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Application of TiN/TiO_2 coatings on stainless steel: composition and mechanical reliability

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Abstract. The paper reports on the effect of the substrate temperature (350 ^{o}C, 380 ^{o}C and 420 °C) during reactive magnetron sputtering of a TiN film on the phase composition, texture and mechanical properties of TiN/TiO_2 coatings on 304L stainless steel substrates. Pure Ti was used as a cathode source of Ti. The texture and unit cell parameters of both TiN and TiO_2 phases of the coating are discussed in relation with the tribological properties and adhesion of the coating. The scratch tests performed showed that the nitride deposited at 380 °C, having the highest unit cell parameter and a predominant (111) texture, possessed the lowest friction coefficient (μ), tangential force and brittleness. The anatase-type TiO_2 with predominant (101) pole density and increased *c* unit cell parameter showed the highest stability on the nitride deposited at 420 °C. The results indicated that the friction coefficient, tangential force and critical forces of fracture could be varied by controlling the coating deposition temperature.

1. Introduction

The demand for better quality of life entails the need of high-quality implant devices making fast recovery possible. The medical grades stainless steel has long been a quite common material used for manufacturing a variety of hard implantable devices, such as orthopedic prostheses, valves, or endo-prostheses, as thin-wall stents, and dental brackets [1]. The AISI grade 304L steel has high corrosion resistance, which is an important aspect for the material biocompatibility; still, concerns persist because of steel's poor tribological properties and the metal ions released from it after prolonged exposure [2] that disturb the cell proliferation and differentiation. An approach to minimizing the corrosion phenomenon and the release of metallic ions is the deposition of coatings of more biocompatible materials, like Ti, TiN, and TiO_2. Moreover, the hardness and wear resistance that are beneficial for the medical device could be thus enhanced [3, 4]. The different material properties will affect the coating adhesion, resistance to plastic deformation, fracture toughness, etc. Hence, the aim of this study was to determine the influence of different deposition temperatures of a magnetron

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sputtered TiN/TiO_2 coating on the composition and tribological properties of the implant system. X-ray diffraction (XRD) was employed to characterize the phase composition, texture and crystalline particles of both coating layers. The adhesion, which is the most important element determining the final coating quality, was assessed by means of a macroscratch test analysis in a progressive-load scratching mode.

2. Experimental procedures

Austenitic stainless steel 304L (X2CrNi18-9, 1.4307) with weight composition of C 0.03%, Cr 18%, Ni 8%, Mg 0.2% P 0.045%, Si 0.75% and Fe balance was used for the experiments. The specimens had a dimension of 22.22×19.15×2.9 mm. All the samples were ground by sandpaper down to P800 and mechanically polished.

The TiN/TiO_2 coating was applied by reactive magnetron sputtering. The diameter of the Ti target of 99.8% purity was 100 mm. The TiN layer deposition took a place in Ar-N_2 atmosphere for 90 min at a working pressure of 1.2×10^{-1} Pa. During the deposition process, the substrate was heated to 350 °C, 380 °C and 420 °C. The TiO_2 film was formed in pure O_2 environment for 120 min at the working pressure of 7×10^{-2} Pa, as the substrate temperature was decreased down to 180 °C. The thickness of each coating (TiN and TiO_2) was about 1 μm, as assessed by the resonant frequency of a quartz plate (Intermetalix IL800) coated under 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 room temperature was reached.

The coatings were characterized by X-ray diffraction using a URD6 Seiferd&Co diffractometer with CuK_α radiation. The patterns were registered within the 20° – 80° interval at 2θ scale, a 0.1° step and counting time of 10 s per step. The experiments were conducted in symmetrical Bragg-Brentano (B-B) mode.

The scratch tests were performed on the top surface of the samples with a CSM REVETEST Scratch Macrotester equipped with a Rockwell diamond indenter with a 200-μm tip radius. In scratching mode, a progressive load was applied with a normal force ranging from 0 to 50 N at a speed of 10 N/mm. The scratch track was evaluated visually by a Nikon optical microscope, with a 14-megapixel digital camera adapted for image acquisition within the 16-FMME-02 project of University of Ruse [5]. Also, digital-signals were recorded of the friction coefficient (μ), the tangential force (F_t) and the acoustic emission (AE) fluctuations The scratch hardness (H_S) and fracture toughness (K_{IC}) were calculated by the equations quoted in [6] and [7], respectively.

3. Results and discussions

Figure 1 shows diffractograms of the TiN/TiO_2 coatings on 304L substrates, with the nitride sub layers deposited at different temperatures (350 °C, 380 °C and 420 °C). The results indicate the presence of polycrystalline TiN, TiO_2 phases and austenite reflected from the substrate. The TiO_2 phase is anatase-type.

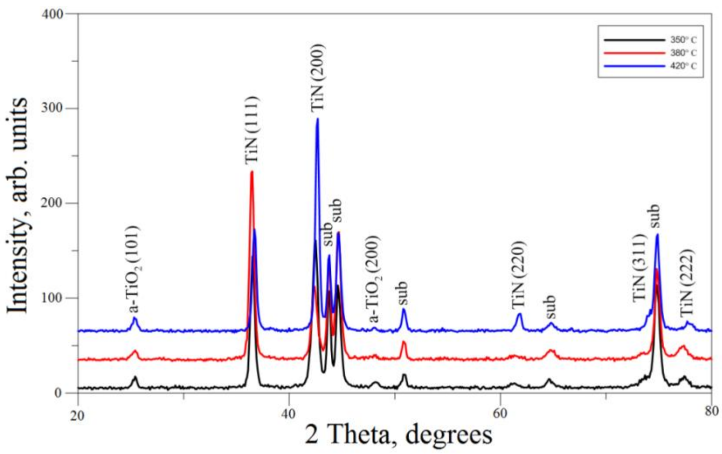

Figure 1. XRD patterns of TiN/TiO_2 coatings deposited on 304L steel substrates under different temperature conditions.

Table 1 illustrates the influence of micro-volume fractions belonging to different texture components, represented by the diffraction pole density P_{hkl} as a function of the substrate temperature during the deposition of TiN. It is clear that at lower temperatures (350 °C and 380 °C) the predominant crystallographic orientation of the TiN coating is (111), while with the substrate temperature increase up to 420 °C the texture changes mainly to the (200) direction. Concerning the TiO_2 film, the texture shifts from the (200) direction at lower temperatures (350 °C and 380 °C) towards the (101) direction at 420 °C. In contrast with the TiN deposited at 350 °C, where the grains size is about 24 nm, the TiN deposited at 380 °C and 420 °C shows larger and similar grain sizes – 27.5 nm and 26.9 nm, respectively. The grain size of TiO_2 rises substantially from 18.86 nm and 18.83 nm for the coatings deposited at 350 °C and 380 °C to 23.3 nm for the one deposited at 420 °C.

Table 1. Texture components presented by diffraction pole density and grain size of the films phases.

T, °C	TiN				TiO_2		Grain size, nm	
P_{hkl},%	$P_{(111)}$	$P_{(200)}$	$P_{(220)}$	$P_{(311)}$	$P_{(101)}$	$P_{(200)}$	TiN	TiO_2
350	41.58	32.96	4.75	20.72	40.86	59.14	24.12	18.86
380	64.54	16.74	4.76	14.02	44.87	55.13	27.52	18.33
420	30.20	46.66	8.25	14.89	58.50	41.50	26.9	23.3

The calculated unit cells parameters of the TiN/TiO_2 coating are summarized in table 2. The unit cell parameters of the TiN films deposited at 350 °C and 380 °C exceed those cited in the ICDD diffraction data. In the case of the substrate temperature of 420 °C, the TiN unit cell is smaller than those quoted in ICDD. For the TiO_2 phase, the *a* unit cell parameters are similar for both temperatures of 350 °C and 380 °C and increase with the increase of TiN deposition temperature. The *c* parameter follows a linear increase in line with the increase of the substrate temperature during the TiN deposition.

Table 2. Calculated unit cells parameters of the deposited films.

	350° C		380° C		420° C		ICDD database	
	TiN	TiO_2	TiN	TiO_2	TiN	TiO_2	TiN	TiO_2
a, Å	4.256	3.776	4.265	3.774	4.237	3.782	4.241	3.785
c, Å	-	9.345	-	9.453	-	9.524	-	9.513

The digital signal recordings from the tribological test of all three coated samples shown in figure 2 a and b indicate that a difference in the friction coefficient of (μ) is seen after a 5-N normal load (figure 2 a). For the film deposited at 350 °C, the friction coefficient's rising trend is accompanied by severe fluctuations of up to 0.4. Once the loading reaches 25 N, μ diminishes because of the joint influence of the nitride and the substrate. The coating deposited at 420 ºC shows a smoothly increasing μ behavior with a maximum value of 0.35. After loading to 20 N, the μ values are also dependent on the complex substrate-coating influence. The coating with nitride deposited at 380 ºC has the lowest coefficient of friction. The surface film is largely stable up to 50 N despite the coating sinking in the substrate at 22.6 N, which does not cause delamination and μ keeps its low values until the end of the test.

The behavior of F_t (figure 2 b) for all three coated samples is of a similar growing nature, with the highest fluctuations shown by the specimen deposited at 350 ºC, and the lowest, by the one deposited at 380 ºC. Additionally, the acoustic emission (AE) signals from the scratch test allow one to assess the coatings' hardness and fracture toughness. All three coated samples indicate a similar scratch resistance up to 5 N. As the load progressively increases, the brittleness of the coating deposited at 350 ºC causes strong fluctuations in the AE. A similar effect occurs for the coating deposited at 420 ºC, but the AE manifests a more uniform variation, while its higher values suggest a higher coating hardness. The AE of lower level and intensity recorded for the coating deposited at 380 ºC is indicative of lower internal stresses in the TiN/TiO_2 film.

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The scratch track micrographs (figure 2 c) of all three coated samples show distinct first cracks (Lc_1) occurring during the progressive loading; the Lc_1 value increases with the increase of the nitride deposition temperature. The shape of the lateral cracks of all samples indicates ductile tensile cracking arising from the plastic deformation around the indenter. The piling up of material in front and sideways of the residual groove is indicative of low substrate hardness. Although total delamination is not observed up to 50 N for all coated samples, the coatings deposited at 350 °C and 420 ºC show a partial detachment at maximum load. The coating deposited at 380 ºC is stable under the indenter up to 50 N.

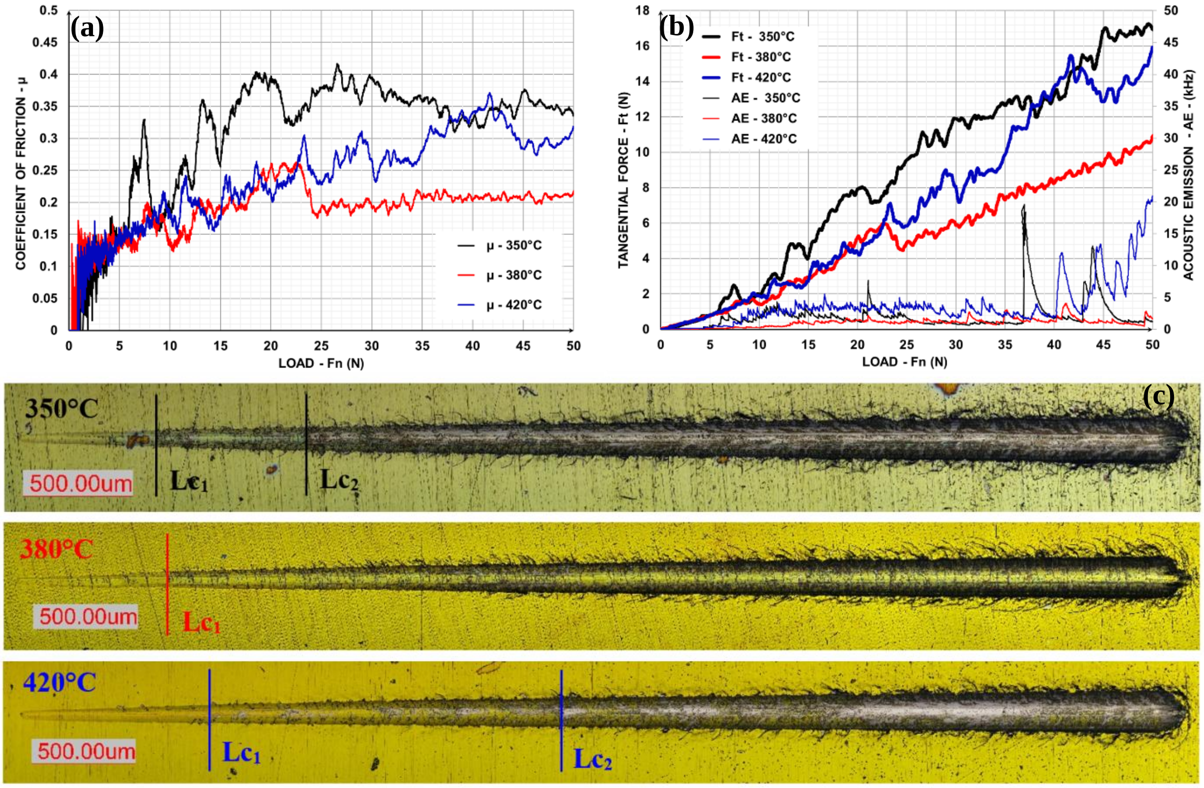

Figure 2. Comparison of the variation in the: **a**) tangential force (F_t); **b**) coefficient of friction (μ) and acoustic emission (AE) and **c**) micrographs of the scratch tracks during progressive 0 N to 50 N scratch tests of the TiN/TiO_2 coatings deposited on 304L steel substrates under different temperature conditions.

As shown in table 3, the scratch hardness values decrease with the increase of the deposition temperature of the nitride. The higher F_t value at Lc_1 for the nitride deposited at 350 º C proves its fragile behavior, but increases its fracture toughness. The lowest K_{IC} value at L_{c1} calculated for the nitride deposited at 380 ºC suggests a higher plasticity of the coating that demonstrates prevailing (111) oriented micro-volume fractions. At 420 °C, the unfavorable slipping planes prevail, which reduces the fracture toughness at L_{c1}. The Lc_2 values reach 14.08 N and 23.36 N for the coatings deposited at 350 °C and 420 ºC, respectively, which suggests a better adhesion of the coating deposited at the higher temperature. Nevertheless, the smaller penetration of the indenter because of the higher strength of the surface of the nitride deposited at 350 ºC gives rise to its fracture toughness value at L_{c2}. The coating deposited at 380 ºC does not show detachment from the substrate, but only deformation and embedding in the stainless steel material.

Table 3. Calculated scratch test parameters of the deposited coatings: Lc_1 – the load inducing the first crack of the coating, Lc_2 – the load inducing partial detachment of the coating, F_t – tangential force at the critical loading, H_S – scratch hardness, K_{IC} – fracture toughness.

T, °C	Lc_1, N	F_t at Lc_1, N	H_S, GPa	K_{IC}, MPa.m$^{1/2}$	Lc_2, N	F_t at Lc_2, N	H_S, GPa	K_{IC}, MPa.m$^{1/2}$
350	7.60	2.40	3.85	0.014	14.08	5.02	3.58	0.019
380	7.80	1.53	3.82	0.0062	>50	-	-	-
420	9.52	1.95	3.40	0.0067	23.36	6.18	3.20	0.012

4. Conclusions

The TiN/TiO_2 coatings deposited on 304L stainless steel at different temperatures have the same phase composition, but different texture and tribological behavior. The TiN deposited at 380 °C, which has predominant texturing in the close-packed (111) direction and the highest unit cell parameters and grain size, exhibits the best tribological test results, as its μ, AE, and Ft values are the lowest. The low (200) and (311) pole density of the nitride sub-layer enhances the tribological performance − adhesion of the coating, but decreases its scratch hardness. As the deposition temperature increases, a reorientation to the (200) direction occurs, which is a prerequisite for a higher brittleness of the coating. At the deposition temperature of 350 ºC, the allocation of the crystallographic planes of the nitride is more balanced, as the unfavorable directions exceed, in aggregate, the favorable one, which explains the lower plasticity of the coating. On the other hand, the low stability of the anatase oxide on the nitride deposited at 350 °C could be explained by the higher stresses at the oxide-nitride interface and the (200) texture of the surface layer that causes higher scratch hardness and fracture toughness. The oxide obtained on the nitride deposited at 420 ºC has the highest stability due to the change of its texture to the (101) direction and the increased *c* unit cell parameter and grain size.

Acknowledgments

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