MICROSTRUCTURAL CHARACTERIZATION OF TiN/ZrN MULTILAYER COATINGS ON TITANIUM ALLOY PRODUCED BY POWDER METALLURGY*

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Abstract

The development of multilayered structures has attracted attention from scientific community during recent years. TiN/ZrN coatings with a number of alternate layers have high potential for use in optical, electromagnetism and wear areas. In this work, three sets of multilayered TiN/ZrN coatings presenting variable thickness were designed and deposited by electron beam-physical vapor deposition (EB-PVD). Ti-35Nb-7Zr-5Ta substrates were produced by powder metallurgy from a mixture of hydrided powders with subsequent cold pressing steps and sintering at 1400°C, in high vacuum. TiN/ZrN coatings were obtained by evaporation of alternating Ti and Zr cylindrical targets under a nitrogen flow. The multilayer coatings were characterized by means of scanning electron microscopy (SEM), chemical analysis via energy dispersive spectrometry (EDS) and Vickers indentation. The multilayer produced showed homogeneous thickness and a consistent columnar structure.

Keywords: Multilayer coatings; Powder metallurgy; EB-PVD; Titanium alloys.

CARACTERIZAÇÃO MICROESTRUTURAL DE RECOBRIMENTOS MULTICAMADAS TiN/ZrN EM LIGA DE TITÂNIO PRODUZIDA POR METALURGIA DO PÓ

Resumo

O desenvolvimento de estruturas multicamadas tem atraído a atenção da comunidade científica nos últimos anos. Recobrimentos de TiN/ZrN com camadas alternadas apresentam um elevado potencial para uso nas áreas de resistência ao desgaste e magnetismo. Neste trabalho, três seqüencias de recobrimentos multicamadas TiN/ZrN com espessuras variáveis foram obtidas por deposição física de vapores via feixe de elétrons (EB-PVD). Substratos da liga Ti-35Nb-7Zr-5Ta foram produzidos por metalurgia do pó a partir de pós hidrogenados com etapas de prensagem a frio e sinterização a 1400°C, em alto vácuo. Os recobrimentos de TiN/ZrN foram obtidos pela evaporação alternada de alvos cilíndricos de Ti e Zr sob um fluxo de nitrogênio. Os recobrimentos foram caracterizados por meio de microscopia eletrônica de varredura (MEV), análise química via espectrometria de energia dispersiva (EDS) e indentação Vickers. As multicamadas produzidas apresentaram espessuras homogêneas e uma estrutura colunar consistente.

Palavras-chave: Recobrimentos multicamadas; Metalurgia do pó; EB-PVD; Ligas de Titânio.

*Dedicated to the memory of Professor Carlos de Moura Neto.

1 INTRODUCTION

Titanium and its alloys are classified by Donachie [1] as highly strategic materials for aerospace, chemical and biomedical applications due to its high strength-to-weight ratio, good corrosion resistance to many corrosive environments, and high biocompatibility. Despite of their great potential, the high production costs of titanium-based parts by conventional processes have limited their applications in industry. This fact, explain why the development of titanium alloys by different processing techniques is a necessity of the modern metallurgy.

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German [2] demonstrated that powder metallurgy (P/M) may lead to the production of components having low material loss, uniform grain structure and higher homogeneity compared with conventional wrought products. According to German [3], new P/M-based manufacturing techniques, including direct laser sintering and metal injection molding (MIM) offer an increasing potential for the application of titanium and its alloys. Furthermore, Henriques et al. [4] found that the production of titanium alloy by P/M starting from blended elemental powders might be a production-effective route considering its lower costs (a necessary prerequisite to expand the use of titanium and its alloys), versatility and also for allowing the manufacture of complex parts.

According to Long et al. [5], Ti–35Nb–7Zr–5Ta alloy has lower modulus of elasticity (55GPa) closer to that of bone than other alloys typically used. This alloy does not include any elements, which have been shown or suggested as having short-term or long-term potential adverse effect. Taddei et al. [6] found that the production of Ti–35Nb–7Zr–5Ta by P/M is governed by the control of the dissolution of Nb and Ta particles in order the stabilization of a homogenous β-phase microstructure.

Guo et al. [7] found that although the high mechanical and chemical properties, the use of titanium and its alloys is restricted to non-tribological applications due their high friction coefficients and low resistance to wear, which are resulted from the low hardness and low shearing resistance of the oxide surface layer. Because of these reasons, in applications which high shearing resistance is required, titanium alloys components just can be used after a specific surface treatment, normally coating.

According to Smith [8], the great advantage of the coatings is that, changing only the surface of the component, it is possible to modify the response to the environment, giving properties completely different to the component. Surface coating is an effective method for increasing the durability of the materials used in aggressive environments and applications as well as to add superior surface characteristics to the based material.

Though a single layer coating enables a wide range of applications at various sectors of engineering, there is a growing number of applications where the properties of a single material is not sufficient. PalDey and Deevi [9] found that one way to overcome this problem is depositing a multilayer coating that combines the properties of the different materials deposited.

Multilayered structures have attracted a large amount of attention from both the scientific and the industrial community during recent years because of their promising properties. These structures consist of alternating layers of two different materials with nano or micrometer-scale dimensions deposited over a surface.

According to Tavares et al. [10], the alternative multilayer design is credited to the introduction of more interfaces, which permit cracks to be deflected, thereby dissipating energy and enhancing toughness. Multilayers are suited for tribological applications owing to their elevated hardness and strength, due either to differences in dislocation line energies or coherency strain fields developed between adjacent layers

The electron beam-physical vapor deposition (EB-PVD) has constantly gaining reputation and confidence in a wide range of applications including thermal barrier ceramic coatings and wear-resistant hard coatings. With this technique it is able to produce coatings with high deposition rate, formed by a columnar structure that is favorable to the accommodation of tensions generated during mechanical cycles. DeMasi-Marcin and Gupta [11] demonstrated that the EB-PVD process offers an extensive possibility of structures and compositions of the coatings by the control of the process parameters. Thus, coatings with alternate layers of different compositions can be produced.

The aim of this paper is to investigate the microstructural evolution of the TiN/ZrN multilayer coatings obtained by EB-PVD and determines the influence of the key process variables like beam current and coating time on the microstructure, thickness and adhesion of multilayer deposited on Ti-35Nb-7Zr-5Ta substrates obtained by P/M.

2 MATERIAL AND METHODS

2.1 Production of Substrates

Titanium and zirconium powders were obtained by hydriding treatment from sponge fines. Hydriding was carried out at 500°C, in a vacuum furnace, for 3 h, under a positive pressure. After cooling to room temperature, the friable hydride was milled in a titanium container, in vacuum condition (10^{-3} Torr) for 6h. Nb and Ta powders were obtained using the same route, however, using machining chips and hydriding temperatures significantly higher (800°C). The starting hydrided powders for Ti-35Nb-7Zr-5Ta stoichiometry were weighed in batches of 100 g, dried at 110°C for 1 h and blended for 90 min in a Y-shaped blender at 65 rpm. After blending, hydrided powders were cold uniaxially pressed at 100 MPa in a cylindrical 15 mm diameter steel die without lubricants. In sequence, the green compacts were encapsulated in vacuum and cold isostatically pressed at 400 MPa during 30 s to increase their green density. Sintering was carried out at 1,400°C for 1 h in high vacuum (10^{-7} Torr), with total elimination of hydrogen. After sintering, Ti-35Nb-7Zr-5Ta samples were embedded in bakelite, ground and polished. Then, the inlay was removed and the samples submitted to an ultrasound cleaning for 15 min. The Ti-35Nb-7Zr-5Ta samples were kept in acetone until their fixation in the substrate holder for the subsequent deposition in order to prevent contamination.

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2.2 Production of Ti and Zr Targets

Titanium and zirconium targets were obtained by melting of commercially pure ingots and by powder metallurgy, respectively. Purified titanium ingot targets were obtained after two melting steps in an electron beam furnace. After that, a machining step was carried out to achieve the targets in the appropriate dimensions (cylinders of 20 mm diameter). The zirconium targets were obtained from 35 g of zirconium hydrided powder, uniaxially cold pressed at 150 MPa in cylindrical 25 mm diameter die, with later steps of cold isostatic pressing at 400 MPa for 1 min and sintering at 1,300°C in vacuum for 1 h.

2.3 Production of TiN/ZrN Multilayer Coatings

The multilayer coatings were obtained using an electron beam furnace specially modified for metallic and ceramic coatings production. The equipment consists of an electron gun with accelerating voltage of 25 kV and beam current ranging from 0 to 1.2 A. The vacuum system allows reaching a final pressure of 10^{-6} Torr in the evaporation chamber. A substrate holder assembly is situated above the vapor source at a vertical distance of 170 mm. A tungsten filament is used to heat the substrate by Joule effect to the desired temperature (600°C),

which is measured and maintained by a thermocouple and programmable temperature controller. A water-cooled copper crucible was used for evaporation of the targets. The evaporation occurs when the electron beam is focused alternately on titanium or zirconium targets. The metal vapor combines chemically with nitrogen released by a duct, depositing layers of TiN and ZrN on Ti-35Nb-7Zr--5Ta substrate. The detailed description of the deposition system is shown in Figure 1.

For this paper, it was carried out three depositions. In order to obtain layers of TiN and ZrN, some parameters were common for all depositions: distance between the target and the substrate: 17 cm, nitrogen gas flow: 50 sccm (standard cubic centimeters per minute), substrate temperature: 600°C, and acceleration voltage: 25 kV. Specific parameters for each deposition are presented in Table 1. These parameters were specified in function of the evaporation properties of the targets in order to obtain homogeneous multilayer coatings.

After the multilayer deposition, the metallographic preparation of the samples was carried out using conventional techniques. Multilayer coatings were analyzed in cross section. The microstructure of the multilayer was investigated using light optical microscopy (LOM) and scanning electron microscopy (SEM) in the backscattered mode (BSE). The chemical composition of the layers was
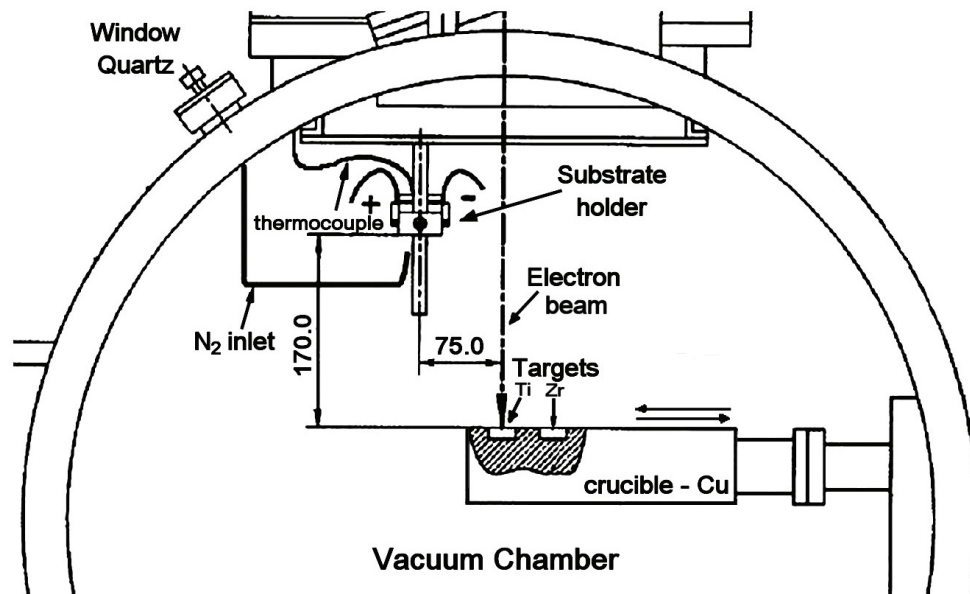

Figure 1. Schematic configuration of the electron beam-physical vapor equipment for multilayer deposition.

Table 1. Specific parameters for the multilayer coatings*

Deposition	Number of Layers	Evaporation time –Zr**	Evaporation time –Ti**	Current- Zr evaporation	Current- Ti evaporation
I	4	15 min	15 min	0.17 A	0.07 A
II	4	30 min	10 min	0.33 A	0.07 A
III	8	20 min	3 min	0.28 A	0.07 A

*The layers were deposited alternately; The first layer of the samples was always ZrN; **For each layer deposition.

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analyzed via energy dispersive spectrometry (EDS). The hardness measurements were carried out in Micromet 2004 equipment (Buehler) with load of 0.05 kgf with 5 indentations for each deposition.

3 RESULTS AND DISCUSSIONS

3.1 Ti-35Nb-7Zr-5Ta Substrates

Ti-35Nb-7Zr-5Ta substrates sintered at 1,400°C presented a microstructure composed basically of β-metastable grains (Figure 2). Some areas riches in niobium and tantalum (bright ones) and microporosity (dark sites) were observed. The densification was found above 94% of the theoretical density. According to Taddei *et al.* [6], homogeneous β-phase microstructure during sintering of Ti-35Nb-7Zr-5Ta is obtained in the whole sample extension with the increase of the sintering temperature. With the beginning of the β-stabilizers dissolution, at low sintering temperatures, there is the formation of an intermediary Widmanstätten (α+β) phase. With the increase of the dissolution of Nb and Ta particles in the titanium matrix at high temperatures, the stabilization of β phase regions occurs. The residual porosity can become an important property for osteointegration in surgical implants.

3.2 TiN/ZrN Multilayer Coatings

The deposition I presented a structure with 4 layers exposed in the sequence of ZrN/TiN/ZrN/TiN (Figure 3). The most noticeable microstructural features are that the TiN layers are much thicker than ZrN layers. During the deposition process, it was observed that the evolution of zirconium vapor is less effective than that of titanium vapor at the same beam current. This fact is related to vapor pressure of the targets materials. Blocher and Campbell [12] found that the vapor pressure of titanium is 0.49Pa at 1,660°C, while Skinner *et al.* [13] found that the vapor pressure of titanium is 0.00168Pa at 1,852°C. Since the vapor pressure of titanium is higher than that of zirconium, the evaporation of the titanium targets is more effective and consequently the TiN layers are thicker. This first deposition showed that specific conditions for ZrN deposition were required. Thus, the bean current and the coating time were increased in the subsequent experiments.

The deposition II was a try to increase deposition I (4 layers). The evaporation time for Zr target was improved to 30 min. The evaporation time for Ti target was reduced to 10 min and the beam current used for Zr was about five times stronger than that used for Ti. Microstructural analyses (Figure 4) reveal that it was possible to obtain alternating layers with more homogenous thick-

ness. It was observed that the thickness of TiN and ZrN layers were about 2 μm. With the changes in the current and time of deposition, ZrN layers showed approximately the same thickness of TiN layers. At this experiment, the TiN layers were obtained from a deposition rate of 0.18μm/min, while the ZrN layers were obtained from a deposition rate of 0.067μm/min.

The next step was the deposition of a coating composed by eight layers with homogenous thickness obtained by the deposition III from the optimization of the parameters used in the deposition II (Figure 5). The deposition time for ZrN layers was seven times longer than that for TiN layers, with almost the same current parameters of the deposition II.

At this experiment, the TiN layers were obtained from a deposition rate of 0.67μm/min, while the ZrN layers were obtained from a deposition rate of 0.1μm/min. From the use of these conditions, it was possible to produce multilayer with homogeneous thickness. The thickness of each layer is about 1.8μm, producing a coating with thickness of 14.65 μm. It is important to emphasize
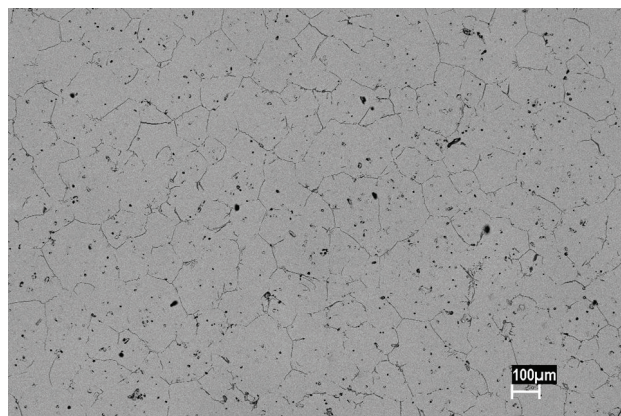

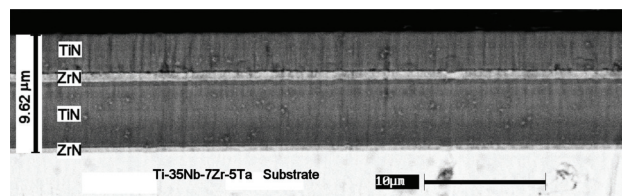**Figure 2.** Microstructure of Ti-35Nb-7Zr-5Ta substrate sintered at 1400°C.

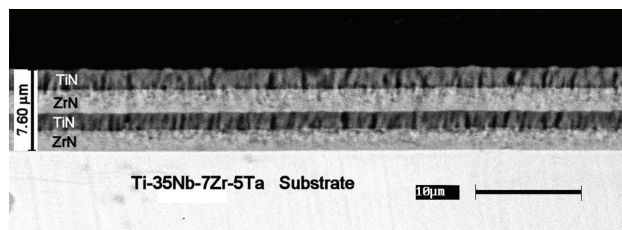**Figure 3.** Micrograph of multilayer coatings obtained by deposition I

Figure 4. Micrograph of multilayer coatings obtained by deposition II.

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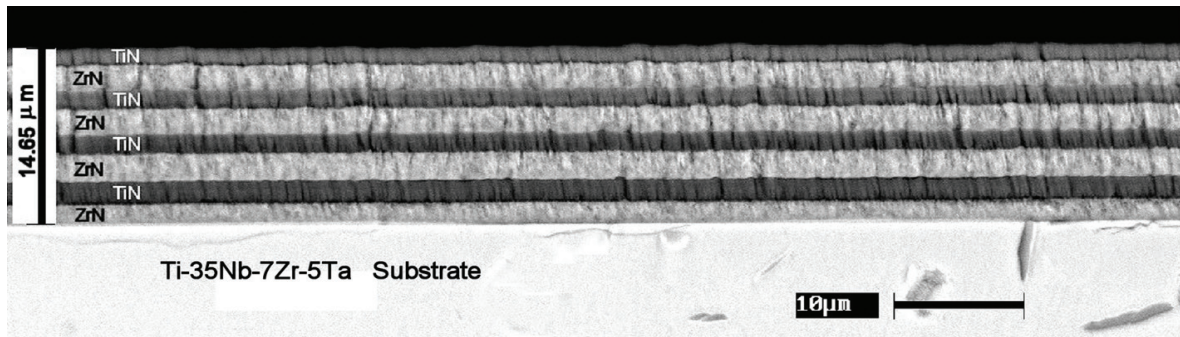
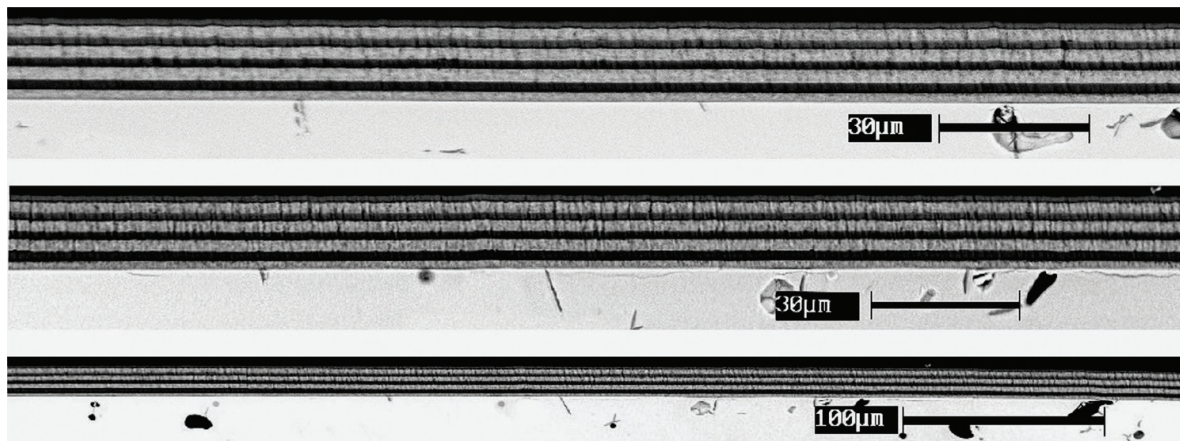**Figure 5.** Micrograph of multilayer coatings obtained by deposition III.

Figure 6. Details of the multilayer coatings obtained by deposition III (several magnitudes), showing the integrity and homogeneity of the coatings along the substrate.

that the residual porosity of the substrates seems do not interfere at the adhesion properties. The good adhesion to the substrate and the integrity of the coating along the substrate can be observed with more details in Figure 6.

A point to be highlighted is the sharpness of the multilayer in micrographs after metallographic preparation. It is unusual the observation of layers with as much distinction between them. This fact facilitates the measurement of its thickness and indicates the efficiency of the process.

The EB-PVD process enables the obtainment of coatings with unique properties. A columnar grain structure perpendicular to the interface results from adjusted process parameters. Figure 7 presents a section of a TiN/ZrN multilayer fractured after the deposition III. The columnar structure of the multilayer obtained by EB-PVD is evident. According to Almeida *et al*. [14] this structure due to a weak bond between the monocrystalline individual columns is responsible for accommodation of mechanical stress that arises from mechanical shock of particles in use or during thermal cycles, optimizing the useful life of the material.
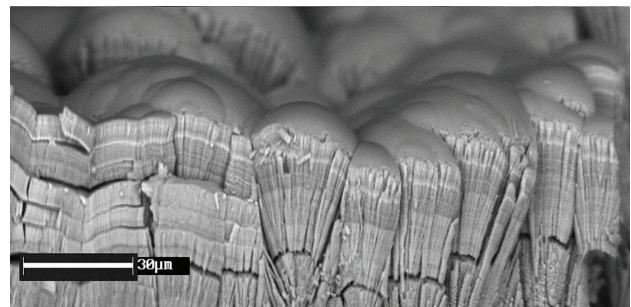

Figure 7. Columnar microstructure and surface morphology of a fractured multilayer coating from deposition III.
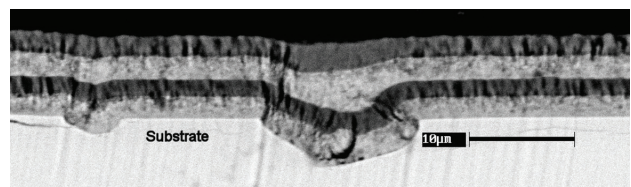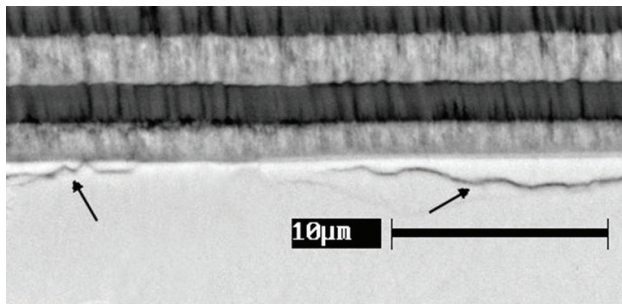

Figure 8. Pore coverage after TiN/ZrN EB-PVD multilayer coatings (deposition II).

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Figure 9. Cracks near the interface (indicated by the arrows) between the substrate and the first layer deposited (ZrN).

The analysis of the surface morphology (Figure 7) shows a dense TiN/ZrN coating without texturing. Porosity and voids were not observed at the surface of the coating. High magnification observations revealed an average grain size of the TiN coating in the range of 10-20 μm. Almeida *et al*. [15] found that properties as density, crystalline orientation and microstructure of EB-PVD coatings are influenced by the deposition parameters such as, substrate temperature, distance from the source to the substrate, pressure in the evaporation chamber, angle of incidence and effects of shading.

An interesting characteristic observed is related to TiN/ZrN deposition inside the superficial pores of the substrate (Figure 8). The microstructural analysis revealed that these pores are penetrated by the multilayer coatings. Since that TiN/ZrN layers are very thick, the first layer is deposited along the relief of the pore and the remaining layers act in the planning of the microstructure correcting these defects. These results reinforce the concept that porosity has low influence on the adhesion properties of the multilayer coatings.

Other microstructural issue is related to the lines like cracks near the interface between the substrate and the first layer deposited (ZrN) in some samples (Figure 9). Godoy *et al*. [16] found that these defects are probably related to residual stresses that arise from two sources: (i) shrinkage of the layer after solidification (primary cooling process) and (ii) difference between the thermal expansion coefficients between the substrate (titanium alloy) and nitride layer deposited. Therefore, a means to prevent the creation of these cracks includes the deposition of a first layer containing a material with similar characteristics to the substrate, such as titanium. Thus, internal tensions would be reduced preventing the crack formation. Good results were obtained using this technique and will be presented in a future paper.

From the hardness measurements, a comparative analysis can be established. Taddei *et al*. [6] found that P/M samples of Ti-35Nb-7Zr-5Ta alloy presented hardness values around 350 HV, while samples coated with TiN/ZrN multilayer after deposition III presented hardness values around 830 HV. Thus, the multilayer coatings promoted an increase of almost 250% in the alloy hardness, which is an important factor to increase the wear resistance. Future experiments will be carried out in order to increase the hardness of TiN/ZrN multilayer based on the influence of chemical composition, thickness and number of layers in the final hardness.

4 CONCLUSIONS

From the development of this work, it was possible to establish a complete process for production of titanium alloy parts with multilayer surface structure based in simple and reliable techniques, which can enhance and expand the use of these structures to more strategic applications. Based on the microstructural characterization carried out after the deposition of TiN/ZrN multilayer coatings on Ti-35Nb-7Zr-5Ta substrates, the following conclusions can be drawn: (a) The layers produced by the EB-PVD process are larger than that obtained by other techniques of deposition, presenting a consistent columnar structure, high adhesion and integrity along the substrate. (b) Since the evaporation of zirconium was less effective than the evaporation of titanium, related to the difference between the vapor pressures of these materials, it is necessary to increase current and time of deposition in order to obtain TiN/ZrN multilayer with homogeneous thickness. (c) The analysis showed that the surface hardness was substantially increased, indicating that the multilayer coatings can contribute significantly to increase the wear resistance of titanium alloys.

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