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Comparison of the Phase Composition and Nanohardness of Gradient TiN/TiO_2 Coatings on Ti5Al4V Alloy Deposited by Different PVD Methods

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Abstract. The effect of the deposition technology of gradient TiN/TiO_2 coatings, applied on Ti5Al4V substrate, on the phase composition and mechanical properties has been studied. The films have been applied by reactive magnetron sputtering and cathodic arc and glow-discharge techniques. The coatings' properties have been studied by X-ray diffraction (XRD) and nanoindentation tests. The results in the present study show that the application of both methods are capable to form polycrystalline TiN and TiO_2. The coatings deposited by magnetron sputtering are monophasic and polycrystalline as TiO_2 is in the form of anatase. Those, applied by cathodic arc and glow-discharge technique, TiO_2 layer is in the form of double-phase structure of rutile and anatase. The measured hardness is similar for the coatings deposited via both methods. The hardness of magnetron sputtered coatings is 6.3±1.1 GPa. The values for coatings obtained by glow-discharge is 6.1±1.4 GPa.

1. Introduction

Titanium alloys have been widely used as hard tissue replacement materials. However, poor tribological properties and possible release of metal products from the alloy in the physiological environment could compromise the biocompatibility of the alloy. The deposition of a stable titanium dioxide films on hard and wear resistant TiN film could overcome the major drawbacks of the Ti alloys whilst promote positive interaction between the metallic implant and the existing bone tissue. These materials are applicable in many branches, such as fabrication of different tools which work in abrasive environments, food processing industries, where surfaces must be cleanable and resistant to microbial contamination, for manufacturing of implants due to their biocompatibility [1-3]. They can also be used as self-cleaning and bio-sensor coating, biomedical materials, etc. [4,5].

The discussed coatings can be obtained by a number of different techniques. The ones used by us are different physical vapor deposition methods. It should be noted that both magnetron sputtering and cathodic arc and glow-discharge provide advantages for controlling the deposition process. This guarantees the reproducibility of the film formation and control of its properties [6-9].

The aim of our present study is to investigate the influence of different deposition methods on the mechanical properties and phase composition of the as-deposited multilayer TiN/TiO_2.

2. Experimental procedures

The chemical compositions of the bare Ti substrate and the target material used for the experiment, determined by JEOL JXCA-733 Microprobe scanning electron microscope (SEM) equipped with wavelength dispersive spectrometers (WDS), were shown in table 1. Samples with dimensions 14×14×4 mm were cut out of 16 mm thick sheet material using the electro-erosion cutting method. The as-received samples were single solution treated (ST) for 30 min at 920 °C and water quenched. Half of the specimens were precipitated (P) for 4 hours at 500 °C and air cooled. All treatments were carried out in ≤ 1 Pa vacuum. The surfaces of the samples were grounded and polished before the EBSM. To study the effect of the surface treatment, the EBSM was applied to as-received, ST and ST and precipitated (ST+P) samples.

Table 1. Chemical composition (wt. %) of the substrate material.

Element	**Al**	**V**	**Fe**	**Mn**	**Co**	**Cr**	**Mo**	**Pd**	**Nb**	**Hf**	**Ti**
Substrate	5.21	4.40	0.14	0.11	0.06	-	0.17	0.15	0.36	0.04	Bal.

The electron beam surface modification (EBSM) was carried out by electron beam installation Leybold Heraeus (EWS 300/15–60). The following technological parameters were applied: electron beam current – I = 20 mA, accelerated voltage – U = 52 kV, speed of the samples motion – V = 0.5 cm/s, electron beam frequency – f = 1 kHz, scanning electron beam with sinusoidal dithering. Afterwards, all samples were ultrasonically washed with absolute ethanol, acetone, isopropanol, rinsed with distilled water for 5 min and dried.

The TiN/TiO_2 coating was applied by two different methods: reactive magnetron sputtering and cathodic arc and glow-discharge method using Ti targets with purity of 99.8%. The deposition of the magnetron deposited TiN layer took a place in the $Ar\text{-}N_2$ atmosphere, as the working pressure was 1.2×10^{-1} Pa, during the deposition process, the substrate had been heated to 350° C. The TiO_2 film was realized in the pure O_2 environment, the working pressure was 7×10^{-2} Pa, as the substrate temperature was decreased down to 180° C. The thickness of each coating (i.e. TiN and TiO_2, respectively) was about 1 μm assessed by the resonant frequency of quartz plate (Intermetalix IL800) coated within the same process conditions. In order to minimize the residual stresses and the oxidation, the samples with deposited coating were retrieved from the vacuum chamber after the achievement of room temperature.

For the cathodic arc deposition of the TiN, a sidewall positioned evaporating system in a cubic vacuum chamber with water-cooled walls was used. The samples were hanged near the center of a clockwise-rotating with a frequency of 0.5 Hz turntable. To ensure the coating stress relaxation and necessary adhesion a very thin pure layer from the target (at 2.5×10^{-1} Pa in Ar atmosphere for 5 min., bias 600 V, 110 A arc current) was applied. The TiN film was made in a pure N_2 atmosphere at 340 °C substrate temperature for a time of 60 min., 110 A arc current, bias 250 V and 7.5×10^{-1} Pa pressure in the working chamber. The TiO_2 film was made by glow plasma discharge using the uppermost located sputtering system in the same chamber. A bias voltage of 1340 V (720 mA current) in a pure O_2 atmosphere at a pressure of 6×10^{0} Pa were applied for a deposition time of 240 min. Both layers' thickness was attained by means of calotest measurements: TiN ~ 1.6 μm, TiO_2 ~ 0.6 μm.

The coatings were characterized by X-ray diffraction analysis using URD6 Seiferd&Co diffractometer with CuKα radiation. The registration of the patterns was within 20° to 70° at 2θ scale with 0.1° step and counting time of 10 s per step. The experiments were conducted in symmetrical Bragg-Brentano (B-B) mode.

The mechanical properties of the coatings were characterized by Nanomechanical Tester (Bruker, USA). The software program prepared for this experiment consisting of 4 lines with 12 indentations each (total of 48 indentations) and 80 μm spacing was utilized. The applied force for each indentation was 50 mN.

3. Results and discussions

Figure 1 and 2 presents the XRD patterns of the multilayer coatings, deposited on Ti5Al4V alloy. Peaks corresponding to α-Ti from the substrate, as well as TiN and a-TiO_2 can be seen in the diffractogram of the sample obtained by magnetron sputtering (figure 1). Diffraction maxima corresponding to r-TiO_2, β-TiO_2, etc. were not observed, which means that the coatings are mono-phase (polycrystalline TiN and TiO_2).

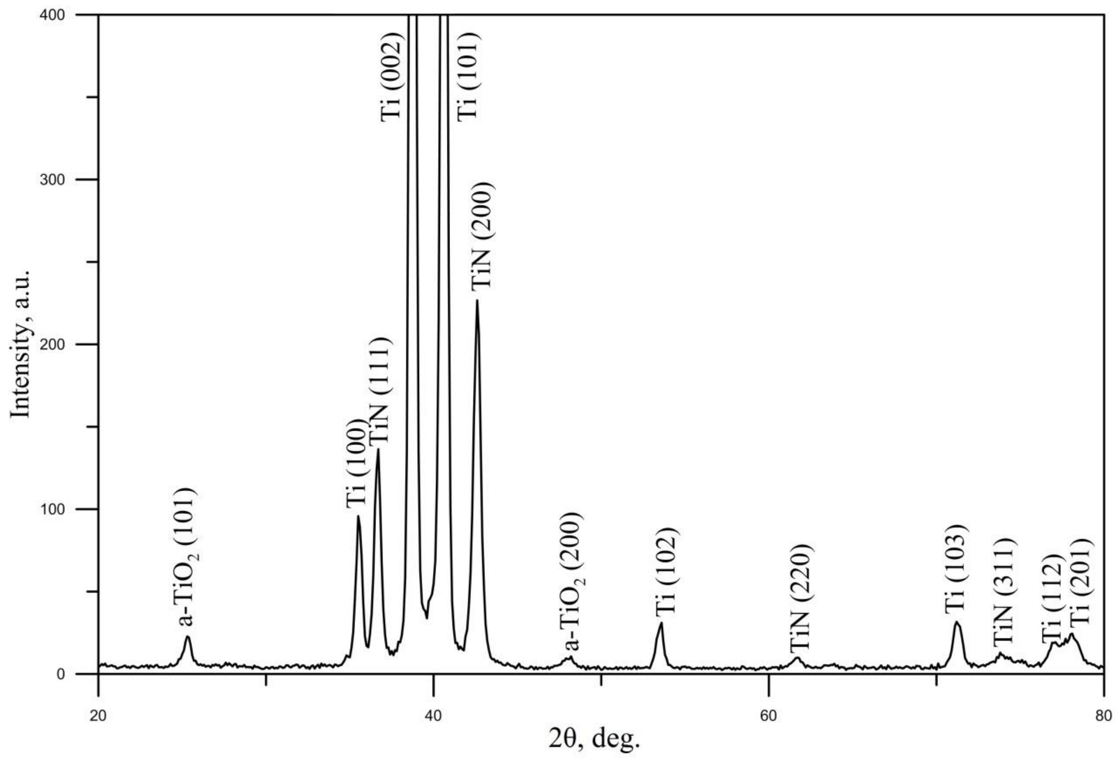

Figure 1. XRD of multilayer TiN/TiO_2 deposited by magnetron sputterring

The diffractogram of the sample obtained by cathodic arc and glow-discharge (figure 2) shows also peaks belonging to α-Ti from the substrate, as well as TiN and a-TiO_2. Also, diffraction maxima corresponding to r-TiO_2 are observed, which means that the obtained coatings are double-phase.

These results are in agreement with those published in other studies, where the formation of TiO_2 coatings has been studied. It should be noted that in our case, during the deposition process via magnetron sputtering, no bias voltage was applied. This is the reason for the TiO_2 to be in single phase with absence of rutile. This result correlates with the results published in ref. [10]. The presence of rutile phase in the glow-discharge deposited coatings is due to the applied high bias voltage. As stated in other studies [10, 11] the rutile phase can be induced in the TiO_2 coating by applying bias voltage.

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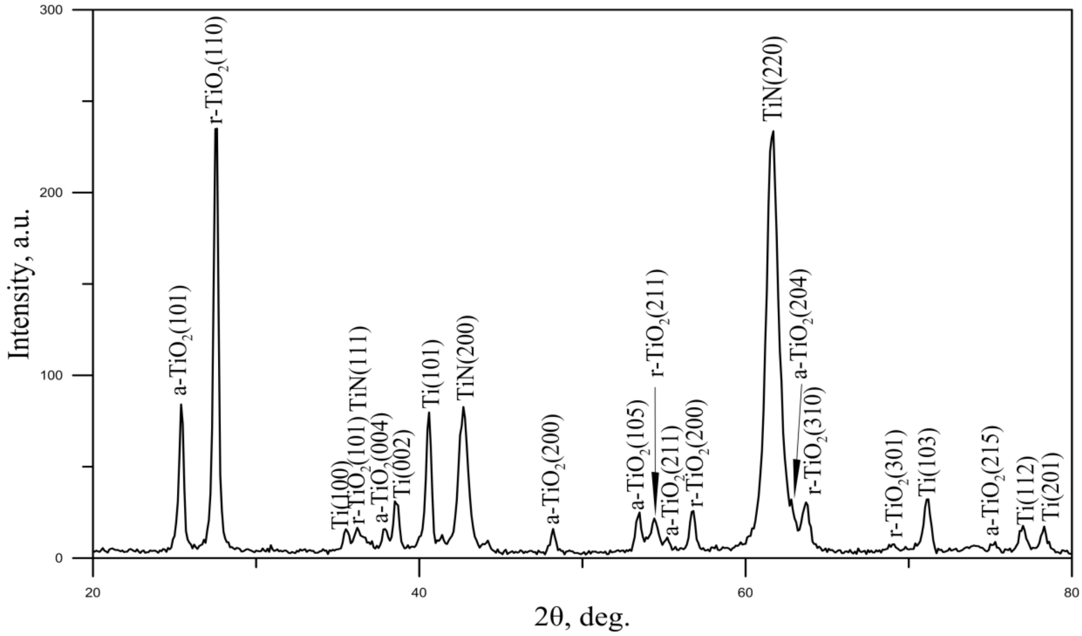

Figure 2. XRD of multilayer TiN/TiO_2 deposited by cathodic arc and glow-discharge

The mechanical properties of the coatings have been studied by nanoindentation tests and the results are summarized in table 2. Both coatings were tested by a load of 50 *mN*. The hardness values were evaluated from the load displacement curves [12, 13], which are shown in figure 3 and 4. From the figures it can be seen that the penetration depth of the indentor after each load is different. This scattering of the penetration depths can be explained by the very different surface topography. The treatment of the substrates by scanning electron beam is capable to increase the surface roughness leading to a larger number of peaks and valleys with higher amplitude. The penetration of different surface formation strongly reflects on the penetration level during the measurement.

Table 2. Nanohardness of the deposited multilayer TiN/TiO_2 coating

Deposition method	Hardness, GPa
Magnetron sputtering	6.3 ± 1.1
Cathodic arc and glow-discharge	6.1 ± 1.4

The measured hardness of the TiN/TiO_2 coatings deposited on Ti5Al4V substrates by the two different methods show similar values, namely 6.3 *GPa* for the specimen deposited by magnetron sputtering and 6.1 *GPa* for the one deposited by glow-discharge.

The authors [10] have reported that the application of bias voltage and presence of double phase structure of rutile and anatase when considering TiO_2 film results in increase the hardness. However, the results obtained in the present study can be explained by the nature of the two deposition methods. Using magnetron sputtering yields denser coatings than cathodic arc [14]. The denser coatings leads greater hardness. In our case, the application of bias voltage during the cathodic arc and glow discharge method leads to an increase in density of the atoms near the substrate, hence increase the density and change the phase composition (figure 2) of TiO_2 film in the coating. The results obtained in present study show that the mechanical properties of the deposited TiN/TiO_2 coatings depend on the phase composition and on the deposition method. This is the reason that both methods are capable to produce coatings with similar hardness.

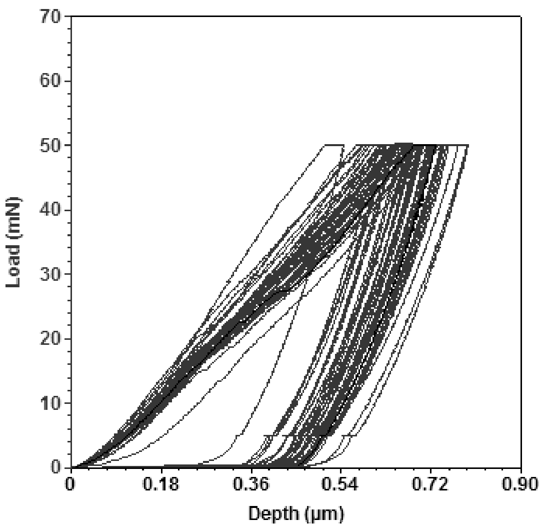

Figure 3. Load displacement curves of multilayer TiN/TiO_2 deposited by magnetron sputtering

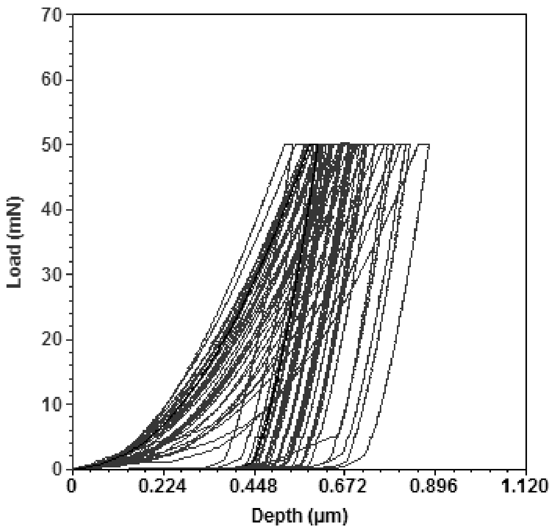

Figure 4. Load displacement curves of multilayer TiN/TiO_2 deposited by cathodic arc and glow-discharge

4. Conclusions

The results in the present study show the difference in phase composition of multilayer TiN/TiO_2 coatings on Ti-5Al-4V substrate obtained by two PVD methods, magnetron sputtering and cathodic arc and glow-discharge. Magnetron sputtered coatings are monophasic and polycrystalline with presence of anatase TiO_2, whereas the samples obtained by the cathodic arc and glow-discharge method are double-phase and polycrystalline with the presence of anatase and rutile TiO_2.

It is shown that the samples have similar hardness. The coatings obtained by the magnetron sputtering method have hardness about 6.3 *GPa*, while those obtained by the cathodic arc and glow-discharge method have 6.1 *GPa*.

5. References

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