IASJ المجلات الاكاديمية العراقية

Tikrit Journal of Pure Science

ISSN: 1813 – 1662 (Print) --- E-ISSN: 2415 – 1726 (Online)

Journal Homepage: http://tjps.tu.edu.iq/index.php/j

The bulk modulus of β-type Titanium Alloys for Hip and Bone Replacement

Adnan Mahmood Khalid

Laboratory Sciences Department, University of Tikrit, Tikrit, Iraq

https://doi.org/10.25130/tjps.v28i1.1263

ARTICLE INFO.

Article history:

-Received: 2 / 8 / 2022

-Accepted: 6 / 10 / 2022

-Available online: 20 / 2 / 2023

Keywords: Bulk modulous β-titanium alloys, biomaterial, hip, and bone replacement.

Corresponding Author:

Name: Adnan Mahmood Khalid

E-mail: adnan.mahmod@tu.edu.iq

Tel:

ABSTRACT

Although aluminum (Al) and vanadium (V) have been shown to be cytotoxic, titanium and its Ti-6AI4V alloy have been utilised extensively as implant materials for many years. This is due to new titanium alloys consisting of non-cytotoxic substances like molybdenum (Mo), tantalum (Ta), niobium (Nb), zirconium (Zr), or tin (Sn) have advanced when treated as a cubic β-phase alloy, which has led to the investigation of Al and V free titanium alloys. When configured as a cubic β-phase alloy, they exhibit abnormal corrosion resistance as well as decreased elasticity moduli that are comparable to the substance of the bone they are repairing.

This work uses synchrotron x-ray diffraction to calculate the unit cell volume of beta-phase gum metal (Ti–23Nb–0.7 Ta–2Zr–1.2O-TNTZ-O system) at pressures 50, 45, 24, and 40 GPa respectively. The Murnaghan, Viet and Birch-Murnaghan equation of state has been applied using the bulk modulus measurement it was about 88.7GP . Additionally, applying the same technique, the bulk moduli of Ti-7.5Mo-1O, Ti-7.2Mo, and Ti2448 have been determined to be 116.1, 50.2, and 116.2 GPa, respectively. The Ti-7.2Mo system has a below-average bulk modulus when compared to all other alloys. For biomedical applications like hip and human bone replacement, which will be the subject of the study, it would be most appropriate to change the (Ti-xMo-xNb-xTa) alloy and investigate its mechanical properties.

1. Introduction

The study of the mechanical properties and microstructure of pure Ti and its alloys for biomedical applications is significant nowadays; because they have a high specific strength, excellent corrosion resistance and are good biocompatible materials [1] compared to stainless steels and Co-Cr alloys [2]. Pure titanium is found at room temperature in the hexagonal closed packed (hcp) α-phase structure. An allotropic transformation at 880°C takes place to a body-centred cubic (bcc) β-phase, which is stable up to the melting point of 1668°C. It is possible to stabilize the β-phase at lower temperatures with so-called β-stabilizer elements added to titanium; this leads to the decrease of the temperature of the allotropic (α to β) transformation [3]. β -stabilizing elements include molybdenum, vanadium, tantalum, and niobium [4]. Mixed-phase $\alpha+\beta$ type alloys like Ti-6Al-4V are extensively utilized for biomaterials, however, it's Young's modulus of about 110 GPa is much higher than that of human bone (9-29 GPa). This mismatch causes bone loss, implant loosening and premature failure of the artificial hip [5]. Moreover, titanium alloys with vanadium or aluminum can cause potential cytotoxicity damage to the human body [6]. Recently biomedical titanium alloys with β-phase Ti alloys have been developed, which typically have a lower Young's modulus, with non-cytotoxic elements such as Nb, Zr, Ta, Mo or Sn, for example Ti-12Mo-3Nb [7], Ti-25Nb-3Zr-3Mo-2Sn [8] Ti–29Nb–13Ta–4.6Zr [9], Ti–12Mo–6Zr–2Fe[10] , Ti-Mo-Nb-Zr alloy [11], TiNbZrTa [12] and TNZTS alloy[13] .

2. Experimental procedure

Alloys are produced by arc melting in an argon environment; Metals in the appropriate ratios (up to about
(20-25 g) are placed when an electric current is fed through a copper crucible that has been cooled by water, producing melting temperatures of up to 3500°C as shown in fig1. The phase composition of the ingots (crushed to produce a powder sample) are determined by X-ray diffraction at the ESRF, in France, using (Siemens D5000 or Bruker D8) to gain information on crystal structure, as shown in table1. The lattice parameter (*a*,*b*,*c*) with angles for BCC (body-centered cubic gum metal. Also, lattice strain, state of ordering, and chemical composition can be taken with this instrument shown in fig.2 , then analyzed by Rietveld profile refinement as shown in figs. 3,4,5,6. Ingots will be subjected to controlled heat-treatment, under either an inert environment or under a dynamic vacuum, in a purpose-built annealing rig.

Table 1: Shows the lattice parameter with angles for body centered cubic for TNTZ-O metal.

a **(Å)** lattice parameter	***b*** **(Å)** lattice parameter	***c*** **(Å)** lattice parameter	**U.C.V** Unit cell volume	**α, β, γ (°)** angles
3.109	3.109	3.109	30.051	90, 90, 90
3.011	3.011	3.011	27.298	90,90,90
3.110	3.110	3.110	30.080	90,90.90
3.877	3.877	3.877	58.275	90,90,90

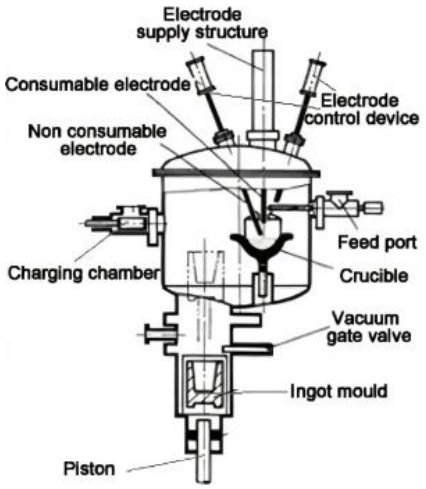

Fig.1: Schematic diagram of arc-melter [14].

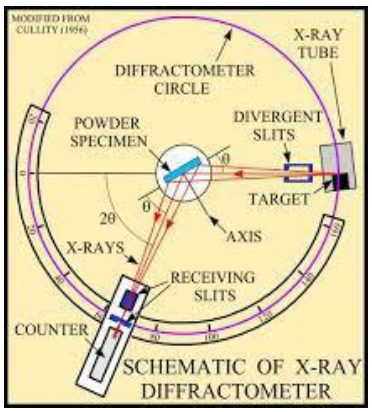

Fig. 2: Shows the major parts of x-ray diffraction [15]

3. Equations of state

For forming solids, the equation of state adequate in continuum mechanics is simply rather several from the ideal gas law. A solid has an assured equilibrium volume V0, and then the energy rises quadratically as volume rises or collapses a little amount from that value. A harmonic solid would be the easiest reasonable reliance of energy on volume, as shown [16]:

$$E = E_0 + \frac{1}{2} B_0 \frac{(V-V_0)^2}{V_0} \quad \ldots\ldots (1)$$

When V_0 is equilibrium volume
V is volume
E is energy
B_O is the isothermal bulk modulus
A constant bulk modulus is followed by the next uncomplicated equation:

$$B = -V \left(\frac{\partial P}{\partial V}\right)_T \quad \ldots (2)$$

P is pressure

$$E = E_0 + B_0 \left(V_0 - V + V \, ln \, ln \left(\frac{V}{V_0}\right)\right) \ldots (3)$$

3.1 Murnaghan equation of state

The equation of state was also obtained in 1944 at Johns Hopkins University by Francis D. Murnaghan To start with, deal with the pressure [16].

$$P = -\left(\frac{\partial E}{\partial V}\right)_S \quad \ldots (4)$$

Bulk modulus in this cause given:

$$B = -V \left(\frac{\partial P}{\partial V}\right)_T \quad \ldots (5)$$

Analytically, the bulk modulus pressure coming from:

$$\underline{B} = -V \left(\frac{\partial B}{\partial P}\right)_T \quad \ldots\ldots (6)$$

If take $B' = B'_0$ to be a constant, then it is established to modify little with pressure:

$$B = B_0 + \underline{B_0} P \quad \ldots\ldots (7)$$

In this case, equate this with (2) and readjust as where B_0 is the value of B when $P = 0$.

$$\frac{dV}{V} = -\frac{dP}{B_0 + \underline{B_0} P} \quad \ldots\ldots\ldots (8)$$

Integrating this outcome in:

$$P(V) = \frac{B_0}{\underline{B_0}} \left(\left(\frac{V_0}{V}\right)^{\underline{B_0}} - 1\right) \quad \ldots\ldots\ldots\ldots\ldots \quad (9)$$

or comparably:

$$V(P) = V_0 \left(1 + \underline{B_0} \frac{P}{B_0}\right)^{\frac{-1}{\underline{B_0}}} \quad \ldots\ldots\ldots\ldots\ldots \quad (10)$$

Substituting (6) into: $E = E_0 - \int \quad PdV$
The equation of state for energy outcomes:

$$E(V) = E_0 + \frac{B_0 V}{B_0}\left(\frac{\left(\frac{V_0}{V}\right)^{B_0}}{B_0 - 1} + 1\right) - \frac{B_0 V_0}{B_0 - 1} \quad \ldots\ldots\ldots (11)$$

3.2 Birch–Murnaghan equation of state

Francis Birch of Harvardis announced in 1947 the third-order Birch–Murnaghan isothermal equation of state, followed by [17]:

$$P(V) = \frac{3B_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left\{1 + \frac{3}{4}(B_0 - 4)\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]\right\} \quad \ldots\ldots\ldots (12)$$

E(V) is achieved by integration of the pressure repeatedly:

$$E(V) = E_0 + \frac{9V_0B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^3 B_0 + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2\left[6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\} \ldots\ldots\ldots (13)$$

3.3 Vinet equation of state

A group of equations used to define the equation of the state of solid objects is called the Vinet equation of state. It is a modification of the Birch–Murnaghan equation of state[18]. There are four inputs that the equation is placed on, which are: the isothermal bulk modulus B0, the derivative of bulk modulus regarding pressure (B'0), the volume V0, and the thermal expansion; they are all calculated at zero pressure (P=0) at a single temperature. The same equation holds for all classes of solids and an expanded range of temperatures.

The cube root of the particular volume would be [19]:

$\eta = (V/V_O)^{1/3}$

The state of the equation will be given as:

$P = 3B_0(1 - \eta/\eta^2)\, e^{(3/2(B_0 - 1)(1 - \eta)}$

4. Results

Bulk modulus were determined from experimental values of *P* versus *V* by using EosFit7 software for four materials: Gum alloy presented with (TNTZ-O), Ti-7.5Mo-1O, Ti-7.2Mo and Ti2448 (Ti-24Nb-4Zr-8Sn). Bulk moduli have been calculated by using three different equations, Murnaghan,Vient and the Birch-Murnaghan, the results of which are given in table 1 . The fig.3, 4, 5 and 6 (a, b ,c, and d) show fits of the Birch-Murnaghan equation of state, a comparison of the bulk modulus shows that the Ti-7.2Mo system has the lowest value, 50.2 GPa. Notably, this value is lower than that of the commercial shape-memory alloy TNTZ-O, 88.7 GPa. The reason behind that is the presence of the β-Ti phase, adding a percentage of Mo a presenting a β-Ti phase which reduces the mechanical properties [20, 21].

Table 2: Shows Bulk modulus for materials used in the present work with different equations of state

Material	Murnaghan K (GPa)	Birch-Murnaghan K (GPa)	Vinet K (GPa)
TNTZ-O	94.2	88.7	88.5
Ti-7.5Mo-1O	118.5	116.1	117.4
Ti-7.2Mo	61.3	50.2	51.4
Ti2448	118.4	116.2	117.2

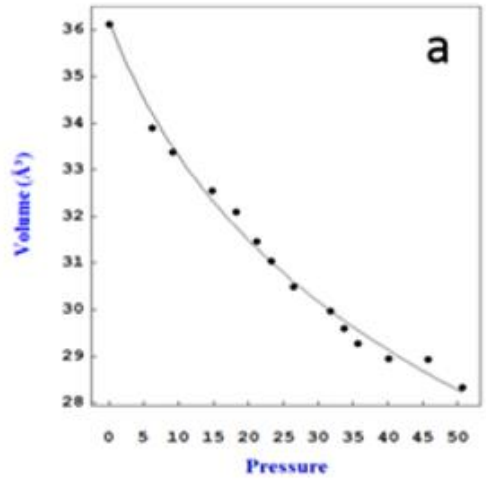

Fig. 3: Unit cell volume as a function of pressure (in GPa) obtained from Reitfeld refinement of the X-ray diffraction data for TNTZ-O metal, the solid lines are fits of the of Birch-Murnaghan equation state.

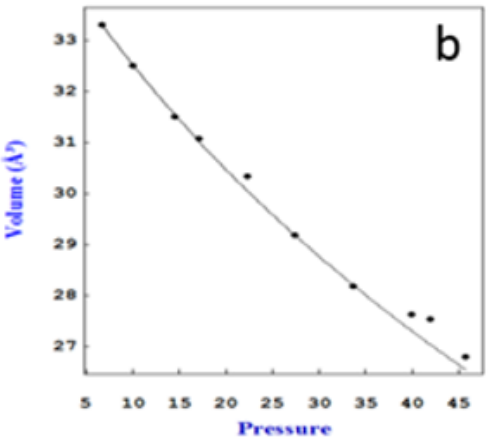

Fig. 4: Unit cell volume as a function of pressure (in GPa) obtained from Reitfeld refinement of the X-ray diffraction data for Ti7.5-Mo-1O, the solid lines are fits of the of Birch-Murnaghan equation state.

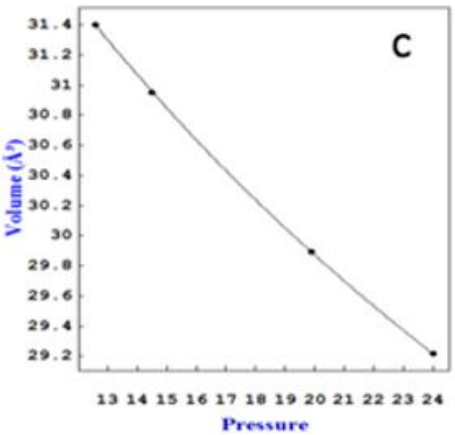

Fig. 5: Unit cell volume as a function of pressure (in GPa) obtained from Reitfeld refinement of the X-ray diffraction data for Ti7.2-Mo, the solid lines are fits of the of Birch-Murnaghan equation state.

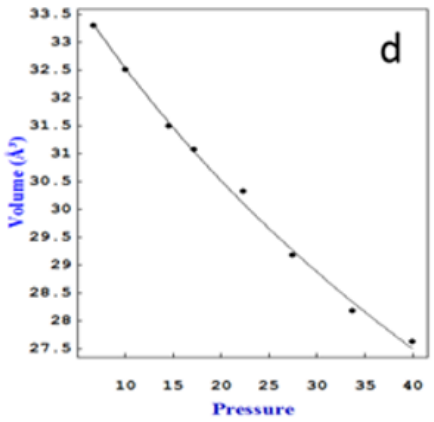

Fig. 6: Unit cell volume as a function of pressure (in GPa) obtained from Reitfeld refinement of the X-ray diffraction data for Ti2248, the solid lines are fits of the of Birch-Murnaghan equation state.

Depending on modeling, a set of experimental parameters can be used to characterize the powder neutron diffraction pattern. The background, crystal lattice and symmetry, crystal structure, crystal microstructure, instrumental factors, and others are among the many contributions to the pattern that are included in these parameters. Modern software really allows users to add, edit, and enhance any parameter, making the process modular.

In addition, Reitfeld refinement gets good experimental parameters such as unit cell and profile of samples before fitting structure it can also be estimated the best possible fit when profiles are irregular and fit an additional phase where the structure is not known. Then the parameters can be simultaneously refined until the calculated pattern matches the experimentally collected data. Once a satisfactory match is achieved, the crystal structure is considered refined.

5. Conclusion

This study uses synchrotron x-ray diffraction to estimate the unit cell size of β-type TNTZ-O system at different pressures. These computations resulted in the measurements of the following bulk modulus

- TNTZ-O = 88.7 Gpa.
- Ti-7.5Mo-1O =116.1 Gpa.
- Ti-2448= (Ti-24Nb-4Zr-8Sn) 116.2 Gpa.
- Ti-7.2Mo= 50.2 Gpa.

Moreover, different equations of state have been used in this work such as;

Murnaghan, Birch-Murnaghan and Vient equation of state. It has been seen that Birch-Murnaghan gives us more accurate results compared to the others that obtained the bulk modulus of biomedical materials.

Future research will be focused on the situation of changing the (TMNT) alloys going forward and will investigate their mechanical qualities best suitable for biomedical applications.

References

[1] Wang, X., Li, Y., Xiong, J., Hodgson, P. D., and Wen, C. E. (2009). Porous TiNbZr alloy scaffolds for biomedical applications. *Acta biomaterialia*, ***5*(9):** 3616-3624.

[2] Niinomi, M. (2008). Mechanical biocompatibilities of titanium alloys for biomedical applications. *Journal of the mechanical behavior of biomedical materials*, ***1*(1):** 30-42.

[3] Jackson, M. J., Handy, R. G., Whitfield, M. D., Burgess, J. W., Robinson, G. M., Novakov, T., Phoenix, D. A. (2014). 9.1 Metallurgical Aspects. *Anti-Abrasive Nanocoatings: Current and Future Applications*, 225.

[4] Welsch, G., Boyer, R., & Collings, E. (1993). *Materials properties handbook: titanium alloys*: ASM international.

[5] Wang, X., Chen, Y., Xu, L., Xiao, S., Kong, F., & Woo, K. D. (2011). Ti–Nb–Sn–hydroxyapatite composites synthesized by mechanical alloying and high frequency induction heated sintering. *J Mech Behav Biomed Mater*, ***4*(8):** 2074-2080.

[6] Wang, X., Chen, Y., Xu, L., Liu, Z., & Woo, K.-D. (2013). Effects of Sn content on the microstructure, mechanical properties and biocompatibility of Ti–Nb–Sn/hydroxyapatite biocomposites synthesized by powder metallurgy. *Materials & Design*, ***49*(0):** 511-519.

[7] Niinomi, M., Nakai, M., & Hieda, J. (2012). Development of new metallic alloys for biomedical applications. *Acta Biomater*, *8*(11), 3888-3903. http://dx.doi.org/10.1016/j.actbio.2012.06.037.

[8] Tian, Y., Yu, Z., Ong, C. Y. A., Kent, D., & Wang, G. (2015). Microstructure, elasticdeformation behavior and mechanical properties of biomedical β-type titanium alloy thin-tube used for stents. *J Mech Behav Biomed Mater*, ***45*(0):** 132-141. http://dx.doi.org/10.1016/j.jmbbm.2015.02.001.

[9] Y.L. Hao, M. Niinomi, D. Kuroda, K. Fukunaga, Y.L. Zhou, R. Yang, A. Suzuki . Metall. Mater. Trans., A, 33A (2002), p. 3137

[10] Rack, H.J. and Qazi, J.I., 2006. Titanium alloys for biomedical applications. *Materials Science and Engineering: C*, *26*(8), p: 1269-1277.

[11] Nnamchi, P. S., Obayi, C. S., Todd, I., & Rainforth, M. W. (2016). Mechanical and electrochemical characterisation of new Ti–Mo–Nb–Zr alloys for biomedical applications. Journal of the Mechanical Behavior of Biomedical Materials, 60, 68-77.

[12] Luo, X., Yang, C., Li, R. Y., Wang, H., Lu, H. Z., Song, T., ... & Li, Y. Y. (2022). Effect of silicon content on the microstructure evolution, mechanical properties, and biocompatibility of β-type TiNbZrTa alloys fabricated by laser powder bed fusion. Biomaterials Advances, 133, 112625.

[13] Luo, X., Liu, L. H., Yang, C., Lu, H. Z., Ma, H. W., Wang, Z., ... & Li, Y. Y. (2021). Overcoming the strength–ductility trade-off by tailoring grain-

boundary metastable Si-containing phase in β-type titanium alloy. Journal of Materials Science & Technology, 68, 112-123.

[14] Edmund Bühler GmbH. 2014. Compact Arc Melter MAM-1.

[15] Connolly, J. R. (2007). Introduction to X-ray powder diffraction. *Material in this document is*.

[16] F.D. Murnaghan, 'The Compressibility of Media under Extreme Pressures', in Proceedings of the National Academy of Sciences, vol. 30: p. 244-247, 1944.

[17] Francis Birch, 'Finite Elastic Strain of Cubic Crystals', in Physical Review, vol. 71, pp. 809-824 (1947).

[18] Pascal Vinet, John R. Smith, John Ferrante and James H. Rose (1987). "Temperature effects on the universal equation of state of solids". Physical Review B. 35 (4): 1945–1953. doi:10.1103/physrevb.35.1945. hdl: 2060/19860019304 .

[19] F.D. Stacey; B. J. Brennan; R. D. Irvine (1981). "Finite strain theories and comparisons with seismological data". Surveys in Geophysics. **4** (4): 189–232. doi:10.1007/BF01449185.

[20] Cardoso, G.C., de Almeida, G.S., Corrêa, D.O.G., Zambuzzi, W.F., Buzalaf, M.A.R., Correa, D.R.N. and Grandini, C.R., 2022. Preparation and characterization of novel as-cast Ti-Mo-Nb alloys for biomedical applications. Scientific Reports, 12(1), pp.1-9.

[21] Raganya, L., Moshokoa, N., Obadele, B.A., Olubambi, P.A. and Machaka, R., 2021. Investigation of the tensile properties of heat treated Ti-Mo alloys. Materials Today: Proceedings, 38, pp.1044-1048.

معاملات الحجم لسبائك بيتا تيتانيوم لاستبدال الورك والعظام

عدنان محمود خالد

كلية الصيدلة ، جامعة تكريت ، تكريت ، العراق

الملخص

على الرغم من أن الألمنيوم والفاناديوم قد ثبت أنهما سامان للخلايا ، فقد تم استخدام التيتانيوم وسبائك Ti-6AI4V على نطاق واسع كمواد للزرع لسنوات عديدة. ويرجع ذلك إلى أن سبائك التيتانيوم الجديدة المكونة من مواد غير سامة للخلايا مثل الموليبدينوم ، والتنتالوم ، والنيوبيوم ، والزركونيوم، والقصدير قد تقدمت عند معالجتها على أنها سبيكة مكعبة طورها بيتا، مما أدى إلى التحقيق في سبائك التيتانيوم الخالية من الألمنيوم والفاناديوم. عند تكوينها على شكل سبيكة مكعب طورها بيتا، فإنها تُظهر مقاومة غير طبيعية للتآكل بالإضافة إلى انخفاض معدلات المرونة التي يمكن مقارنتها بمادة العظام التي يتم إصلاحها. يستخدم هذا العمل حيود الأشعة السينية السنكروترونية لحساب حجم خلية وحدة طور بيتا ل (نظام Ti – 23Nb – 0.7 Ta – 2Zr – 1.2O-TNTZ-O) عند ضغوط 50 و 45 و 24 و 40 جيجا باسكال على التوالي. تم تطبيق معادلة الحالة Murnaghan و Viet و Birch-Murnaghan باستخدام قياس معامل الحجم الذي كان حوالي GP88.7. بالإضافة إلى ذلك، بتطبيق نفس التقنية ، تم تحديد معاملات الحجم لـ Ti-7.5Mo-1O و Ti-7.2Mo و 2448Ti لتكون 116.1 و 50.2 و 116.2 جيجا باسكال، على التوالي. يحتوي نظام Ti-7.2Mo على معدل مرونة أقل عند مقارنته بجميع السبائك الأخرى. بالنسبة للتطبيقات الطبية الحيوية مثل الورك واستبدال العظام البشرية ، والتي ستكون موضوع الدراسة ، سيكون من الأنسب تغيير سبيكة (Ti-xMo-xNb-xTa) والتحقق من خصائصها الميكانيكية.