REVISTA MATÉRIA V.26 N.04
ISSN 1517-7076 articles e13111, 2021

Influence of zirconium addition on microstructure, hardness and oxidation resistance of tantalum nitride thin films

Jonh Yago Erikson Santos[1], André Romão Terto[1],
Daniel Angel Ramirez[1], Júlio César Valeriano dos Santos[1],
Beatriz dos Santos Silva Brito[1], Luís Fernando Sabino[1],
Iago Lemos Dias[1], Roberto Hübler[2], Eduardo Kirinus Tentardini[1]

[1] Universidade Federal de Sergipe, Departamento de Ciência e Engenharia de Materiais, Programa de Pós-Graduação em Ciência e Engenharia de Materiais, Laboratório de Filmes Finos, Avenida Marechal Rondon, S/N, CEP: 49100-000, São Cristóvão, SE, Brasil.
[2] Pontifícia Universidade Católica do Rio Grande do Sul , Faculdade de Física, Gepsi - Grupo de Estudos de Propriedades de Superfícies e Interfaces, Avenida Ipiranga, 6681, CEP: 90619-900, Porto Alegre ,RS, Brasil.
e-mail: jonhyagoo@gmail.com, arterto@outlook.com, daniel.angel0275@gmail.com, juliocesarvaleriano@gmail.com, beatrizsilva867@gmail.com, luisfernandosabino@hotmail.com, iagolemos18@gmail.com, hubler@pucrs.br, etentardini@academico.ufs.br

ABSTRACT

$Ta_{1-x}Zr_xN$ thin films were deposited by reactive magnetron sputtering aiming to investigate the influence of zirconium addition on the microstructure, hardness and high temperature oxidation resistance of the coatings. GAXRD showed that all $Ta_{1-x}Zr_xN$ thin films maintained ZrN crystalline structure, forming a TaZrN solid solution. Zr incorporation did not alter hardness values of $Ta_{1-x}Zr_xN$ coatings, however, promoted significant improvements in the oxidation resistance when compared to pure TaN thin films.

Keywords: Thin films; Magnetron sputtering; Tantalum nitride; Nanohardness; High temperature oxidation.

1. INTRODUCTION

Use of thin films as an approach to modify superficial properties of materials has been attracting increasing attention from metal mechanic industry, given their utilization provides substantial improvements on tools properties such as hardness, abrasion and corrosion resistance [1, 2].

Transition metal nitride thin films (MeN), in special those composed by titanium, chromium, zirconium and tantalum, represent a class of materials capable of generating several types of protective coatings, which present valuable properties for numerous scientific and industrial applications [3-8].

In this context, tantalum nitride thin films (TaN) have been attracting attention in the last decade, due to promising properties such as good wear and corrosion resistance, high hardness, resistance to high temperatures, good chemical stability and thermal conductivity [9-11].

Despite such good properties, TaN thin films possess inferior hardness and oxidation resistance values when compared to other commonly used refractory nitrides [11-13].

In this sense, a well-studied approach to enhance MeN properties is the production of ternary systems by the incorporation of a third chemical element to the binary nitride [14, 15]. For instance, TiZrN, TiNbN and TiTaN are a few examples of ternary nitrides with superior hardness, wear rates and corrosion resistance when compared to their correspondent binary nitrides [16]. Analogously, the addition of a third element to TaN ($Ta_{1-x}Me_xN$) is a potential measure to achieve improvements in these coatings [17, 18]. CHEN *et al.* [19] observed an enhancement on oxidation resistance and a slight increase in hardness of TaSiN thin film when compared to pure TaN.

Among the existing options for a third chemical element, zirconium addition shows great promise, seeing that this element has been used in other systems. KHAMSEH e ARAGHI [20] reported the increase of

Autor Responsável: Jonh Yago Erikson Santos   Data de envio: 21/12/2020   Data de aceite: 05/04/2021

10.1590/S1517-707620210004.1311

(cc) BY

oxidation temperature from 873 K to 1073 K for CrZrN (0.4 at.%) thin films while maintaining an elevated hardness.

CUI *et al.* [21] showed that Zr addition promoted an improvement in chemical and mechanical properties of TiN coatings. TiZrN ternary system presented higher hardness, corrosion resistance and lower friction coefficient when compared to the binary nitride. Other reports also demonstrate that Zr addition resulted in increments to mechanical properties when compared to pure binary nitrides de TiN e CrN [22-24].

In particular, tantalum nitride thin films with zirconium addition (TaZrN) showed considerable improvements in hardness, oxidation and wear resistance, allowing its application on biomedical implants and diffusion barrier layer to copper [25, 26]. However, it is not entirely clear in the literature the influence of zirconium content on microstructure and consequent hardness repercussions of TaZrN thin films.

This work aims to evaluate the influence of Zr content on the microstructure, oxidation resistance and hardness of $Ta_{1-x}Zr_xN$ thin films. To that end, TaN, ZrN e $Ta_{1-x}Zr_xN$ with three different content of Zr were deposited by reactive magnetron sputtering (RMS) and characterized by energy dispersive spectroscopy (EDS), glancing angle x-ray diffraction (GAXRD), nanohardness and high temperature oxidation tests.

2. MATERIALS AND METHODS

TaN, ZrN e $Ta_{1-x}Zr_xN$ thin films were deposited by reactive magnetron sputtering using an AJA Orion 5-HV Sputtering Systems equipment, with direct current (DC) and radiofrequency (RF) power sources, where Zr (99.9%) and Ta (99.7%) targets were placed, respectively. The samples were positioned in a rotating substrate holder, 120 mm distant from the targets. Figure 1 shows a representation of the deposition system used in the present work.

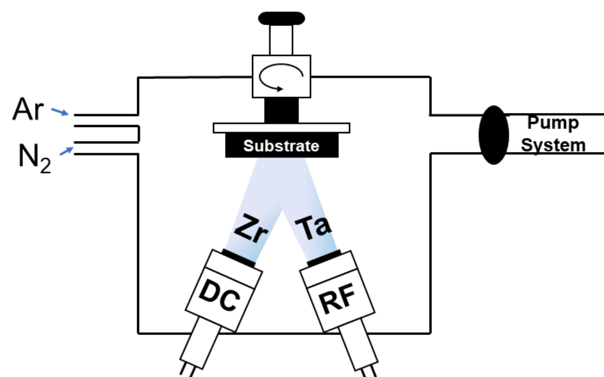

Figure 1: Deposition system scheme.

Monocrystalline silicon wafers were used as substrate for depositions. They were subjected to cleaning procedure with acetone in ultrasound equipment for 30 minutes, followed by a bath in distilled and deionized water in order to achieve good adhesion of coatings on the substrates.

Aiming to verify the influence of zirconium content in TaN thin films, all main deposition parameters were kept constant, such as: 1×10^{-5} Pa base pressure, 4×10^{-1} Pa work pressure, 19 and 2 sccm argon and nitrogen fluxes respectively, 200 W power applied to Ta target and deposition time of 60 minutes for all films. The only varying parameter was the power applied to zirconium target, which was set in 20, 50 and 100 W.

Pure TaN and ZrN were deposited with comparative purposes, using the same aforementioned parameters.

After depositions, quantification of tantalum and zirconium were carried out by EDS in JEOL JCM 5700 equipment. Crystalline structure was evaluated by GAXRD in a Shimadzu XRD-6000 with Cu-Kα radiation ($\lambda = 1.54$ Å), incidence angle of 1°, from 20 to 80°.

Nanohardness tests were carried out in a *Fisherscope* HV 100 nanodurometer, with a Berkovich indenter, applying 10 mN load with indentation depth varying along 20% of films thickness in order to avoid the substrates influence on results.

(cc) BY

To verify coatings oxidation resistance, samples were heated from ambient temperature until 773, 873 and 973 K. A heat rate of 0.17 K/s was used, and test temperature was maintained for 1800 s using a JUNG-7013 furnace, in accordance with ASTM G 54-84 106 norm. After oxidation tests, samples were analyzed one more time by GAXRD.

3. RESULTS AND DISCUSSION

3.1 Elemental and Structural Analyses

$Ta_{1-x}Zr_xN$ thin films were analyzed by EDS in order to verify zirconium concentration in TaN matrix. Figure 2 shows the results obtained for samples deposited with 20, 50 and 100 W of power applied to Zr target.

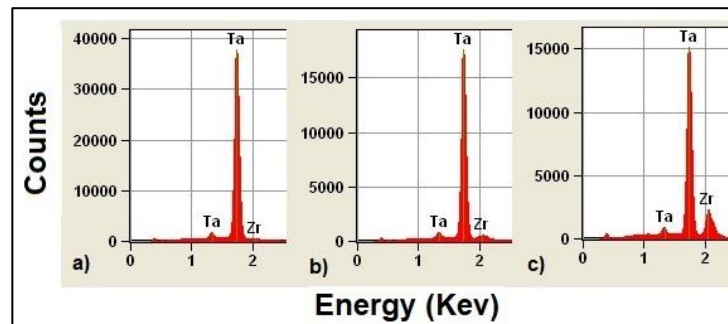

Figure 2: EDS analysis of $Ta_{1-x}Zr_xN$ thin films deposited with the following power applied to Zr target: a) 20 W; b) 50 W and c) 100 W.

Upon comparison of Figures 2a, 2b and 2c it is possible to note that, given the difference in Zr peak size, the higher the applied power on zirconium target, the greater the quantity of this chemical element in the coating. Light elements such as nitrogen and oxygen were not quantitatively analyzed by EDS

In this sense, quantitative results in at.% determined by EDS in the present work refer only to Ta and Zr chemical elements. Samples nomenclature are composed by numbers related to relative atomic concentration of Zr/Ta, as seen in Table 1.

Table 1: Relative contents in at.% of Ta/Zr obtained by EDS for $Ta_{1-x}Zr_xN$ coatings.

SAMPLE	POWER APPLIED IN ZR TARGET (W)	ZR CONTENT (AT.%)	TA CONTENT (AT.%)
TaZrN_26	20	26 ± 3	74 ± 7
TaZrN_52	50	52 ± 5	48 ± 5
TaZrN_77	100	77 ± 8	23 ± 3

ZrN, TaN and $Ta_{1-x}Zr_xN$ coatings were subjected to GAXRD analyses in order to verify the present crystalline phases. Results are shown in Figure 3.

(cc) BY

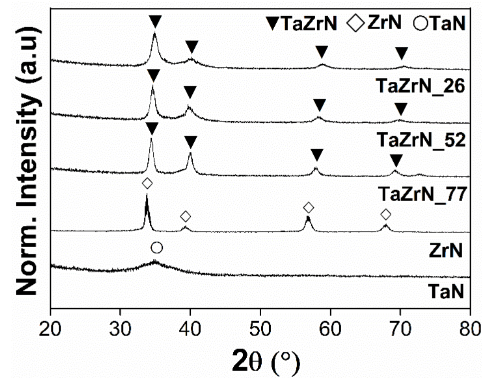

Figure 3: GAXRD patterns obtained for *as deposited* ZrN, TaN and $Ta_{1-x}Zr_xN$ thin films.

According to GAXRD results, the presence of a single diffraction peak in approximately 35° for tantalum nitride sample suggests a tendency for this material to crystallize in TaN face centered cubic phase (FCC), following (PDF 49-1283) pattern, however, the coating notably manifested an overall amorphous behavior. Similar results were previously reported in the literature [12, 27, 28].

Pure ZrN sample presented x-ray diffraction peaks related to its FCC crystalline structure, typical for this material when deposited under the adopted parameters [29]. These peaks are identified in 2θ values of 33.8°, 39.3°, 56.8° and 67.9°, corresponding to crystalline planes (111), (200), (220) and (311) of stoichiometric zirconium nitride (PDF 35-753).

As reported by MATENOGLOU *et al.* [30], transition metal ternary nitrides as $Ta_{1-x}Me_xN$ (Me = Ti, Zr, Hf, Nb, Mo, W) form stable solid solutions with rock-salt crystalline structure, regardless the valence electronic configuration from the component metals. Thus, concerning $Ta_{1-x}Zr_xN$ samples, zirconium has possibly been dissolved into TaN matrix, resulting in the formation of TaZrN structure (PDF 89-5204); this hypothesis is corroborated by thoroughly observing a few aspects in Figure 3:

(a) Tantalum and zirconium nitrides both possess a FCC crystalline structure, thus being mutually miscible, which favors the formation of a solid solution where Ta atoms partially replaced by Zr;

(b) The relative crystallite size for TaN, ZrN and $Ta_{1-x}Zr_xN$ thin films was determined by Scherer's equation using the FWHM value of (111) peaks, resulting in values ranging from 7.2 nm to 10.8 nm for all samples. It is well described in literature that grain growth is limited when the simultaneous nucleation of different grains occurs in a substrate, culminating in a decrease in crystallite size [31, 32]. In the case of ZrN, TaN and $Ta_{1-x}Zr_xN$ deposited in this work, there was no significant modification in the crystallite size value, suggesting that no ZrN and TaN grain growth competition was developed, but a TaZrN structure was formed.

(c) GAXRD results obtained for $Ta_{1-x}Zr_xN$ reveal the presence of ZrN typical diffraction peaks, nevertheless, when compared to pure ZrN patterns, peak shifts can be observed. Probably such phenomenon occurs due to the existing difference in atomic radius between tantalum (0.15 nm) and zirconium (0.16 nm). Given that fact, the replacement of Ta by Zr atoms in the crystalline structure is closely followed by a reduction in interplanar distances, consequently causing the peaks to shift to higher angles regions. Such behavior becomes more evident with the gradual shift of peaks as a function of Zr content for ZrN, TaZrN_77, TaZrN_52 and TaZrN_26 samples, as shown in Table 2;

(d) When compared to pure ZrN, broadening of diffraction peaks for $Ta_{1-x}Zr_xN$ samples occurs, possibly due to the presence of two differently sized chemical elements in the same structure, causing a distortion in the lattice with a subsequent loss of crystallinity.

Table 2: $Ta_{1-x}Zr_xN$ diffraction peaks shift, in comparison with pure ZrN.

SAMPLE	POSITION OF DIFFRACTION PEAKS IN 2Θ (°)			
	(111)	**(200)**	**(220)**	**(311)**
ZrN	33.8	39.3	56.8	67.9
TaZrN_77	34.4	39.9	57.9	69.1
TaZrN_52	34.6	40.0	58.3	69.8
TaZrN_26	34.9	40.1	58.9	70.4

(cc) BY

3.2 Nanohardness Tests

Following microstructural analyses, samples were subjected to nanohardness tests in order to evaluate this property for ZrN, TaN and $Ta_{1-x}Zr_xN$ thin films with different Zr content. Figure 4 shows hardness resulting values for all samples, obtained in accordance to ISO 14577 regulation.

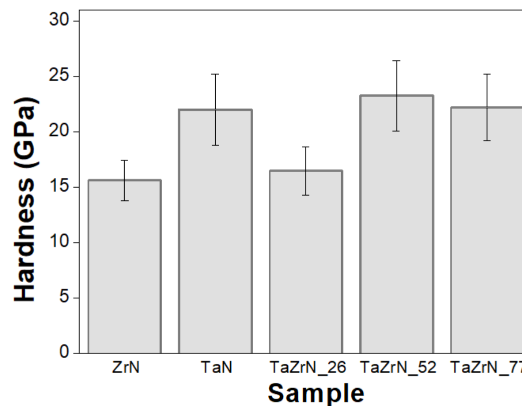

Figure 4:.Hardness values of all samples obtained through nanohardness tests.

The registered hardness value acquired for ZrN sample was 15.6 GPa, similar result to that reported by MUSIL *et al.* [33], in which FCC stoichiometric ZrN thin film was deposited. For TaN sample the obtained value was 22.0 GPa, close to that found by BERNOULLI *et al.* [34], who registered a 21 GPa hardness values for FCC TaN thin films.

Samples TaZrN_26, TaZrN_52 e TaZrN_77 presented hardness values similar to those of pure TaN, with all the values inside the experimental error range.

As shown in the GAXRD results presented in Figure 2, all $Ta_{1-x}Zr_xN$ samples manifested the formation of a TaZrN solid solution. Even with the mutual replacement of Ta by Zr in the microstructure, the resulting distortion was not sufficient to generate a hardness increment, comparing to pure TaN sample. This fact can be explained by the similarity in the atomic radii of Ta and Zr, which was enough to dislocate x-ray diffraction peaks, nonetheless not capable of effectively distorting the crystalline lattice as to generate an increase of residual tensions and a consequent raise in the coatings hardness values.

3.3 High Temperature Oxidation Tests

Samples ZrN, TaN e $Ta_{1-x}Zr_xN$ were subjected to oxidation tests at 773 K, 873 K e 973 K. After the tests, all samples were analyzed by GAXRD in order to verify the formed crystalline phases originating from the coatings oxidation processes.

Figure 5 shows the diffraction patterns of ZrN sample after oxidation tests. The pattern obtained for *as deposited* sample is also explicit in the figure, with comparative purposes.

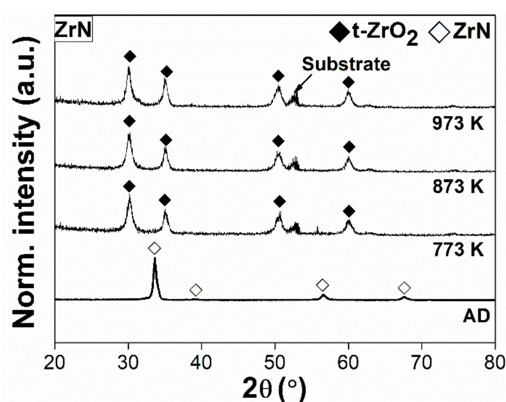

Figure 5: X-ray diffraction patterns obtained for as deposited ZrN thin films and oxidized at 773 K, 873 K and 973 K.

(cc) BY

Results presented in Figure 5 show that ZrN thin film did not resist even the lowest temperature applied of 773 K, given that peaks related to *as deposited* FCC ZrN sample cannot be identified and the only existing peaks refer to tetragonal zirconium oxide (t-ZrO_2), according to PDF 50-1089 pattern. Same behavior is registered for oxidation tests at 873 and 973 K.

Figure 6 shows GAXRD results after oxidation tests obtained for TaN sample.

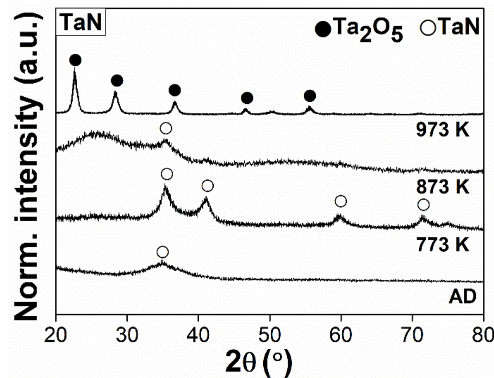

Figure 6: Diffraction patterns obtained for *as deposited* TaN samples and oxidized at 773 K, 873 K and 973 K.

As previously discussed, *as deposited* TaN sample manifested an amorphous behavior while simultaneously indicating a tendency for possible crystallization of FCC TaN structure. Such tendency becomes evident after this sample was exposed to 773 K, where the increased available energy in the system promoted a higher crystallization degree for TaN coating, favoring the formation of FCC TaN with its typical peaks in planes (111), (200), (220) and (311), in accordance to PDF 49-1283 pattern. For this temperature it is not possible to observe peaks derived from tantalum oxide, only the increase of crystallinity degree for this material.

GAXRD results after oxidation tests at 873 K show a single TaN diffraction peak present, at 35°, revealing a considerable loss of crystallinity when compared to the previous temperature. Such fact suggests that a significant change is starting to occur inside the coatings crystalline structure, possibly due to the formation of oxides, which nonetheless coexist with the nitride.

TaN oxidation process is completed when tantalum oxide was formed after oxidation tests at 973 K. At such temperature results show intense and defined diffraction peaks related to Ta_2O_5, according to PDF 25-922 pattern. No peak referring to TaN can be identified, thus, it is possible to conclude that tantalum nitride is fully oxidized in the form of Ta_2O_5 at 973 K.

GAXRD results obtained for $Ta_{x-1}Zr_xN$ samples after oxidation tests presented a similar behavior in all oxidation temperatures applied, hence, aiming to avoid identical and repetitive discussions, only TaZrN_52 results will be shown, though the considerations made for this thin film will be extrapolated for TaZrN_26 and TaZrN_77 samples. Figure 7 shows diffraction patterns obtained for sample TaZrN_52 after oxidation tests.

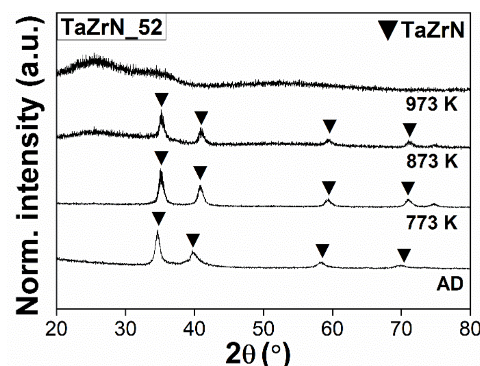

Figure 7: Diffraction patterns obtained for TaZrN thin films containing 52 at.% of Zr, *as deposited* and oxidized at 773 K, 873 K and 973 K.

(cc) BY

The addition of 26 at.%, 52 at.% or 77 at.% Zr into TaN matrix promoted a significant improvement in the coatings oxidation resistance when compared to ZrN sample, seeing that TaZrN structure remains unaltered up to 873 K. Nevertheless, at 973 K, $Ta_{x-1}Zr_xN$ thin films presented an amorphous character, suggesting that the nitride structure has started to partially oxidize. Analogously to pure TaN sample, at this temperature the film structure is probably composed by a mix of oxides and nitrides and, provided the temperature is further raised, the samples shall eventually come to a complete oxidation.

Following the previous discussion, the relative crystallite size for all samples was virtually identical, suggesting the increase in oxidation resistance by $Ta_{1-x}Zr_xN$ samples cannot be explained by the decrease of grains boundaries. However, one possible interpretation to understanding the improvement in oxidation resistance of $Ta_{1-x}Zr_xN$ samples is also observed in GAXRD analysis showed in Fig. 2, once the tantalum and zirconium atoms presence in $Ta_{1-x}Zr_xN$ samples promoted a distortion in the crystal lattice and caused an interplanar distance reduction when compared to ZrN. This shrinkage of the lattice parameters could be responsible to hinder oxygen diffusion derived from external environment to the inside of thin films, increasing oxidation resistance of $Ta_{1-x}Zr_xN$ samples in comparison to pure ZrN and TaN coatings.

4. CONCLUSIONS

TaN, ZrN e $Ta_{1-x}Zr_xN$ thin films were successfully deposited by reactive magnetron sputtering. GAXRD analyses of *as deposited* samples revealed that TaN possess an amorphous character, while pure ZrN presented a FCC crystalline structure. $Ta_{1-x}Zr_xN$ coatings consisted of a TaZrN solid solution maintaining FCC ZrN peaks, which were gradually shifted due to the substitution of Zr and Ta in the structure.

Hardness values obtained for pure ZrN and TaN were similar to those found in the literature, while $Ta_{1-x}Zr_xN$ samples maintained values close to those of TaN. Zirconium addition was not effective for a hardness improvement.

High temperature oxidation tests showed that pure ZrN was fully oxidized at 773 K. Pure TaN samples presented an increment in crystallinity at 773 K, and the formation of Ta_2O_5 only occurred at 973 K.

Zr incorporation promoted a significant improvement in the oxidation resistance of $Ta_{1-x}Zr_xN$ when compared to pure ZrN and TaN results. GAXRD analyses showed an unaltered TaZrN structure up to 873 K. At 973 K all $Ta_{1-x}Zr_xN$ samples presented an amorphous behavior, however, no oxides could be identified in that temperature. Thus, the addition of 26, 52 or 77 at.% Zr in TaN thin films did not alter hardness values in any relevant manner, nevertheless, it was effective in improving the oxidation resistance of this binary nitride.

5. BIBLIOGRAPHY

[1] SERRA, E.C., SOARES, V.F.D., FERNANDEZ, D.A.R., *et al*. "Influence of WS2 content on high temperature wear performance of magnetron sputtered TiN-WSx thin films". *Ceramics International.* v.45(16), pp. 19918–19924, Fev. 2019.

[2] FREY, H., KHAN, H.R. *Handbook of Thin-Film Technology*. pp.1–379 , 2015.

[3] XU, S., MUNROE P., XU, J., *et al*. "The microstructure and mechanical properties of tantalum nitride coatings deposited by a plasma assisted bias sputtering deposition process". *Surface and Coatings Technology,* v.307, pp.470–475, Fev. 2016.

[4] KOLLER, C.M., MARIHART, H., BOLVARDI, H., *et al.* "Structure, phase evolution, and mechanical properties of DC, pulsed DC, and high power impulse magnetron sputtered Ta–N films". *Surface and Coatings Technology,*v.347, pp.304–312, 2018.

[5] RAOUFI, M. "The correlation between tribological properties of nanostructure tin coatings and deposition process parameters in PACVD system". *Revista Materia*,v.22(2), 2017.

[6] VASYLYEV, M.A., MORDYUK, B.N., SIDORENKO, S.I., *et al.* "Characterization of ZrN coating low-temperature deposited on the preliminary Ar+ ions treated 2024 Al-alloy". *Surface and Coatings Technology*, v. 361, pp. 413–424, Mar 2019.

[7] SILVA NETO, P.C., FREITAS, F.G.R., FERNANDEZ, D.A.R., *et al.,* "Investigation of microstructure and properties of magnetron sputtered Zr-Si-N thin films with different Si content". *Surface and Coatings Technology*. v. 353, pp. 355-363, Nov. 2018.

[8] ABDALLAH, B., NADDAF, M., A-KHARROUB, M., "Structural, mechanical, electrical and wetting properties of ZrNx films deposited by Ar/N2 vacuum arc discharge: Effect of nitrogen partial pressure".

Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms.v. 298, pp.55–60, Mar. 2013.

[9] SHEN H., RAMANATHAN R., "Fabrication of a low resistivity tantalum nitride thin film". *Microelectronic Engineering*, v. 83 n. 2, pp. 206–212. Fev. 2006.

[10] ZHOU Y., JIN P., CHEN S., *et al.,* "Tantalum nitride nanowires: Synthesis and characterization". *Materials Letters*, v. 136, pp. 168–170, Dez. 2014.

[11] PIERSON, H.O., Handbook of Refractory Carbides and Nitrides: Properties, Characteristics, Processing and Applications, 1 ed., Norwich, Noyess Publications, 1996.

[12] ARYASOMAYAJULA, A., VALLETI, K., ARYASOMAYAJULA, S., *et al.,* "Pulsed DC magnetron sputtered tantalum nitride hard coatings for tribological applications". *Surface and Coatings Technology, v.* 201, n. 7, pp. 4401–4405, Dez. 2006.

[13] TSENG, C.C., HSIEH, J.H., JANG S.C., *et al.*, "Microstructural analysis and mechanical properties of TaN–Ag nanocomposite thin films", *Thin Solid Films*, v. 517 n. 17, pp. 4970–4974, Jul. 2009.

[14] NARVAEZ, D.M.D, RESTREPO, J.M.V., PARRA, E.R. "Bias voltage influence on the mechanical and tribological properties of titanium aluminum nitride coatings produced by triode magnetron sputtering". *Revista Materia*, v.20(1), pp.115–126, 2015

[15] CHOI, H., JANG, J., ZHANG, T., *et al.*, "Effect of Si addition on the microstructure, mechanical properties and tribological properties of Zr–Si–N nanocomposite coatings deposited by a hybrid coating system". *Surface and Coatings Technology*, v. 259, n. PC, pp. 707–713, Nov.2014.

[16] ABADIAS, G., KANOUN, M.B., GOUMRI-SAID, S., *et al.,* "Electronic structure and mechanical properties of ternary ZrTaN alloys studied by ab initio calculations and thin-film growth experiments". *Physical Review B*, v. 90, n. 14. pp. 144107-1 - 144107-18, Out. 2014.

[17] HERNÁNDEZ-NAVARRO, C., RIVERA, L.P., FLORES-MARTÍNEZ, M., *et al.,* "Tribological study of a mono and multilayer coating of TaZrN/TaZr produced by magnetron sputtering on AISI-316L stainless steel". *Tribology International*, v. 131, pp. 288–298, Mar. 2019.

[18] MANAUD, J.P., POULON, A., GOMEZ, S., *et. al.,* "A comparative study of CrN, ZrN, NbN and TaN layers as cobalt diffusion barriers for CVD diamond deposition on WC–Co tools". *Surface and Coatings Technology*, v. 202, n. 2, pp. 222–231, Nov 2007.

[19] CHEN, Y.I., LIN, K.Y., WANG, H.H., *et al.* ,"Characterization of Ta-Si-N coatings prepared using direct current magnetron co-sputtering". *Applied Surface Science*,v.305, pp.805–816, Set. 2014.

[20] KHAMSEH, S., ARAGHI, H., "A study of the oxidation behavior of CrN and CrZrN ceramic thin films prepared in a magnetron sputtering system". *Ceramics International*, v. 42, n. 8, pp. 9988–9994, Jun. 2016.

[21] CUI, W., CHENG, J., LIU, Z. "Bio-tribocorrosion behavior of a nanocrystalline TiZrN coating on biomedical titanium alloy". *Surface and Coatings Technology* , v.369, pp.79–86, Abr. 2019.

[22] LIN, Y-W., HUANG, J-H., CHENG, W-J., *et. al.,* "Effect of Ti interlayer on mechanical properties of TiZrN coatings on D2 steel". *Surface and Coatings Technology*,v. 350 n. 2017, pp. 745–754, Set. 2018.

[23] LIN, Y-W., HUANG, J-H., YU, G-P., "Microstructure and corrosion resistance of nanocrystalline TiZrN films on AISI 304 stainless steel substrate". *Journal of Vacuum Science & Technology A*, v. 28, n. 4 pp. 774–778, Jul. 2010.

[24] CHANTHARANGSI, C., DENCHITCHAROEN, S., CHAIYAKUN, S., *et al.,* "Structures, morphologies, and chemical states of sputter-deposited CrZrN thin films with various Zr contents". *Thin Solid Films*, v. 589, pp. 613–619, Ago. 2015.

[25] AOUADI, S.M., FILIP, P., DEBESSAI, M. "Characterization of tantalum zirconium nitride sputter-deposited nanocrystalline coatings". *Surface & Coatings Technology*, v.187, pp. 177 -184, 2004.

[26] RUAN, J-L., HUANG, J-L., LU, H-H., *et al.*," Effects of the Ta content on the microstructure and electrical property of reactively sputtered TaxZr1−xN thin films". *Thin Solid Films*, v. 519, p. 4987–4991, 2011.

[27] TSUKIMOTO, S., MORIYAMA, M., MURAKAMI, M., "Microstructure of amorphous tantalum nitride thin films". *Thin Solid Films*, v. 460, n. 1–2, pp. 222–226, Jul. 2004.

[28] WANG W-L., CHEN W-C., PENG K-T., *et al*., "The influence of amorphous TaNx under-layer on the crystal growth of over-deposited Ta film". *Thin Solid Films*, v. 603, pp. 34–38, Mar. 2016.

[29] FREITAS F.G.R., HÜBLER R., SOARES, G., *et al.*, "Structural and Mechanical Properties of Zr-Si-N Thin Films Prepared by Reactive Magnetron Sputtering", *Materials Research*, v. 18, n. supl. 2, pp. 30–34, Out. 2015.

[30] MATENOGLOU, G.M., KOUTSOKERAS, L., LEKKA, C.E., *et al.*, "Structure, stability and bonding of ternary transition metal nitrides". *Surface and Coatings Technology*, v. 204, n. 6–7, pp. 911–914, Dez. 2009.

[31] QI Z., WU Z., ZHANG D., *et al.,* "Effect of sputtering power on the chemical composition, microstructure and mechanical properties of CrNx hard coatings deposited by reactive magnetron sputtering", *Vacuum*, v. 145, pp. 136–143, Nov. 2017.

[32] SOARES, V.F.D., FERNANDEZ, D.A.R., JUNIOR, A.S.F., *et al.*, "Structure and high temperature oxidation of Zr(1-x)Mo(x)N thin films deposited by reactive magnetron sputtering". *Applied Surface Science*, v. 485, pp. 490–495, Ago. 2019.

[33] MUSIL, J., DANIEL, R., ZEMAN, P., *et al.,* "Structure and properties of magnetron sputtered Zr–Si–N films with a high (≥25 at.%) Si content". *Thin Solid Films*,v. 478, n. 1–2, pp. 238–247, Mai. 2005.

[34] BERNOULLI, D., MÜLLER, U., SCHWARZENBERGER, M., *et al.*, "Magnetron sputter deposited tantalum and tantalum nitride thin films: An analysis of phase, hardness and composition". *Thin Solid Films*, v. 584, n. 2, pp. 157–161, Dez. 2013.

ORCID

Jonh Yago Erikson Santos https://orcid.org/0000-0002-7933-8623
André Romão Terto https://orcid.org/0000-0003-0229-6928
Daniel Angel Ramirez https://orcid.org/0000-0002-5327-2654
Júlio César Valeriano dos Santos https://orcid.org/0000-0002-1686-4597
Beatriz dos Santos Silva Brito https://orcid.org/0000-0001-5242-5535
Luís Fernando Sabino https://orcid.org/0000-0002-2455-1961
Iago Lemos Dias https://orcid.org/0000-0002-9136-906X
Roberto Hübler https://orcid.org/0000-0002-8625-5607
Eduardo Kirinus Tentardini https://orcid.org/0000-0001-5898-2973