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Compositional library of β Ti-Nb-Zr alloy coatings applied to biomedical prostheses

Biblioteca composicional de recobrimentos da liga Ti-Nb-Zr β aplicada às próteses biomédicas

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ABSTRACT

The β Ti-based alloys have attracted considerable interest as biomedical materials due to their unique characteristics, such as excellent biocompatibility, low elastic modulus, low density, and corrosion and wear resistances in biological environment. Ti, Nb, and Zr are non-toxic and non-allergenic biocompatible metals, and the addition of Nb and Zr to Ti favors the mechanical compatibility between the alloy and the bone. The addition of Nb to Ti yields to the stabilization of the β phase, and the addition of Zr to the Ti-Nb system increases the β stabilizing effect. However, the ideal amounts of the constituent elements in the Ti-Nb-Zr ternary system are uncertain. Combinatorial strategies allow for the production and characterization of many alloys simultaneously, and magnetron sputtering has been used to generate compositional libraries for ternary thin films and coatings. In this study, Ti-Nb-Zr ternary alloy coatings were deposited by magnetron sputtering on a Si (100) wafer substrate. The Ti, Nb, and Zr targets were positioned in a triangular configuration below the Si substrate. A composition gradient was formed over all the substrate area. Chemical, structural, and morphological analyses were performed by energy dispersive spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and atomic force microscopy.

KEYWORDS: Compositional library, Titanium-based alloy coatings, Biomedical prosthesis.

RESUMO

As ligas à base de Ti β tem atraído considerável interesse como materiais biomédicos por causa das suas características únicas, tais quais excelente biocompatibilidade, baixo módulo de elasticidade, baixa densidade e resistências à corrosão e ao desgaste em ambiente biológico. Ti, Nb e Zr são metais biocompatíveis atóxicos e não alergênicos, e a adição de Nb e Zr a Ti favorece a compatibilidade mecânica entre a liga e o osso. A adição de Nb a Ti leva à estabilização da fase β, e a adição de Zr ao sistema Ti-Nb aumenta o efeito estabilizador de β, entretanto as quantidades ideais dos elementos constituintes ainda são incertas. As estratégias combinatórias permitem a produção e a caracterização de muitas ligas simultaneamente, e a pulverização magneto-catódica tem sido usada para gerar bibliotecas composicionais de filmes finos e recobrimentos ternários. Neste estudo, recobrimentos de ligas ternárias Ti-Nb-Zr foram depositados por pulverização magneto-catódica sobre um substrato de bolacha de Si (100). Os alvos de Ti, Nb e Zr foram posicionados em uma configuração triangular abaixo do substrato de Si. Um gradiente de composição foi formado sobre toda a área do substrato. As análises químicas, estruturais e morfológicas foram feitas por espectroscopia de energia dispersiva, espectroscopia de fotoelétrons excitados por raios X, difração de raios X e microscopia de força atômica.

PALAVRAS-CHAVE: Biblioteca composicional, recobrimentos de ligas à base de titânio, Próteses biomédicas.

INTRODUCTION

The most commonly metal alloy employed in orthopedic and dental implants is the 316L stainless steel, due to its easy fabrication and low cost of production[1]. However, recent studies have shown that its low corrosion resistance and fretting in the human organism enhance the occurrence of premature failure of the device, and its compositional elements cause hypersensitivity to the human body[2,3]. The corrosion of stainless steel in the body environment causes the release of Ni and Cr ions, which have toxic effect[4]. This is a strong motive for the use of alternative alloys in biomedical applications.

Ti-based alloys present excellent properties for biomedical applications, such as biocompatibility, low elastic modulus, low density, and corrosion and wear resistances in biological environment[1,3]. β (body centered cubic – BCC) phase Ti alloys stand out due to their low elastic modulus, which is important because of the charge transfer between the implant and the tissue around it[3,5]. Nb is a non-toxic and non-allergenic element, and its addition to Ti helps to stabilize the β phase[6], but, depending on the composition, undesirable phases can precipitate, such as ω-Ti, a metastable phase with trigonal or hexagonal close packed structure[7]. Zr, which is also a non-toxic and non-allergenic element, can be added to the Ti-Nb alloys to suppress the formation of the ω phase[8]. Ti, Nb, and Zr have total solubility among themselves, but the ideal amounts of the constituent elements in the Ti-Nb-Zr ternary system are uncertain.

Combinatorial strategies allow for the production and characterization of many alloys simultaneously[9,10]. The magnetron sputtering technique is adequate to generate compositional libraries for ternary coatings[10,11]. The main objective of this work was to establish the optimal composition of the Ti-Nb-Zr system. The ternary alloy coatings were deposited by magnetron sputtering on a Si (100) substrate, and the compositions, structures, and morphologies were evaluated by energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and atomic force microscopy (AFM).

EXPERIMENTAL SETUP AND METHODOLOGY

The Ti-Nb-Zr thin film coatings were manufactured with the magnetron sputtering equipment AJA Orion 8 Phase II J. The substrate chosen for this research was a Si (100) wafer with diameter of 4 in and thickness of 0.5 mm, and the targets employed were Ti, Nb, and Zr disks having diameter of 2 in and thickness of 6 mm, with purities of 99.995% (Ti) and 99.95 (Nb and Zr). All the targets were positioned under the substrate in a triangular geometry, as illustrated in Fig. 1. The deposition rates used in this work were 1.0 Å s^{-1} for Ti, 0.5 Å s^{-1} for Nb, and 0.3 Å s^{-1} for Zr, and they were determined accordingly to the elemental composition desired, which were between 20-30 at.% Nb and 10-20 at.% Zr in the effective plasma region. The deposition conditions were: base pressure of 1.0×10^{-5} Pa, working pressure of 0.67 Pa, argon flux of 20 sccm, and applied bias of 30 V.

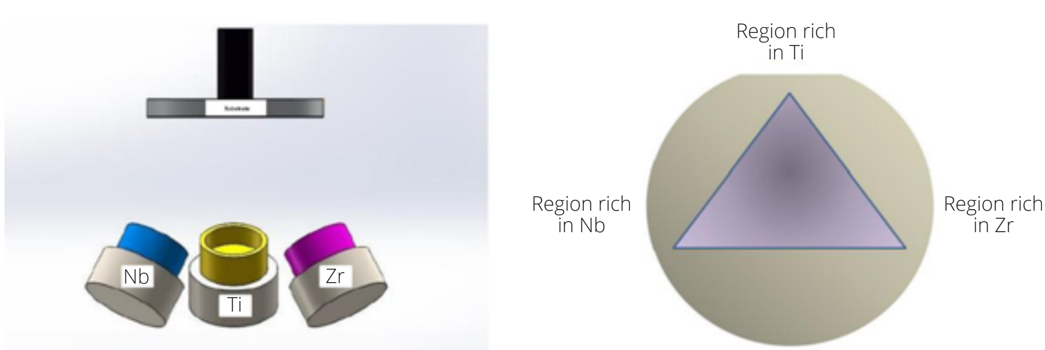

Figure 1: Schematics of the Ti, Nb, and Zr targets and the Si (100) substrate configuration used in the coating processing.

Chemical, structural, and morphological analyses were performed by EDS, XPS, XRD, and AFM. EDS analysis was carried out using an Oxford Link Tentafet X-ray detector. XRD data were acquired by a Bruker diffractometer, model D8 Advance ECO, using a Cu Kα source (λ = 1.5405 Å), acceleration voltage of 40 kV, and current of 20 mA. The AFM images were acquired with a Bruker nanoscope V multimode microscope, using a peak force mode; the surface area and grain size values were obtained using NanoScope Analysis software. XPS analysis was performed using a Scienta Omicron spectrometer, model ESCA+, with a monochromatic Al Kα source (hν = 1486.6 eV), and the data analysis was done with the CasaXPS© software.

RESULTS AND DISCUSSION

The chemical analysis performed by EDS allowed to know the compositions of four distinct regions of the Ti-Nb-Zr ternary alloy coating deposited on a Si (100) wafer substrate. The compositional results are indicated on the Ti-Nb-Zr ternary diagram displayed in Fig. 2. The four selected coatings have the following compositions (in at.%): $Ti_{49}Nb_{14}Zr_{37}$, $Ti_{68}Nb_{12}Zr_{20}$, $Ti_{67}Nb_{21}Zr_{12}$, and $Ti_{67}Nb_{28}Zr_{5}$.

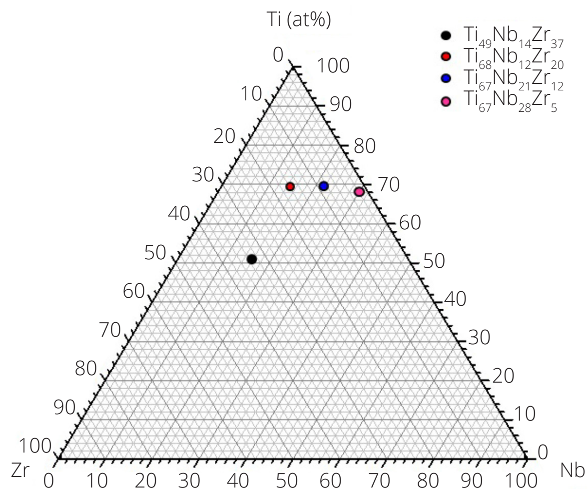

Figure 2: Compositions obtained by energy dispersive spectroscopy for the Ti-Nb-Zr coatings deposited on a Si (100) wafer substrate.

It was also performed a crystallographic analysis by XRD, and the diffractograms are displayed in Fig. 3. The most intense peak was associated to the Si substrate, and the observed (110), (200), and (211) diffraction peaks at 40°, 59°, and 72°, respectively, were characteristic of the β (BCC) phase, according to JCPDS data file No. 44-1288[12,13]. A very small peak at 76° was related to the α (hexagonal close packed – HCP) phase. These results indicate that the addition of both Nb and Zr to Ti stabilized the β phase.

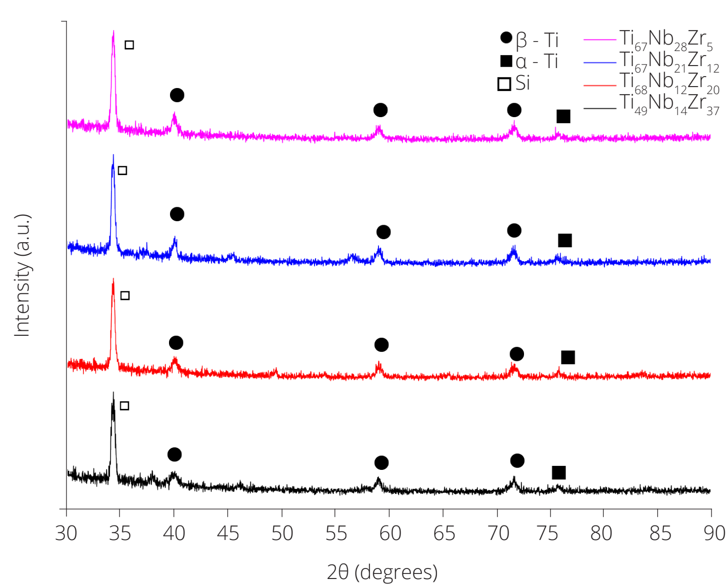

Figure 3: Diffractograms for the four deposited coatings.

Figure 4 displays the images obtained by AFM for (Fig. 4a) $Ti_{49}Nb_{14}Zr_{37}$, (Fig. 4b) $Ti_{68}Nb_{12}Zr_{20}$, (Fig. 4c) $Ti_{67}Nb_{21}Zr_{12}$, and (Fig. 4d) $Ti_{67}Nb_{28}Zr_{5}$ coatings deposited on a Si (100) wafer substrate. The respective roughness (Ra) values are: 5.9, 3.0, 3.2, and 3.9 nm. The highest Ra value corresponds to the coating with the greatest amount of Zr.

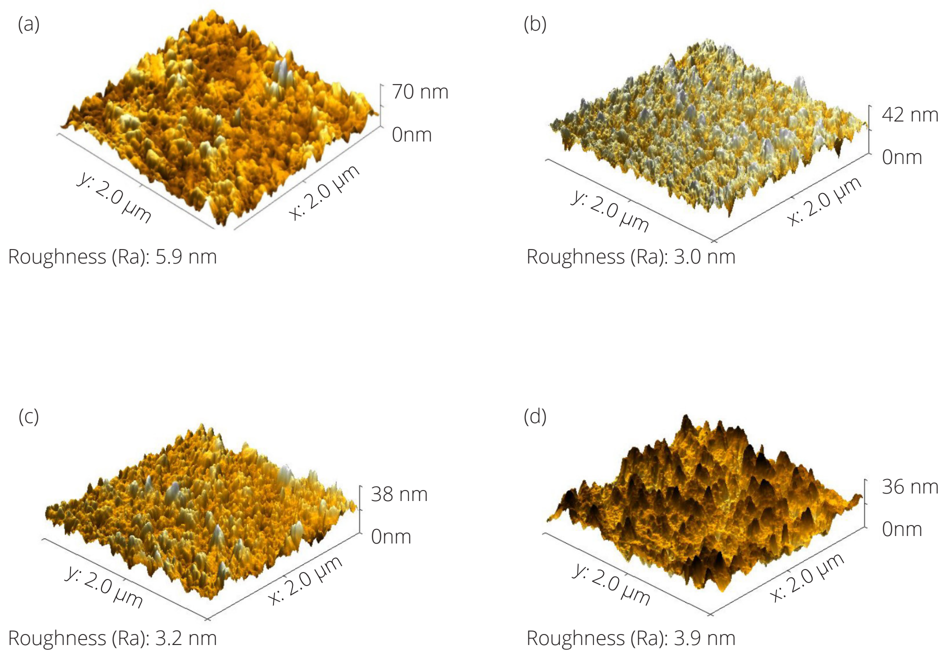

Figure 4: Atomic force microscopy images of the (a) $Ti_{49}Nb_{14}Zr_{37}$, (b) $Ti_{68}Nb_{12}Zr_{20}$, (c) $Ti_{67}Nb_{21}Zr_{12}$, and (D) $Ti_{67}Nb_{28}Zr_{5}$ coatings deposited on a Si (100) wafer substrate.

Figures 5-8 present the XPS long scans for the $Ti_{49}Nb_{14}Zr_{37}$, $Ti_{68}Nb_{12}Zr_{20}$, $Ti_{67}Nb_{21}Zr_{12}$, and $Ti_{67}Nb_{28}Zr_{5}$ coatings, respectively. All spectra show that the coating surfaces have C, O, Ti, Nb, and Zr, confirming the formation of the ternary alloy coatings. The main peaks of the metal constituents of the ternary alloy coatings were Ti $2p_{3/2}$, Nb $3d_{5/2}$, and Zr $3d_{5/2}$. The binding energies of these Ti $2p_{3/2}$, Nb $3d_{5/2}$, and Zr $3d_{5/2}$ peaks were 458.5 eV, 207.0-207.5 eV, and 182.0-182.5 eV, which correspond to TiO_2, Nb_2O_5, and ZrO_2[14,15]. Carbon is commonly detected by XPS, and it is due to adsorbed hydrocarbon molecules on the surface[15]. Oxygen is also detected and related to adsorbed CO and/or CO_2, and metallic oxides formed on the surface[15].

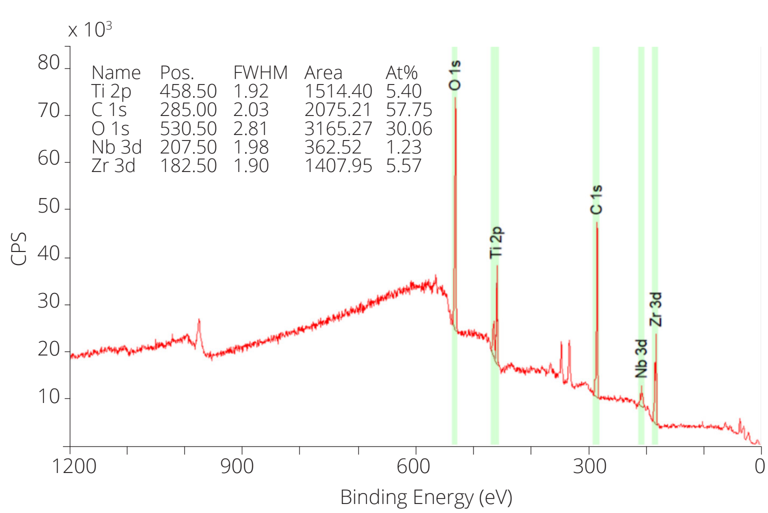

Figure 5: X-ray photoelectron spectroscopy long scan for the $Ti_{49}Nb_{14}Zr_{37}$ coating.

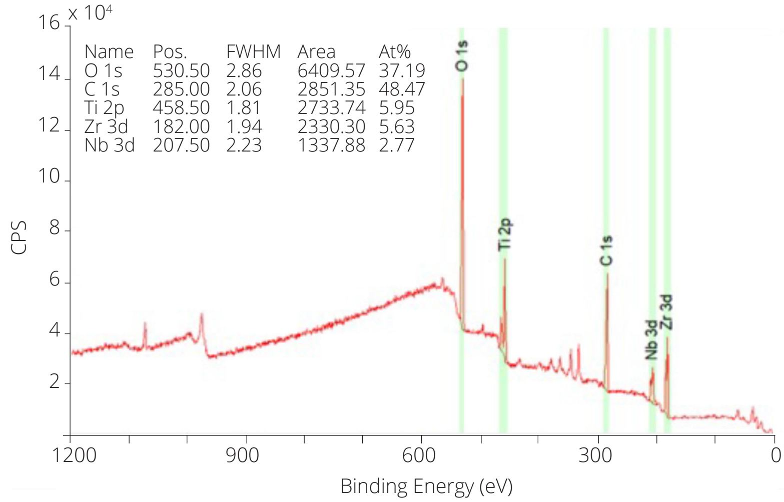

Figure 6: X-ray photoelectron spectroscopy long scan for the $Ti_{68}Nb_{12}Zr_{20}$ coating.

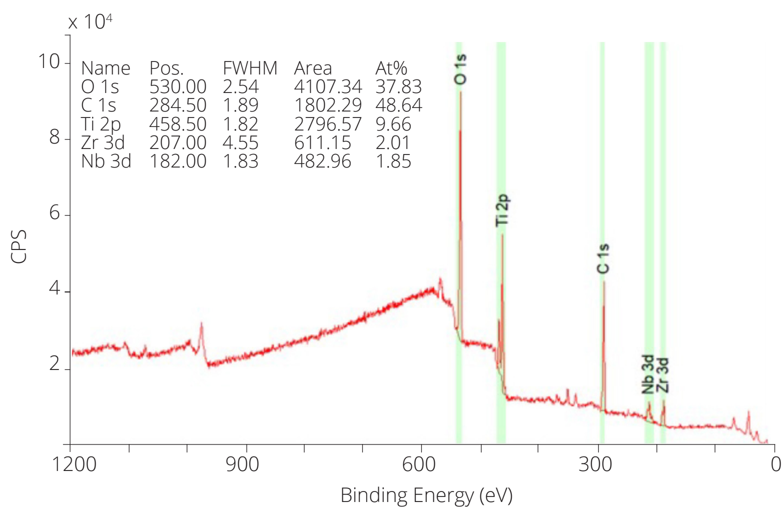

Figure 7: X-ray photoelectron spectroscopy long scan for the $Ti_{67}Nb_{21}Zr_{12}$ coating.

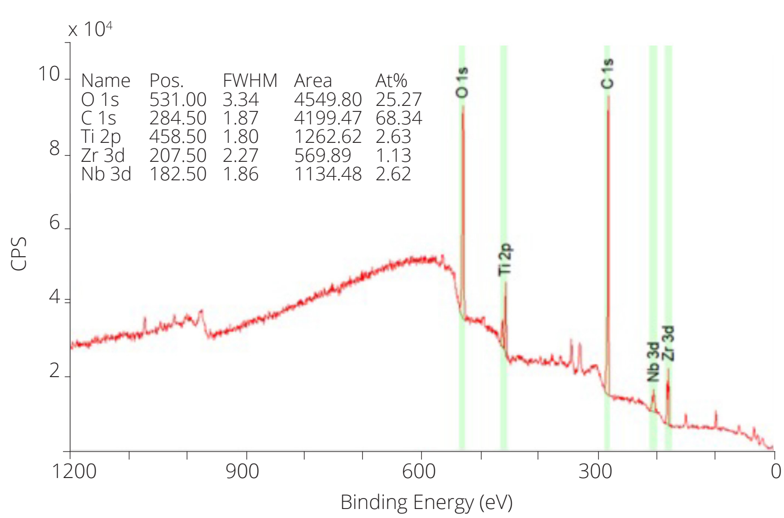

Figure 8: X-ray photoelectron spectroscopy long scan for the $Ti_{67}Nb_{28}Zr_{5}$ coating.

Table 1 presents the Ti/(Ti + Nb + Zr), Nb/(Ti + Nb + Zr), and Zr/(Ti + Nb + Zr) atomic ratios obtained by XPS for the $Ti_{49}Nb_{14}Zr_{37}$, $Ti_{68}Nb_{12}Zr_{20}$, $Ti_{67}Nb_{21}Zr_{12}$, and $Ti_{67}Nb_{28}Zr_{5}$ coatings deposited on a Si (100) wafer substrate, considering only Ti, Nb, and Zr contributions. The atomic ratios obtained by XPS agreed reasonably with those obtained by EDS for the $Ti_{49}Nb_{14}Zr_{37}$, and $Ti_{67}Nb_{21}Zr_{12}$ coatings, but differed significantly for the other two coatings. For comparison, in a previous study on a Ti-Nb-Zr thin film deposited on Si (111), with thickness of 460 nm, the Ti/(Ti + Nb + Zr), Nb/(Ti + Nb + Zr), and Zr/(Ti + Nb + Zr) atomic rations obtained by EDS were 0.64, 0.18, and 0.18, respectively, while the values obtained by XPS were 0.50, 0.30, 0.20[15].

Table 1: Atomic ratios obtained by X-ray photoelectron spectroscopy for the $Ti_{49}Nb_{14}Zr_{37}$, $Ti_{68}Nb_{12}Zr_{20}$, $Ti_{67}Nb_{21}Zr_{12}$, and $Ti_{67}Nb_{28}Zr_{5}$ coatings.

Coating	Ti/(Ti + Nb + Zr)	Nb/(Ti + Nb + Zr)	Zr/(Ti + Nb + Zr)
$Ti_{49}Nb_{14}Zr_{37}$	0.44	0.10	0.46
$Ti_{68}Nb_{12}Zr_{20}$	0.42	0.19	0.39
$Ti_{67}Nb_{21}Zr_{12}$	0.71	0.15	0.14
$Ti_{67}Nb_{28}Zr_{5}$	0.41	0.18	0.41

CONCLUSIONS

Magnetron sputtering was used to produce compositional libraries for the Ti-Nb-Zr ternary alloy coatings deposited on a Si (100) substrate. Chemical, structural, and morphological analyses were performed by EDS, XPS, XRD, and AFM. Four compositions (in at.%) were selected: $Ti_{49}Nb_{14}Zr_{37}$, $Ti_{68}Nb_{12}Zr_{20}$, $Ti_{67}Nb_{21}Zr_{12}$, and $Ti_{67}Nb_{28}Zr_{5}$. XRD characterization of the coatings revealed the formation of the β (BCC) phase for the four compositions. AFM images showed that the roughness values ranged from 3.0 to 5.9 nm. XPS results indicated that the ternary alloy coating surfaces were oxidized. The nanostructured and oxidized surface provided high corrosion protection and good cellular responses that are desirable for biomedical prostheses.

AUTHORS' CONTRIBUTION

Data curation, Formal analysis, Investigation, Visualization, Writing – original draft: Castro AL; **Data curation, Formal analysis, Visualization:** Lemos LLA; **Investigation, Methodology, Resources:** Gobbi AL; **Investigation:** Gontijo LC; **Conceptualization, Investigation, Validation:** Afonso CRM; **Data Curation, Investigation, Resources:** Mastelaro VR; **Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing – review & editing:** Nascente PAP.

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DATA AVAILABILITY STATEMENT

The research data is available under request.

REFERENCES

1. Niinomi M. Recent metallic materials for biomedical applications. Metal Mater Trans A. 2002;33:477-86. https://doi.org/10.1007/s11661-002-0109-2

2. Liu X, Chu PK, Ding C. Surface modification of titanium, titanium alloys, and related materials for biomedical applications. Mater Sci Eng R. 2004;47(3-4):49-121. https://doi.org/10.1016/j.mser.2004.11.001

3. Niinomi M. Biologically and mechanically biocompatible titanium alloys. Mater Trans. 2008;49(10):2170-8.

4. McGregor DB, Baan RA, Partensky C, Rice JM, Wibourn JD. Evaluation of the carcinogenic risks to humans associated with surgical implants and other foreign bodies - a report of an IARC Monographs Programme Meeting. International Agency for Research on Cancer. Eur J Cancer. 2000;36(3):307-13. https://doi.org/10.1016/s0959-8049(99)00312-3

5. Ozaki T, Matsumoto H, Watanabe S, Hanada S. Beta Ti alloys with low Young's modulus. Mater Trans. 2004;45(8):2776-9.

6. Chang C, Wang YD, Ren Y. In-situ investigation of stress-induced martensitic transformation in Ti–Nb binary alloys with low Young's modulus. Mater Sci Eng A. 2016;651:442-8. https://doi.org/10.1016/j.msea.2015.11.005

7. Gonzalez ED, Fukumasu NK, Afonso CRM, Nascente PAP. Impact of Zr content on the nanostructure, mechanical, and tribological behaviors of β-Ti-Nb-Zr ternary alloy coatings. Thin Solid Films. 2021;721:138565. https://doi.org/10.1016/j.tsf.2021.138565

8. Pang EL, Pickering EJ, Baik SI, Seidman DN, Jones NG. The effect of zirconium on the omega phase in Ti-24Nb-[0–8] Zr (at.%) alloys. Acta Mater. 2018;153:62-70. https://doi.org/10.1016/j.actamat.2018.04.016

9. Ding S, Gregoire J, Vlassak JJ, Schroers J. Solidification of Au-Cu-Si alloys investigated by a combinatorial approach. J Appl Phys. 2012;111:114901. https://doi.org/10.1063/1.4722996

10. Li Y, Jensen KE, Liu Y, Liu J, Gong P, Scanley BE, et al. Combinatorial strategies for synthesis and characterization of alloy microstructures over large compositional ranges. ACS Comb Sci. 2016;18(10):630-7. https://doi.org/10.1021/acscombsci.6b00040

11. Li J, Gittleson FS, Liu Y, Liu J, Loye AM, McMillon-Brown L, et al. Chem Commun. 2017;53(59):8288-91.https://doi.org/10.1039/C7CC02733H

12. Gonzalez ED, Niemeyer TC, Afonso CRM, Nascente PAP. Ti-Nb thin films deposited by magnetron sputtering on stainless steel. J Vac Sci Technol A. 2016;34:021511. https://doi.org/10.1116/1.4940753

13. Gonzalez ED, Afonso CRM, Nascente PAP. Influence of Nb content on the structure, morphology, nanostructure, and properties of titanium-niobium magnetron sputter deposited coatings for biomedical applications. Surf Coat Technol. 2017;326(Part B):424-8. https://doi.org/10.1016/j.surfcoat.2017.03.015

14. Tallarico DA, Gobbi AL, Paulin Filho PI, Galtayries A, Nascente PAP. Surface characterization of Zr/Ti/Nb tri-layered films deposited by magnetron sputtering on Si(111) and stainless steel substrates. J Vac Sci Technol A. 2012;30:051505. https://doi.org/10.1116/1.4737616

15. Tallarico DA, Gobbi AL, Paulin Filho PI, Maia da Costa MEH, Nascente PAP. Growth and surface characterization of TiNbZr thin films deposited by magnetron sputtering for biomedical applications. Mater Sci Eng C. 2014;43:45-9. https://doi.org/10.1016/j.msec.2014.07.013