Titanium Nitride Deposition in Titanium Implant Alloys Produced by Powder Metallurgy

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Abstract. Titanium nitride (TiN) is an extremely hard material, often used as a coating on titanium alloy, steel, carbide, and aluminum components to improve wear resistance. Electron Beam Physical Vapor Deposition (EB-PVD) is a form of deposition in which a target anode is bombarded with an electron beam given off by a charged tungsten filament under high vacuum, producing a thin film in a substrate. In this work are presented results of TiN deposition in targets and substrates of Ti (C.P.) and Ti-13Nb-13Zr obtained by powder metallurgy. Samples were produced by mixing of hydrided metallic powders followed by uniaxial and cold isostatic pressing with subsequent densification by sintering between 900°C up to 1400 °C, in vacuum. The deposition was carried out under nitrogen atmosphere. Sintered samples were characterized for phase composition, microstructure and microhardness by X-ray diffraction, scanning electron microscopy and Vickers indentation, respectively. It was shown that the samples were sintered to high densities and presented homogeneous microstructure, with ideal characteristics for an adequate deposition and adherence. The film layer presented a continuous structure with 15μm.

1. Introduction

Hard titanium nitride coatings have been widely used in engineering applications as wear-resistant layers. Nevertheless, it is required to further improve their tribological properties since the friction coefficient of TiN against commercial metallic materials is not sufficiently low for practical use. Furthermore, TiN coatings can suffer from severe adhesion to counter materials. A method to improve these tribological properties or to reduce the weight of loss by wear and friction is the Electron Beam Physical Vapor Deposition (EB-PVD) [1-2].

EB-PVD is a derivative of the electron beam melting technique. The electron beam causes atoms from the target to transform into the gaseous phase. These atoms then precipitate into solid form, coating everything in the vacuum chamber with a thin layer of the anode material. The deposition rate in this process can be as low as 1 nm per minute to as high as few micrometers per minute. The material utilization efficiency is high relative to other methods and the process offers structural and morphological control of films. Due to the very high deposition rate, this process has potential industrial application for wear resistant and thermal barrier coatings in aerospace industries, hard coatings for cutting and tool industries, surgical implants and electronic and optical films for semiconductor industries [3].

Due to its high hardness and subsequently good wear resistance, titanium nitride (TiN) is frequently applied to coat Ti base alloys to act as protective coating for improving the wear resistance of alloys which allow its use in producing performant coatings and cutting tools. Because of its intrinsic biocompatibility, TiN is also a suitable material for orthopaedic implants, and has been used as a coating for the heads of hip prostheses to improve their wear and fatigue resistance. Moreover, TiN is the material of choice for hard coating of dental implants and surgery tools [4-5].

Powder Metallurgy (P/M) techniques offer the advantage of manufacturing near net shapes products with a considerable increase in the materials utilization factor in the case of titanium alloys [6]. The P/M blended elemental technique (BE) can attain high relative density, over 99.5%, making use of high diffusivity of titanium powder during sintering, resulting in excellent mechanical properties. Its main advantage over others powder metallurgy methods is the elimination of the high production costs from expensive techniques (such as hot isostatic pressing) for the obtainment of high densification levels [7-8].

This work presents results about titanium alloys substrates and Ti targets developed by P/M, and TiN coatings by EB-PVD aiming its effective utilization in aerospace and orthopedic implants. The main contribution is on the microstructural development searching the establishment of an optimized microstructure and and continous layers in order to reach high wear resistance.

2. Materials and Methods

The blended elemental method followed by a sequence of uniaxial and cold isostatic pressing with subsequent densification by sintering was chosen for the preparation of the Ti (CP) targets and Ti-13Nb-13Zr substrates.

The elemental powders were obtained by hydriding method and sintered in hydride state. Ti powders hydriding was carried out at 500 °C, in a vertical furnace, for 3 hours, under a positive pressure. After cooling to room temperature, the friable hydride was milled in a niobium container without protecting atmosphere. Nb and Zr powder was obtained using the same route, however, hydriding temperatures were significantly higher (800 °C).The starting powders were weighed (100 g) and dried for one hour in stove and blended for 60 minutes in a planetary mill with six drips of alcohol. Particle size distribution and morphology was determined by means of a laser-scattering equipment (Cilas model 1064) and scanning electron microscopy (SEM LEO model 435 VPi).

Sintering was carried out in niobium crucible in high vacuum condition (10^{-7} Torr), using a Thermal Technology Inc. model Astro 1000 equipment at 1200°C for titanium (CP) and 900-1400°C for Ti-13Nb-13Zr with heating rate of 20 °C/min. After reaching the nominal temperature, samples were hold at the chosen temperature for 2h and then furnace cooled. Metallographic preparation was carried out using conventional techniques. Specimens were etched with a Kroll solution: (3mL HF: 6mL HNO_3: 100 mL H_2O). Microhardness measurements were carried out in a Micromet 2004 equipment, Buehler, with load of 0.2 kgf. The micrographs were obtained using a SEM LEO model 435 VPi. The density of the sintered samples was determined by the Archimedes method. Table 1 shows the principal characteristics of those powders.

Table 1 - Characteristics of the powders used in the Ti (CP) and Ti-13Nb-13Zr alloy preparation.

Characteristics	**Ti**	**Zr**	**Nb**
Medium particles size (μm)	10	37	12
Morphology	angular	angular	angular
Melting point (°C)	1668	1850	2468

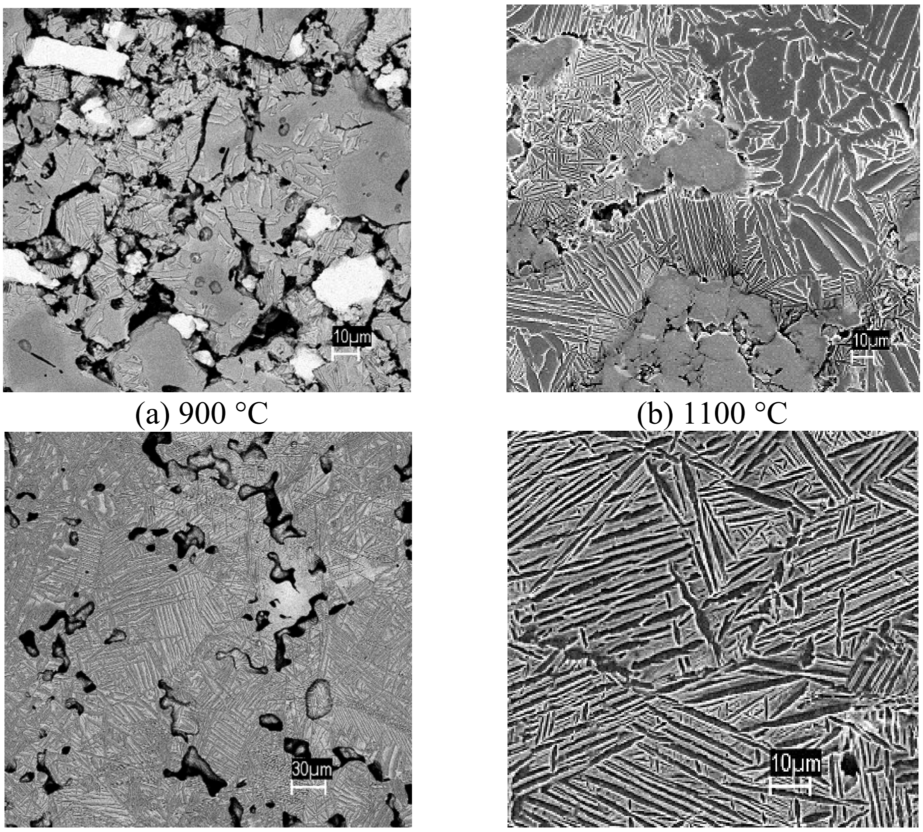
The coating was EB-PVD deposited using one source 30kV electron beam equipment. It consists of an electron gun with an accelerating voltage of 25 kV and beam current variation from 0 to 1.2 A. The vacuum system has an ultimate pressure of 10^{-6} Torr (~ 10^{-4} Pa). A substrate holder assembly is situated above the vapor source at a vertical distance of 150 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 sintered Ti targets. A nitrogen flow directed to the substrates with 10 sccm *(*standard cubic centimeter per minute*)* was used in order to combine with titanium vapor from the targets allowing the deposition of TiN coatings on the substrates. The total time for the deposition was 25 minutes, which in the first 5 minutes only titanium is coated.

3. Results and Discussion

The substrates and targets presented densification varying between 69 up to 71% of the theoretical specific mass, after cold isostatic pressing, and above 95%, after sintering, with homogeneous microstructure.

Ti (CP) prepared as target for posterior evaporation by electron beam in a nitrogen atmosphere presented a monophase (α-Ti) microstructure. It was observed a high densification that it was possible due to the sintering using titanium hydride . The atomic traffic, resulted of the hydrogen removal during sintering, promotes the generation of vacancies that is the base to reach high final densities. The metallografic study showed that the best sintering temperature for pure titanium samples was 1200°C. The microhardness values found in these samples was around 250HV.

Figure 1 presents the microstrutural evolution of the samples after sintering with nominal composition Ti-13Nb-13Zr from 900-1400 °C. Ti-13Nb-13Zr substrates at 1400 °C presented homogeneous microstructure, consisting of hcp-α plates (Widmanstätten) and hcp-martensite (α') dispersed in β matrix. Concerning the alloy microstructure, the dark-contrasting areas are α-phase plates. The β-phase, present among the α-phase areas, gives rise to a white contrast.



(a) 900 °C (b) 1100 °C

(c) 1300 °C (d) 1400 °C

Figure 1- Microstructural evolution of the BE-Ti-13Nb-13Zr during sintering. All samples were sintered at the nominal temperature for 1 h and heating rate equal to 20 °C min^{-1}.

The samples presented hardness values around 300 HV, next to the observed in samples produced by the conventional methods (melting).

The martensite presence seems to demonstrate that the alloy is more likely a α+β alloy instead of a near-β alloy. The microstructure is defined by the control of the β phase precipitation in the cooling that can be retained, to transform into martensitic structures or then allotropicly transform into the α phase [5].

Analyses by EDS were carried out in α and β areas (Figure 2). Table 2 presents the result of the quantitative analysis of the elements. X-ray diffraction analyze in the sample sintered at 1400°C is presented in Figure 3.

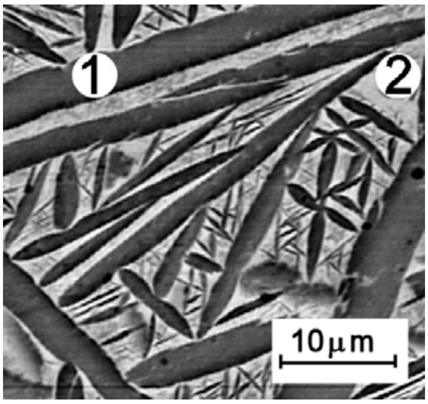


Figure 2- β-phase (1) and α-phase (2) areas analyzed for EDS.

Table 2- Ti, Nb e Zr contents in the areas analyzed for EDS.

Site	Ti (wt. %)	Nb (wt. %)	Zr (wt. %)
(1) α-phase	73,84	13,09	13,07
(2) β-phase	73,15	13,55	13,29

The table 2 shows that the niobium presents a superior content in β-phase, due its power of preferential stabilization of this phase. However, although the niobium, in compositional terms, can be considered a neutral element, it strongly acts in the β-phase stabilization, significantly decreasing the β-transus temperature.

X-ray diffraction analysis revealed only peaks of α and β titanium phases, not being identified peaks related to the hydride, oxide or intermetallics, (Figure 3).

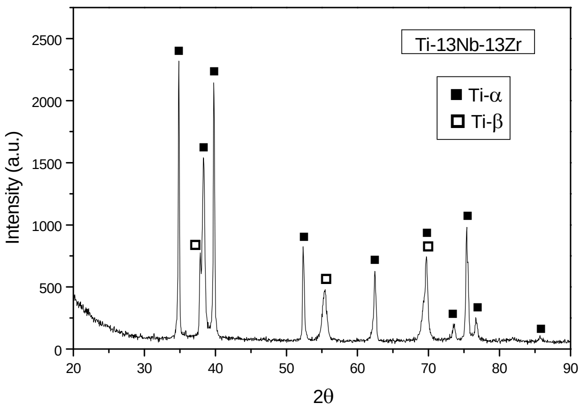


Figure 3- X-ray spectra of Ti-13Nb-13Zr substrate sintered at 1400 °C.

Figure 4 presents Ti-13Nb-13Zr substrates mounting for EB-PVD evaporation and the samples after deposition at 600°C for 25 minutes. The samples present gold to brown color with high level of adhesion.

(a)

(b)

Figure 4- (a) Ti-13Nb-13Zr substrates mounting for EB-PVD evaporation; (b) substrates after deposition at 350°C for 25 minutes.

Figure 5 shows the microstructure of EB-PVD TiN bond layer after deposition by EB-PVD at 600°C for 25 minutes, as seen by SEM on polished cross-section. The bond layer shows color bands associated with chemical composition changes due to the differences in saturation vapor pressure of the individual components as function of the temperature and complex chemical interactions between them. For these reasons, the evaporation of alloy is a selective process, resulting in depletion and enrichment in the melt pool and, consequently, in the coating.

The TiN layer obtained is about 15µm of width, with a continuous film and adequate adhesion conditions. It can be observed in Figure 5 a columnar structure, mainly in the base of the coating. The microhardness values for the TiN film is between 2500-3000HV, indicating elevated wear properties. Further wear analyses are necessary to clear this point, becoming possible surgical implant applications.

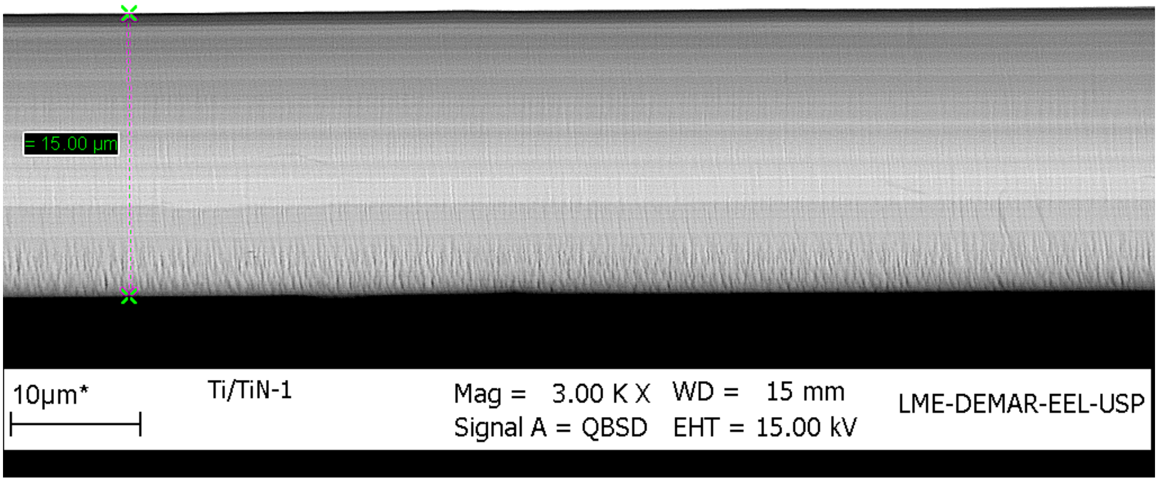


Figure 5- TiN substrates after deposition by EB-PVD at 600°C for 25 minutes.

4. Conclusions

The blended elemental P/M process demonstrated to be efficient for the production of Ti (CP) targets and Ti-13Nb-13Zr substrates. The samples presented high densification and adequate microstructure. Due the complete dissolution of the alloys elements in the titanium matrix, a good combination of microstructure, mechanical properties and densification could be reached. The sintering parameters provided a homogeneous microstructure, with low porosity and contamination. Higher pressing temperatures or longer holding times can lead to intensive grain growth. The hardness values observed in the samples are within the range used in commercially manufactured parts produced by conventional techniques indicates a low interstitial elements pick-up. The TiN layer obtained is about 15μm of width, with a continuous filme with high adhesion and microhardness. High hard values are observed when the color of the coating is near to gold. Brown coatings indicate an oxygen pick-up. A columnar structure and high microhardness values are evidenced becoming possible the application as surgical implants and machining tools.

5. Acknowledgment

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