present as an α-stabilizer due to the high reactivity of titanium with air which promotes oxidization. Therefore, it is important to reduce the oxygen uptake by controlling several parameters such as providing better sintering conditions, i.e. the introduction of argon gas during sintering of titanium alloys. In fact, vacuum sintering should be avoided for titanium alloying because it could cause the leakage of oxygen and nitrogen from the surrounding atmosphere at high temperatures. This consequently oxidizes the metal alloys and further increases their elastic modulus.

3. Phase in Titanium and Its Alloy

Titanium alloys can be classified into three main categories according to the predominant phase(s) in their structures: alpha (α), alpha-beta (α+β), and beta (β). Generally, α phase is used for non-load bearing applications where materials with low strength (240-550 MPa) and good corrosion resistance are required. These include dental implants, maxillofacial and craniofacial implants, screws and staple for spinal surgery, pacemaker case, housings for ventricular-assist device, and implantable fusion drug pump. The higher elastic modulus (116 GPa) in α phase is due to its HCP crystal structure with less slip system than BCC. The less ductile α phase has a lower capability to undergo plastic deformation, which in turn provides a higher elastic modulus to the metal alloy. Ti-6Al-4V alloy consisting of α+β phase appears to be the most popular of titanium alloy in various biomedical applications [18]. This type of titanium alloy shows balanced mechanical properties between α phase and β phase. It also demonstrates moderate strength (600-900 GPa) and slightly lower elastic modulus than cp-Ti (~110 GPa). Ti-6Al-4V alloy is commonly used in hips and knees replacement, fracture fixation plates, and spinal components. Among all the phases in titanium alloys, the β-type titanium alloys show the lowest elastic modulus in the range of 50-80 GPa [19-22]. In addition, the properties of β-type titanium alloys also satisfy the requirements for orthopaedic implants, such as superior biocorrosion resistance, no allergic problems, and excellent biocompatibility [23]. A previous research revealed that the elastic modulus of a non-toxic β-rich Ti-22Nb-10Zr alloy was 47 GPa [24]. On the other hand, according to Jung et al. (2010) [25], the elastic modulus of Ti-35Nb-4Sn alloy was the lowest (40 GPa) among all β-type titanium alloys, which is comparable to that of the human cortical bone. This group of alloy also shows the highest range of strength (650-1100 GPa) which is suitable to be used in load-bearing applications such as implants in hips, knees, shoulders, and elbows.

4. Conclusion

The new generation of β-type titanium alloys is concluded to have low elastic modulus with higher strength, equal to that of the alloy Ti–6Al–4V, which is widely used in the orthopedic field.

Acknowledgement

The authors would like to express gratitude for a financial scholarship from the Ministry of Higher Education of Malaysia and the support provided by Universiti Teknologi MARA (UiTM). They are also would like to thank Universiti Sains Malaysia (USM) for FRGS Grant No. 203/PBAHAN/6071386.

References

1. Y. Li, C. Yang, H. Zhao, S. Qu, X. Lo, X. and Y. Li, Materials (Basel) 7(3) (2014) 1709-1800.
2. A. Khorasani, M. Goldberg, E.H. Doeven, G. Littlefair, Journal of Biomaterials and Tissue Engineering 5(8) (2015) 593-619.
3. V.S. De Viteri, E.Fuentes, IntechOpen 2013.
4. W.F. Ho, S.C. Wu, S.K. Hsu, Y.C. Li, H.C. Hsu, Materials Science and Engineering:C 32 (2012) 517-522.
5. W.F. Ho, C.H. Pan, S.C. Wu, H.C. Hsu, Journal of Alloys and Compounds 472 (2009) 546-550.
6. S. M. Hosnie, M.H. Ismail, M. Yahaya, M., N.A. Haris, I. Todd, Journal of Mechanical Engineering 2(2) (2017) 99-112.
7. A.K. Shukla, R. Balasubramaniam, S. Bhargava, Intermetallics 13 (2004) 631-637.
8. M. Niinomi, Y. Liu, H. Liu, H. Li, Regenerative Biomaterials 3(3) (2016) 173-185.
9. C. Oldani, A. Dominguez, Intech Open (2012) 1-16.
10. N. Mavros, T. Larimian, J. Esqivel, R.K. Gupta, R. Contieri, T. Borkar, , Materials & Design 183 (2019) 108-163.
11. A. Arifin, A.B. Sulong, N. Muhamad, J. Syarif, M.I. Ramli, Materials & Design 55 (2014) 165-175.
12. F.N. Ahmad, Thesis:Mechanical properties and bioactivity of Ti-Nb-HA composite fabricated by mechanical alloying, School of Materials and Mineral Resources Engineering (SMMRE), Universiti Sains Malaysia (2020) 1-210.
13. K. Rajamallu, B.K. Kodli, A. Rajendran, J. Nivedhitha, D.K. Pattanayak, K. Ameyaman, S.R. Dey, Modelling and Simulation in Materials Science and Engineering 25(8) (2017) 085013.
14. Q.-M. Hu, S.-J. Li, Y.-L. Hao, R. Yang, B. Johansson, L. VitosApplied Physics Letters 93(12) (2008) 121902-1 - 121902-3.
15. C. Sutowo, G. Senopati, S. Supriadi, A.W. Pramono, B. Suharno, IOP Conf. Series:Materials Science and Engineering 541 (2019) 1-8.
16. M.K. Han, J.Y. Kim, M.J. Hwang, H.J. Song, Y.J. Park, Materials 8(9) (2015) 5986-6003.
17. G. Lindwall, P. Wang, U.R. Kattner, C.E. Campbell, The Journal of the Minerals, Metals & Materials Society 70(9) (2018) 1692-1705.

18. C. Zhong, J. Liu, T. Zhao, T. Schopphoven, J. Fu, A. Gasser, J.H. Schleifenbaum, Applied Sciences 10(764) (2020) 1-12.
19. M. Geetha, A.K. Singh, R. Asokamani, A.K. Gogia, Progress in Materials Science 54 (2009) 397–425.
20. D. Kuroda, M. Niinomi, M. Morinaga, Y. Kato, T. Yashiro, Materials Science and Engineering:A 243 (1998) 244–249.
21. M. Long, H.J. Rack, Biomaterials 19 (1998) 1621–1639.
22. D. Banerjee, J.C. Williams, Acta Materiala 61 (2013) 844–879.
23. M.T. Mohammed, Z.A. Khan, A.N. Siddiquee, International Journal of Materials and Metallurgical Engineering 8(8) (2014) 822-827.
24. E. Frutos, M. Karlik, J.A. Jimenez, H. Langhansova, J. Lieskovska, T. Polcar, Materials & Design 142 (2018) 44-55.
25. T.K. Jung, H. Matsumoto, T. Abumiya, N. Masahashi, M.S. Kim, S. Hanada, Materials Science Forum 631–632 (2010) 205-210.

© 2020 by the authors. Published by EMS (www.electroactmater.com). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).