

ADHESION ANALYSIS OF TITANIUM OXIDE NANOCOATINGS ON TITANIUM SURFACE

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Abstract: *Ti and its alloys are mostly used for implant production. Their biocompatibility depends on the formation of thin TiO₂ layer on the surface. It can be improved by modification of oxide structure in tubular. For biomedical applications, the adhesion of the coating layers is essential. The aim of the present paper is to investigate the adhesion of TiO₂ nanocoatings on titanium surface.*

Commercially pure Ti (CP Ti) and Ti-6Al-4V alloy samples were grinded, etched and anodized. The anodization was done in 0.5 wt.% HF electrolyte with duration of 7 hours for the CP Ti samples and 6 hours for Ti-6Al-4V alloy samples. The adhesion was investigated by tape and scratch tests. The critical loads that generate the first failures during the scratch test are used for characterization of the adhesion of the TiO₂ nano-tubular coating. The critical loads were measured by CSEM-Revetest macroscratch tester under progressive scratching mode. The samples were characterized by SEM and EDX analysis. The areas around the critical load were further observed by optical and scanning electron microscopy for detail inspection of failure mechanism.

It was established that the higher micro-roughness of the surface of CP Ti sample after anodization is responsible for the detachment only of small areas of the nano-tubular coating situated mainly on the top surface. The lower micro-roughness of the sample made of titanium alloy and the presence of large flat areas lead to detachment of large coating's portions. The scratch test reveals that the TiO₂ nano-tubular coating on the CP Ti fails at an early stage ($L_{c1} \sim 8$ N; $L_{c2} \sim 26$ N), while that on the Ti-6Al-4V sample undergoes cohesive failure and completely fails at higher load values ($L_{c1} \sim 13$ N and $L_{c2} \sim 40$ N respectively). As titanium alloy is ductile material with higher strength than the CP Ti, it provides better support for the coating and produces higher critical loads.

Keywords: TITANIUM, Ti-6Al-4V, TITANIUM OXIDE, NANOTUBES, COATING ADHESION

1. Introduction

Titanium and its alloys are mostly used for implant production. Their biocompatibility depends on the formation of thin TiO₂ layer on the surface [1,2]. It can be improved by modification of oxide structure in tubular, because the TiO₂ nanotubes can mimic the dimensions of the natural bone components. Many research groups work on investigation of the biocompatibility of nano-tubular coatings on titanium implants.

It was established by S.Oh et al. [3] that the addition of nanotubes to the microstructured surface enhances multiple osteoblast behaviors, resulting in better *in vivo* osseointegration. The presence of a vertically aligned TiO₂ nanotube surface on Ti foils improved the proliferation and mineralization of osteoblasts. According to the same group [4] the cell response depends on the nanotubes' diameter, thus on small-diameter nanotubes, increased cell adhesion and growth with minimal differentiation is prevalent, while on larger-diameter nanotubes, mesenchymal stem cells are forced to differentiate specifically into osteoblast cells. It was established by N. Wang et al. [5] that 70 nm diameter is the optimum size for TiO₂ nanotubes implants to obtain favorable osteoconductivity and osseointegration.

TiO₂ nanotubes can be prepared by various techniques: sol-gel method, electrochemical deposition and anodization [4,6]. But anodization is preferred to the rest two processes because it provides strongly adherent TiO₂ layer. The process is rapid, simple and inexpensive ensuring large array of titanium nanotubes [7-9].

For bio-medical applications, the adhesion and mechanical integrity of the TiO₂ layer are essential. The adhesive strength between the anodic oxide films and the titanium substrate was reported to be from 11,7 MPa [3] to 25 MPa [9]. The bond strength between nanocoatings and titanium substrate is investigated mainly by tape test, tensile test or scratch test. Y. Parchaen et al. [10] measured the adhesion of the hydroxyapatite coating to the substrate using ASTM D 3359-02 cross-cut tape test (B). They used 3M Brand Scotch tape which was firmly placed in the area and was pulled off at an angle as close to 180° as possible after 90 s. After that the surface morphology was investigated and the coating delamination was evaluated. During tensile test standard tensile testing machine is used [3,11-13]. The surfaces of the control

samples and that with coatings are attached to the cylindrical rods with glue, adhesive tape or PMMA bone cements. Tensile loads are applied normally to the samples with crosshead speed of 0,5 – 1mm/min until interfacial failure occurs. The mean tensile bonding strength and standard deviation are calculated as well as the interface morphology is examined. The scratch test gives estimation of the adhesion strength of the coatings by determining the critical load L_c , which is defined as the load where film flaking starts [14].

The aim of the present paper is to investigate the adhesion of TiO₂ nanocoatings on the surface of commercially pure titanium and Ti-6Al-4V alloy using both tape and scratch tests.

2. Experimental methods

Anodization

Round samples with dimensions 24 mm x 3 mm (diameter x thickness) were made of commercially pure (CP) Ti Grade-2 (99,5%) and Ti-6Al-4V alloy with chemical composition: Al-5,7%; Fe-0,13%; V-3,8%; O-0,089%; Ti-the rest (wt.%). The samples' surface was grinded with sandpaper 300, 600 and 800. After grinding they were ultrasonically cleaned consecutively in acetone, ethanol and deionized water for 15 min in each media and dried with compressed air. On the next stage the samples were etched for 30 min in 0.5 wt.% HF acid, immediately rinsed with deionized water and dried. They were anodized in an electrolyte, containing 0.5 wt.% HF acid, at 25V for CP Ti and 30V for Ti-6Al-4V alloy. DC power supply and a graphite electrode as cathode were used. The process duration was 7 hours for CP Ti and 6 hours for Ti-6Al-4V alloy. Immediately after anodization the samples were rinsed several times with deionized water and dried with compressed air.

Adhesion tests

Two types of adhesion tests were done. The first one was made with Scotch Transparent Film Tape 640 of 3M with 12,7 mm width and adhesion to steel 30 N/100 mm. As this test gives only relative evaluation of the coatings adhesion we additionally did scratch test. The scratch tests were performed on the top surface of the sample with a CSM REVETEST Scratch Macrotester equipped with a Rockwell C diamond indenter of 200 µm radius. Progressive load scratching mode with normal force range of 1 N to 50 N was used

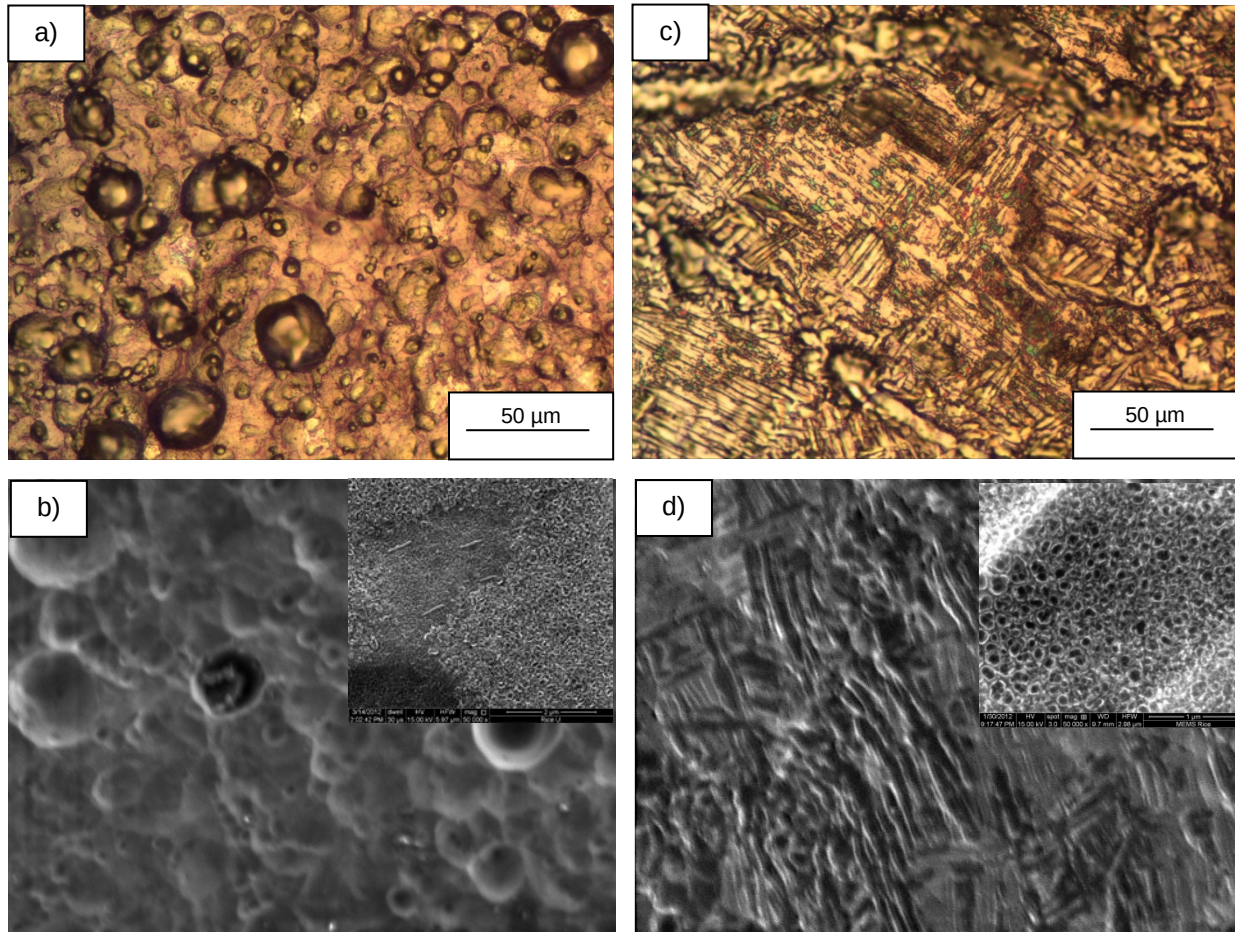


Fig. 1. Surface topography of samples of CP Ti – a), b) and Ti-6Al-4V alloy – c), d) investigated by optical microscopy (a and c) and SEM with original magnification 600x (b and d).

in all experiments and at a speed of 10 N/mm. Critical load values (L_c) at which the failure event occurred for each sample were calculated as an average from at least five tests made in different areas to verified the obtained results. Scratch width at the critical loads was also measured using optical methods of localized regions of poor adhesion and failure for each scratch.

Samples characterization

The surface topography and morphology were observed with optical and scanning electron microscopies. Two SEM were used: high resolution field emission scanning electron microscope FEI Quanta 400 ESEM FEG (ESEM2) and SEM JEOL 733 which was subject to digitalization by a university project 2015 FMME 03. The EDX analysis was made on FEI Quanta 400 ESEM FEG (ESEM2).

3. Results and discussion

Anodization

The superficial morphology of both coated samples, shown in Fig. 1a and Fig. 1b, discloses that the anodization of CP Ti produces step morphology with many small and deep craters that influences the subsequent treatment. Irrespective of their size, all of the present micro voids have defined borders. The anodization of the alloy (Fig. 1c and Fig. 1d) reveals the fully lamellar microstructure between α and β lamellas. It can be stated that the surface micro-roughness of the CP Ti coated sample is higher compared to the alloy coated system.

Our previous investigations [15] showed that after 7 hours

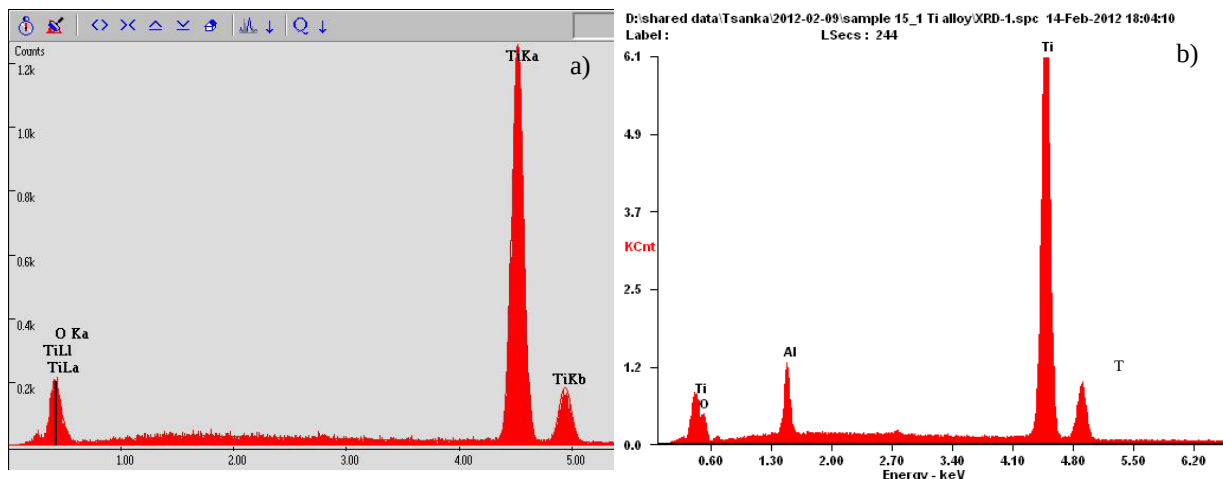


Fig. 2. EDX analysis of the surface of samples of CP Ti – a) and Ti-6Al-4V alloy – b).

anodization the surface of the CP Ti was covered with oxide layer with nanotubular morphology in 70-80% of the area and nanorods in the rest 30-20% (Fig.1b high magnification). The nanotubular structure consisted of nanotubes (NTs) with irregular shape and sizes with average internal diameter about 121 nm. After 6h anodization 80% of the surface of Ti-6Al-4V alloy sample was

covered with comparatively well-shaped NTs (Fig.1d high magnification) with average internal diameter about 109 nm. EDX analysis on Fig. 2 shows that the NTs regions on the CP Ti surface consist of TiO_2 . The presence of Al additionally to the Ti and O in the NTs regions on the Ti-6Al-4V alloy sample are evidence that the all elements take part in the anodization process.

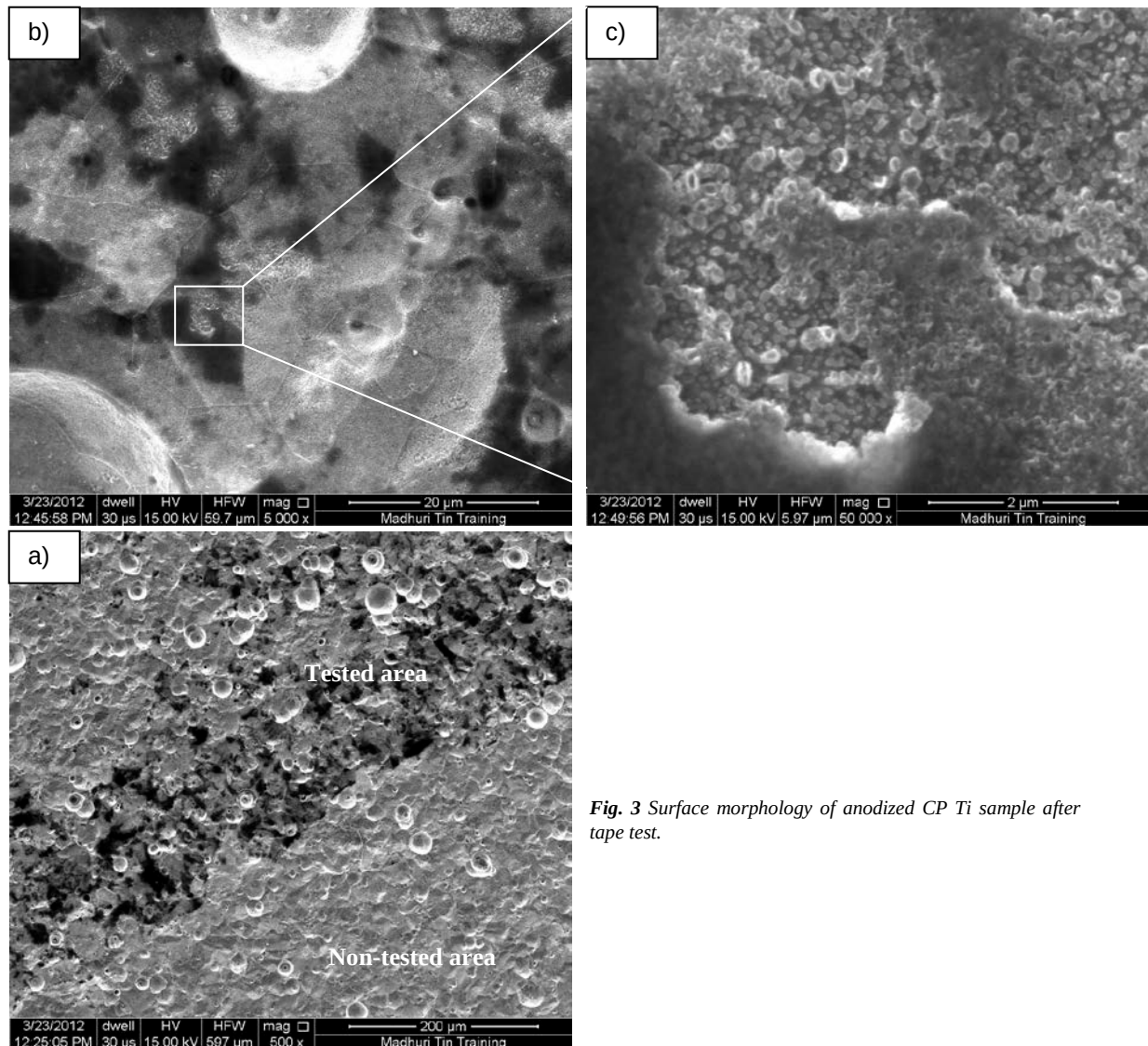


Fig. 3 Surface morphology of anodized CP Ti sample after tape test.

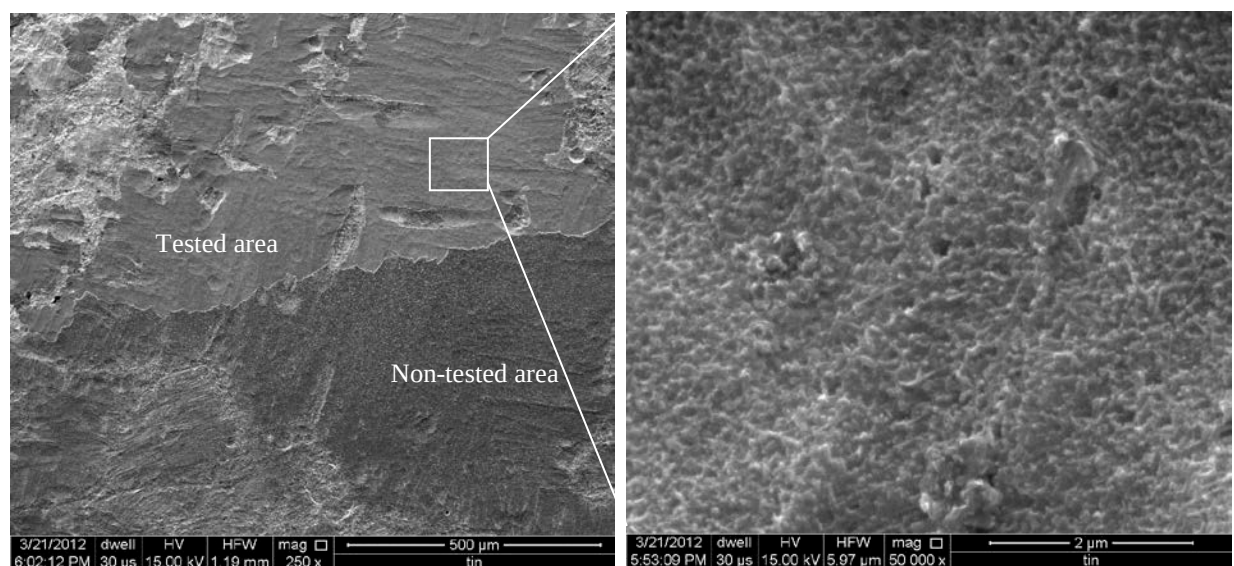


Fig. 4 Surface morphology of anodized Ti-6Al-4V sample after tape test.

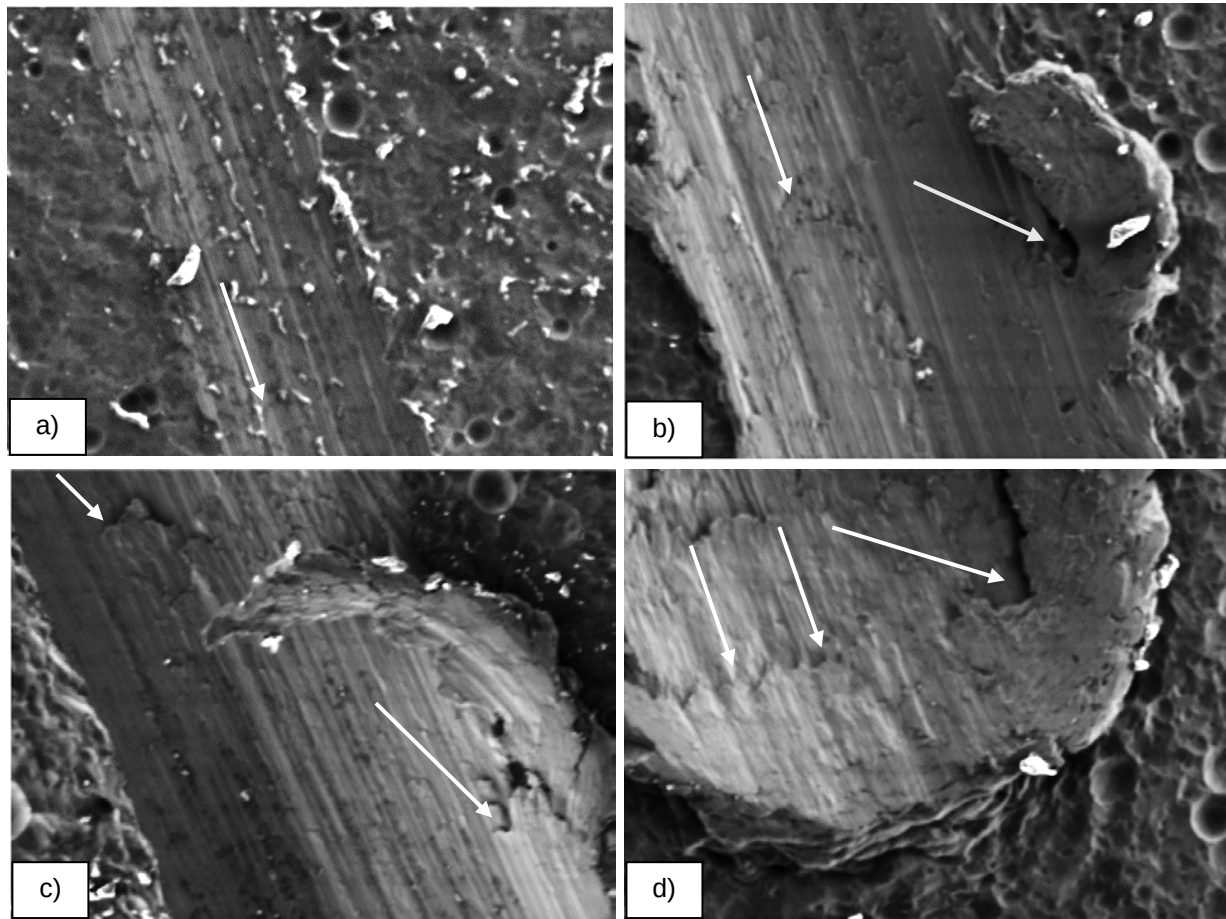


Fig. 5. Morphology of the scratch areas on the CP Ti coated sample: a) initial area of the track (original magnification 400x); b) thin conformal cracks in the track (400 x); c) lateral delamination of the material (400 x); d) damage at the end of the scratch (400 x).

Adhesion (tape test)

Investigation of the coating's adhesion by tape test shows that only small spots of the nano-tubular layer are detached from the surface of the CP Ti (Fig. 3). The detached areas are with round shape and sizes between 5-20 microns. They are situated preliminary on the top of the surfaces while in the grooves the adhesive tapes residues can be seen, as in very deep craters the adhesive cannot penetrate. After the tape test of the sample, made of Ti-6Al-4V alloy, large areas of the nano-tubular coating are detached mainly from the flat surfaces, while in the grooves the coating is not detached (Fig. 4). The alloy's surface under the coating has high nano-roughness and morphology typical for basis of nano-tubular layer. This is an evidence for the mechanism of formation of TiO₂ NTs, proposed in [16].

So, in this experiment the micro-roughness plays important role on the results obtained. As the micro-roughness of the CP Ti sample is high, only the areas on the top surface can adhere well to the tape and can be detached, while no adhesive can penetrate into the deep grooves and craters, which prevents the coating's detachment. The lower micro-roughness of the sample made of titanium alloy and the presence of large flat areas on its surface are preconditions for better adhesion to the tape and detachment of large coating's portions.

Adhesion (scratch test)

Cohesion and adhesion of the coating is closely related to its wear and abrasion resistance during sliding in an increasing load mode because in both cases the failure originates in the coating. This failure is caused by application of the external force via wear/abrasive particles or sliding indenter during scratch test [17].

The experimental results of Chuan Ting Wang et al. [18] shows that the Ti substrate has a relatively low strength and poor wear resistance when it is subject to sliding or wear. Nevertheless the

higher surface roughness, at the beginning of the track of the CP Ti coated sample, there is almost full contact between the stylus and the surface (Fig. 5a). Large asperity contact because of the ductile substrate provokes early spallation of the coating. The TiO₂ nano-tubular coating on the CP Ti fails at an early stage during the scratch test ($L_{c1} \sim 8$ N; $L_{c2} \sim 26$ N) and the indenter causes progressive plastic deformation (Fig. 5b, Fig. 5c and Fig. 5d). The higher degree of deformation at the edge of the track is clearly seen in Fig. 5c. The appearance of high lateral accumulations of material and their size suggest that the coating has a low hardness. The direction of material moving under the influence of the loaded stylus is radial, which is clearly seen at the end of the test (Fig. 5d).

Going further, the acid etching of the metal prior the anodizing increases the hydrogen content near the surface that could lead to a decrease of the fatigue resistance and adhesion strength. The solubility limit of H in α -Ti at room temperature is $\sim 0,04$ at. % and the excess hydrogen could form small hybrid TiH_x phases or microvoids that enhance localized plasticity [19]. The observed semicircular failures along the track in the substrate material area (Fig. 5c and Fig. 5d) prove the reduction in the surface ductility of CP Ti substrate. However the circumferential cracking outside the scratch area is small and severe delamination or brittle failures are not found.

The SEM examination of the Ti-6Al-4V coated sample reveals that the TiO₂ nano-tubular film undergoes cohesive failure at higher load values ($L_{c1} \sim 13$ N) which means that 62,8% higher initial stage of failure than the other sample is measured. Although the higher loading, the type of the scratch track at the initial stage shows a small width (Fig. 6a) that is related to the higher hardness of the coating/substrate system. As shown in Fig. 6c the TiO₂ nano-tubular coating on the alloy completely fails at a higher load ($L_{c2} \sim 40$ N) or 53,8 % higher than the CP Ti coated sample. The ductile alloy material with high strength provides better support for the coating and produces higher critical loads.

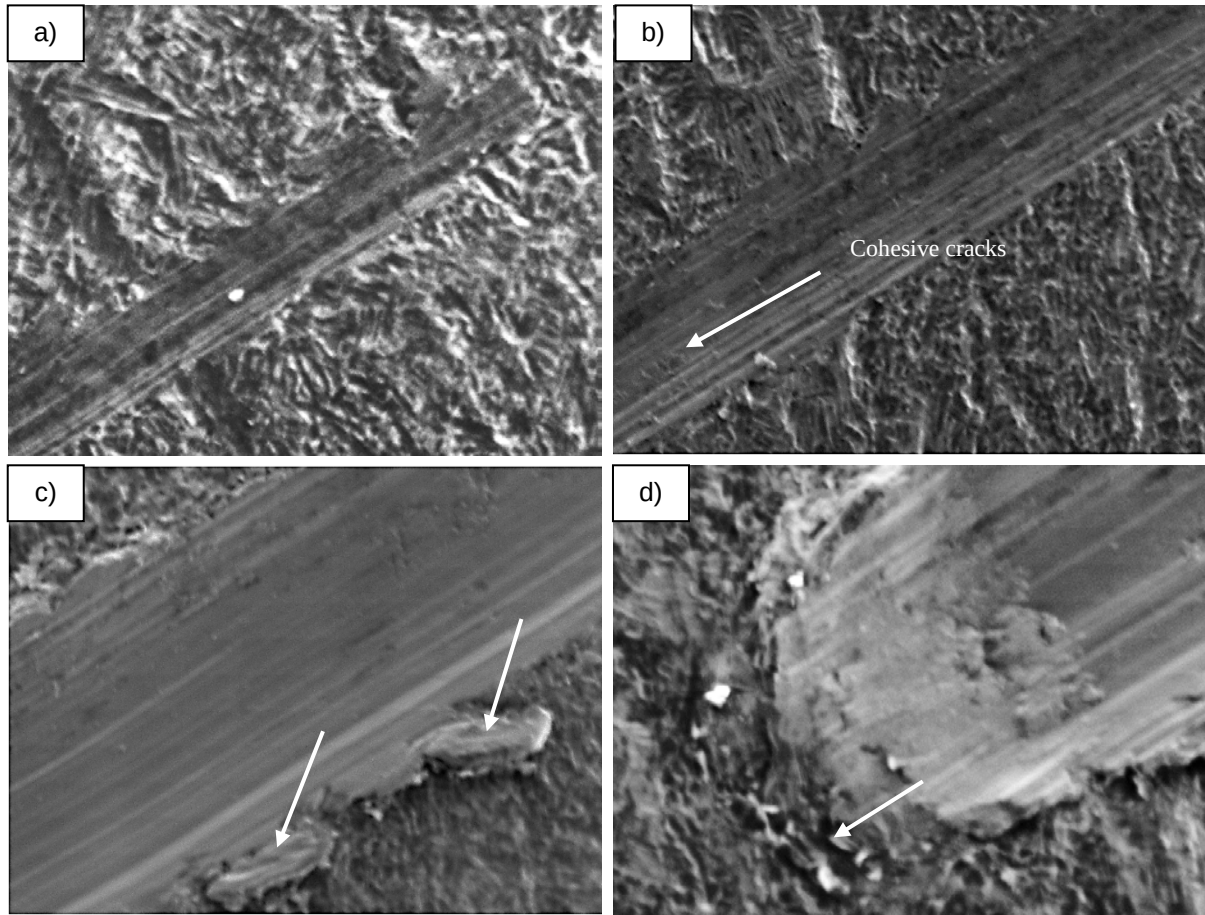


Fig. 6 Morphology of the scratch track area on Ti-6Al-4V coated alloy: a) initial area of the track (original magnification 400x); b) thin conformal cracks in the track (400 x); c) lateral delamination of material (400 x); d) damage at the end of the scratch (200 x).

The dark lanes seen in Fig. 6a and Fig. 6b in the scratch path are regions stripped of the coating that contains some cohesive cracks (Fig. 6b). The increasing pulling force results in pushing aside some detached portions (Fig. 6c) of the surface material parallel to the scratch direction due to tensile cracking behind the stylus. These portions are significantly less in size which is a characteristic feature of harder materials or this fact could be related with the initial surface etching. At the end of the groove (Fig. 6d) the plastic push pad shows small semicircular cracks in front of the indenter.

Since the rate of hydrogen diffusion is higher by several orders of magnitude in β -phase than in α -phase [19], the absorbed hydrogen could be dissolved in the ductile β -phase and below the terminal solubility limit in β the hydrogen could diffuse in between the phases and the embrittlement of the substrate/coating interface should be less pronounced. In the place corresponding to the substrate material no failures of the ductile alloy are observed. The critical indentation widths of 0,112 mm and 0,147 mm (at L_{c2}) are observed for CP Ti and Ti-6Al-4V coated systems, respectively. It is obvious that the critical load increases with the increase of the coating/substrate hardness. This finding does not conflict to the results observed by the microstructural images.

4. Conclusions:

In this study the adhesion of titanium oxide nanocoatings on the surface of CP Ti and Ti-6Al-4V alloy were investigated by tape and scratch tests.

It was established that the higher micro-roughness of the surface of CP Ti sample after anodization is responsible for the detachment only of small areas of the nano-tubular coating situated mainly on the top surface. The lower micro-roughness of the sample made of titanium alloy and the presence of large flat areas lead to detachment of large coating's portions.

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