

NANOSTRUCTURED YSZ COATINGS ON TITANIUM

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Abstract. An approach providing yttrium-stabilized zirconia coatings deposition on titanium is suggested. High-quality YSZ coatings with 5-6 μm thickness were studied using SEM and XRD, the mechanical properties (Brenell and Moos hardness) of covered samples were compared with pure titanium characteristics. The regimes of titanium wafer pretreatment were optimized. It was shown that both $8\text{Y}_2\text{O}_3\text{-}92\text{ZrO}_2$ and $9\text{Y}_2\text{O}_3\text{-}10\text{TiO}_2\text{-}92\text{ZrO}_2$ coatings increase the material hardness.

1. INTRODUCTION

Titanium and its alloys are widely used as biomaterials for different types of implants and prosthesis manufacturing [1]. A bright combination of such properties as lightness, chemical inertness, and sufficient biocompatibility makes it possible to use them for new types of knee and hip joints, cardiac valves, as well as dental implants development. Nevertheless, a number of important problems related to low hardness and a need of bioactivity increment are still being unsolved. Latter is mostly caused by possible allergic reactions, implant abrasion, and long-time osseointegration taking place during the exploitation of titanium materials. Following esthetical problem occurring in dentistry should be mentioned: the discoloration of the gums in the point of metallic implant and tissue contact [2].

It is shown that higher surface area of the material facilitates the tissue and implant binding, and

consequently, faster osseointegration [3]. Herein, following techniques are conventionally used to achieve high micro-roughness: chemical etching in HF [4] and HF/HNO₃ mixtures [5], sandblasting [3], and titanium plasma spraying. Hydroxyapatite (HA), calcium bisphosphonate, and phosphonate, collagen and stabilized zirconia coatings or layers production on the titanium surface are considered as alternative ways to surface modification [6,7]. Recent studies report stabilized zirconia coatings as the most promising among listed above [8-10]. It is due to their fast osseointegration, from the one hand, and significant mechanical properties improvement of composite materials comparing to pure titanium, from the other. It is well known that the required properties of designed materials can be achieved by use of high symmetry zirconia modifications (i.e. tetragonal and cubic) only. A number of detailed reviews on tetragonal zirconia for bioapplications are available [2,11,12], as well as papers describing the

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investigation of physical, chemical, and mechanical characteristics of obtained materials, their biocompatibility [11]; their comparison with the materials based on pure titanium can be found in [13]. However, G. Chevallier in his paper "What future for zirconia as biomaterial?" [14] analyzed the data of Prozyl femoral heads based on tetragonal zirconia failure. The conclusions about the limitations of tetragonal zirconia ($t\text{-ZrO}_2$) as biomaterial and the prospects of composite materials application were stated. Crack propagation was proved to be related to irreversible tetragonal to monoclinic transition in zirconia in the presence of moisture. Despite the fact that cubic modification concedes $t\text{-ZrO}_2$ in mechanical properties, it is also widely used for advanced materials fabrication.

The production of stabilized zirconia coatings on titanium is challenging because of low adhesion of ceramic particles to the metal surface. To date, magnetron sputtering is considered to be the most effective technique to produce high-quality coatings on titanium. In our recent work [15], the attempt of nanostructured zirconia coating sputtering on HTP titanium using nanostructured cubic zirconia target was reported. As a result, amorphous coating hardened by nanosized crystalline inclusions with the uniform Zr-to-Y and Zr-to-O distributions was obtained. Resulted coating structure is attributed to well-known difference in the zirconium and yttrium oxide volatilities. Based on recent data of [16], the deposition of zirconia layers on preliminarily modified titanium surface by sol-gel technique is considered as the alternative method. The present work reports the deposition of cubic yttrium-stabilized zirconia (YSZ) coatings on the preliminary modified surface of the titanium by means of reversed co-precipitation technique.

2. EXPERIMENTAL

Conventional titanium (VT-0 in Russian classification similar to US Grade 2) was used as a wafer for all coatings. However, the modification of its surface was necessary to provide required wafer-coating binding, the main aim of such modification was to form some well-developed surface of the wafer. Oxidation in air resulting in TiO-TiO_2 layer formation was used here. To do so, titanium plates were mechanically polished and degreased. Then, these pre-treated samples were oxidized in the furnace in oxygen ambience at 400, 500, 600, 800, and 900 °C for 2 hours. The obtained samples were investigated by scanning electron microscopy (SEM), Hitachi S-3400N with 20 kV accelerating voltage was

used. The composition of the oxide layers was examined by EDX. SEM and EDX analysis were performed at the center for Geo-Environmental Research and Modeling (GEOMODEL) of research park of St. Petersburg State University". According SEM data, see discussion below, temperatures of 400 and 500 °C were chosen as optimal conditions to produce well-developed surface for further YSZ coatings deposition.

Two YSZ compositions were used as coating materials:

- conventionally used 92 mol.% ZrO_2 - 8 mol.% Y_2O_3 composition ($8\text{Y}_2\text{O}_3\text{-}92\text{ZrO}_2$). This ceramic composition is studied in detail and widely used in materials science due to its excellent mechanical properties and the availability of starting materials. Numerous reports about the properties of YSZ as a bulk material allow to predict the final properties of YSZ layers.
- 9 mol.% Y_2O_3 - 10 mol.% TiO_2 - 81 mol.% ZrO_2 composition ($9\text{Y}_2\text{O}_3\text{-}10\text{TiO}_2\text{-}81\text{ZrO}_2$). According to [17], partial zirconia substitution by titanium dioxide allows to improve sintering and crack resistance of the final materials. Moreover, TiO_2 addition could facilitate stabilized zirconia layering on the oxidized titanium.

Regardless of the chosen composition, two techniques were used for stabilized zirconia deposition on the oxidized titanium surface: sol-gel co-precipitation from aqueous solution (1) and freeze-drying (2). The conditions of co-precipitation and freeze-drying were chosen following the results of process optimization reported in [18].

The first approach (1) can be briefly described as follows. Sol-gel synthesis was performed in the version of reverse co-precipitation from aqueous salts solution. Following starting materials were used for the synthesis: $\text{ZrO}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ (Acros Organics), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Acros Organics), $\text{TiSO}_4 \cdot 8\text{H}_2\text{O}$, ammonium hydroxide. Starting salts solution was acidified up to $\text{pH} = 4$ in order to eliminate hydrolysis. 0.1M salts solution was added to 1M NH_4OH solution by drops with the rate of 2 ml/min under vigorous stirring by multiblade mechanical agitator. The synthesis was performed at 1-2 °C at constant $\text{pH} = 9\text{-}10$. The oxidized titanium plate was placed in the reaction volume just before the synthesis procedure. The plate was removed after the end of the synthesis and washed by distilled water until neutral wash water pH and then thermally treated at 550 °C for 5 hours in the air ambience. The resulted gel of mixed hydroxides was also washed until neutral wash water pH and used in YSZ coatings production according the second technique.

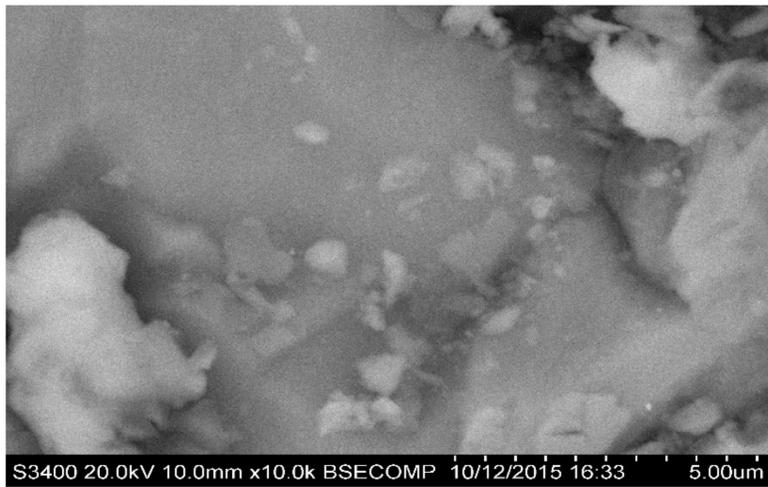


Fig. 1. SEM image of titanium surface after oxidation at 400 °C.

In the second version of the synthesis technique (2), titanium wafers were covered by a layer of gel, manufactured by the above described synthesis. Then, the wafers covered with the gel were freeze-dried at $P = 0.018$ atm. for 24 hours, the temperature of freeze-drying was -50 °C (Labconco, Chamber 1L, USA). The excess of obtained nanosized powder after dehydration was removed from the titanium plate surface. The wafers covered by the dried gel layer were also thermally treated at 550 °C for 5 hours.

Note that the conditions of thermal treatment were chosen according to STA data for final nanosized precursor powders, manufactured via reversed co-precipitation following freeze-drying performed in our previous work [19]. In both approaches, the transition «amorphous precursor \rightarrow cubic zirconia solid solution» takes place in the range 490 - 520 °C.

The samples produced by both approaches were investigated by XRD analysis (SHIMADZU XRD-6000, Cu- K_{α} , $\lambda = 1.54$ Å at room temperature, PDF database [20] was used to interpret XRD patterns).

Both qualitative and quantitative hardness tests were performed: Moos and Brinell hardness were measured. In order to measure Brinell hardness values, mechanical tests were performed using NEMEZIS-9001 (Innovatest, Netherlands). In order to determine Moos hardness, the scratch test set Avanta (Cortest, USA) was used. Titanium plate (VT-0 brand, 30×30 mm, 1 mm thickness) was used as a reference sample. A ball of 2 mm in diameter was used for the test, the applied load was 500 N, the load duration was 20 seconds, the technique of nonreductive indentation was applied here. The reference normalized hardness of non-treated titanium VT-0 was determined as 170 HB. To provide nondestructive impact on the coated samples, the flat-spherical indenter N YBS 51 was used for their tests.

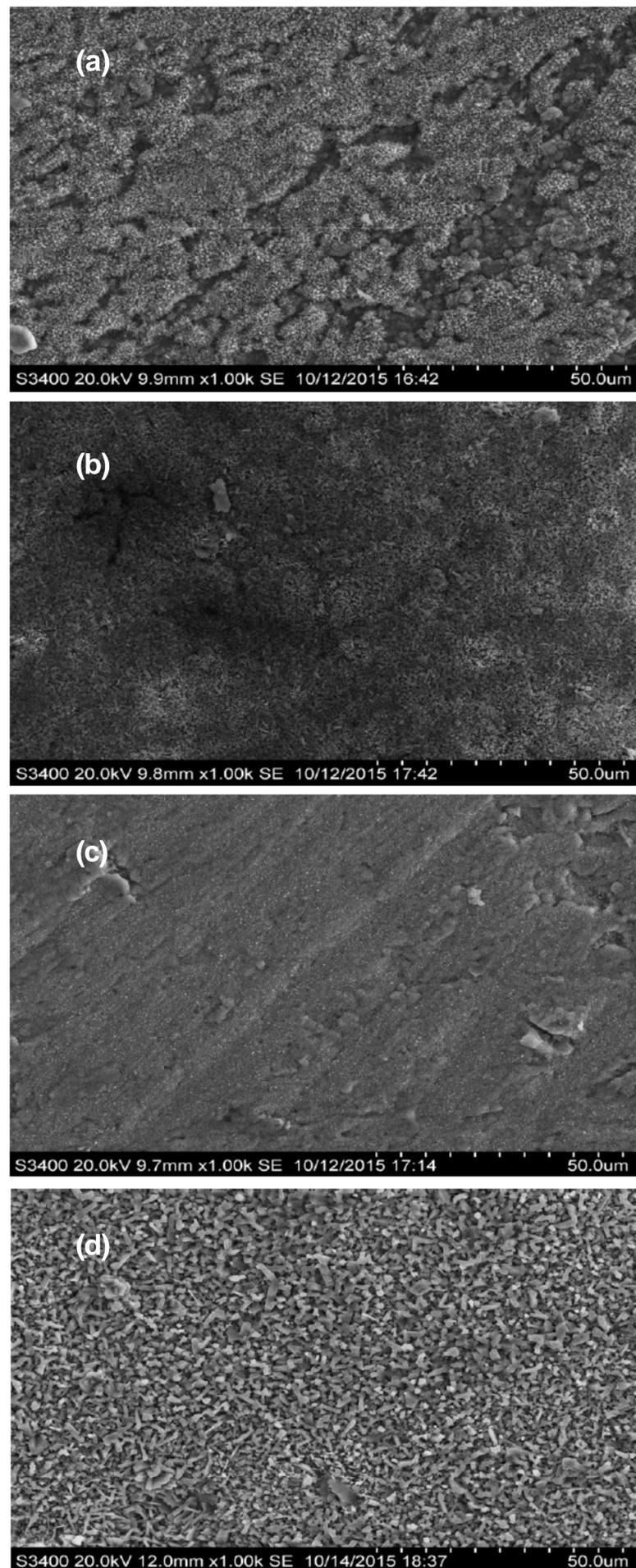


Fig. 2. SEM image of titanium surface oxidized at a) 500, b) 600, c) 700, d) 900 °C.

3. RESULTS AND DISCUSSION

The optimal oxidation temperature was chosen according to SEM data on the structure of the oxidized titanium surface. Such parameters as surface area, structural elements size, and TiO_2 layer thickness were taken into account. As it can be seen from SEM data presented in Fig. 1, the onset of TiO_2 phase nucleation on titanium surface can be ob-

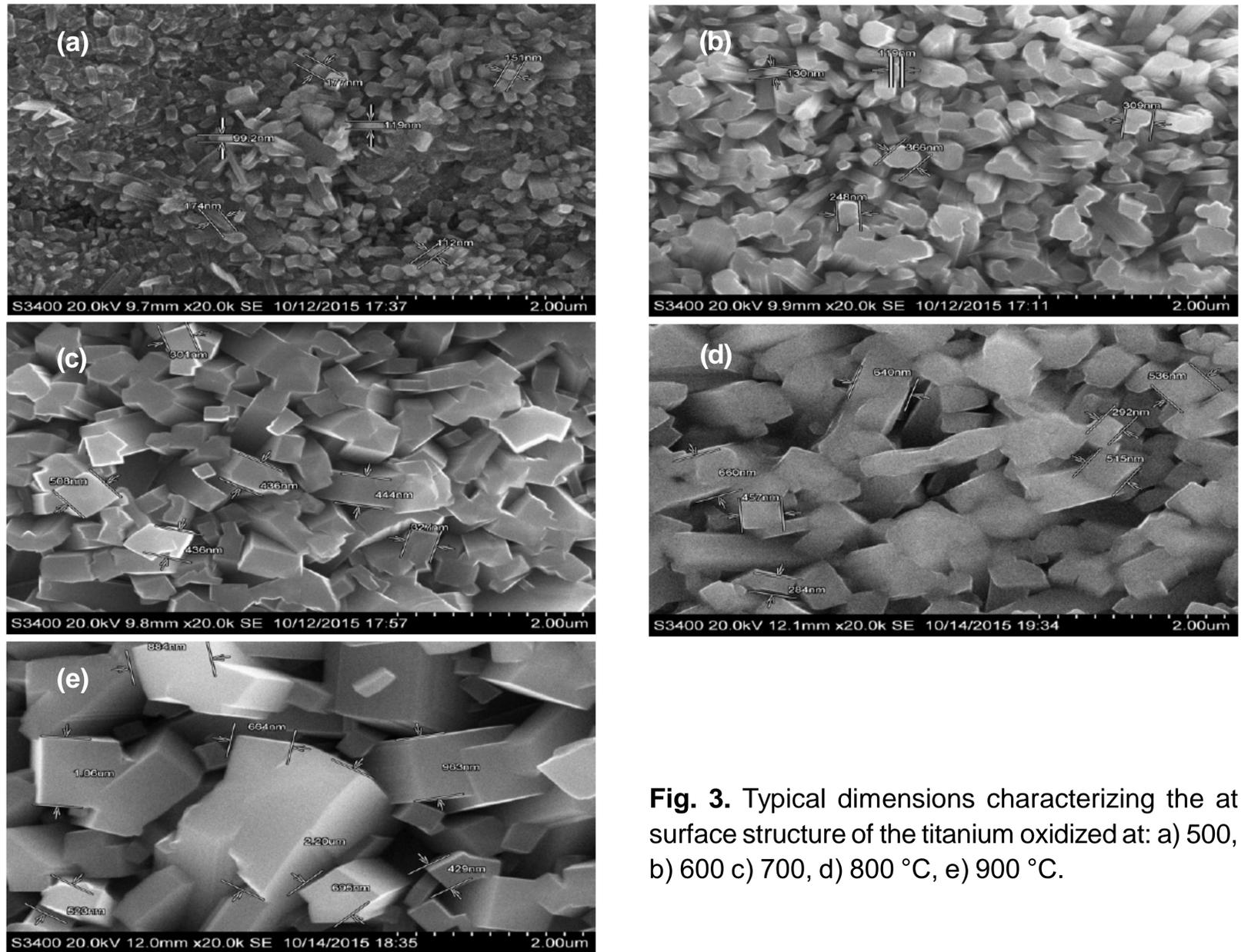


Fig. 3. Typical dimensions characterizing the at surface structure of the titanium oxidized at: a) 500, b) 600 c) 700, d) 800 °C, e) 900 °C.

Table 1. Mass increase of the titanium plates after oxidation 400-900 °C.

Temperature, °C	400	500	600	700	800	900
Δm , %	<0.01	0.01	0.25	0.82	2.35	3.51

served at 400 °C. The increase in oxidizing temperature leads to well-developed surface formation. Fig. 2 illustrates the overview of wafer surface structure after thermal treatment at 500-900 °C. From the microphotos taken with the higher magnification (see Fig. 3) one can conclude that titanium oxidation leads to the columnar structure formation. The characteristic linear dimensions of the columns increase from 100-150 nm at 500 °C up to 800-2000 nm at 900 °C; the voids between them with similar typical linear dimensions also increase. The thickness of the oxidized layers is shown in Fig. 4. The obtained data were compared with the mass change during titanium plates thermal treatment in the temperature range 400 - 900 °C, (see Table 1). The thickness of TiO_2 layers increases from $\sim 3 \mu\text{m}$ at 500 °C to $60 \mu\text{m}$ at 900 °C. Coupling the data of Table 1 and Fig. 4, one can make a conclusion about positive correlation between the titanium plates mass

change after the oxidation and TiO_2 layer thickness on Ti surface.

Thus, summarizing the above information, we conclude that the formation of the structure comprised of characteristic nanosized columns and voids between them takes place already at 500 °C. The homogeneous voids distribution on the surface should be mentioned. Further increase in oxidation temperature leads to the characteristic dimensions growth of all the structural components and, thereby, the layer surface area reduction, i.e. surface energy fall. Herewith, the micro roughness significantly decreases. Latter makes the retention of stabilized zirconia layer on Ti more difficult. It is worth to note, that both the oxide surface and layer thickness on titanium at 500 °C are enough for further stabilized zirconia deposition.

As was mentioned above, the surface modification of titanium wafers after the heat treatment at

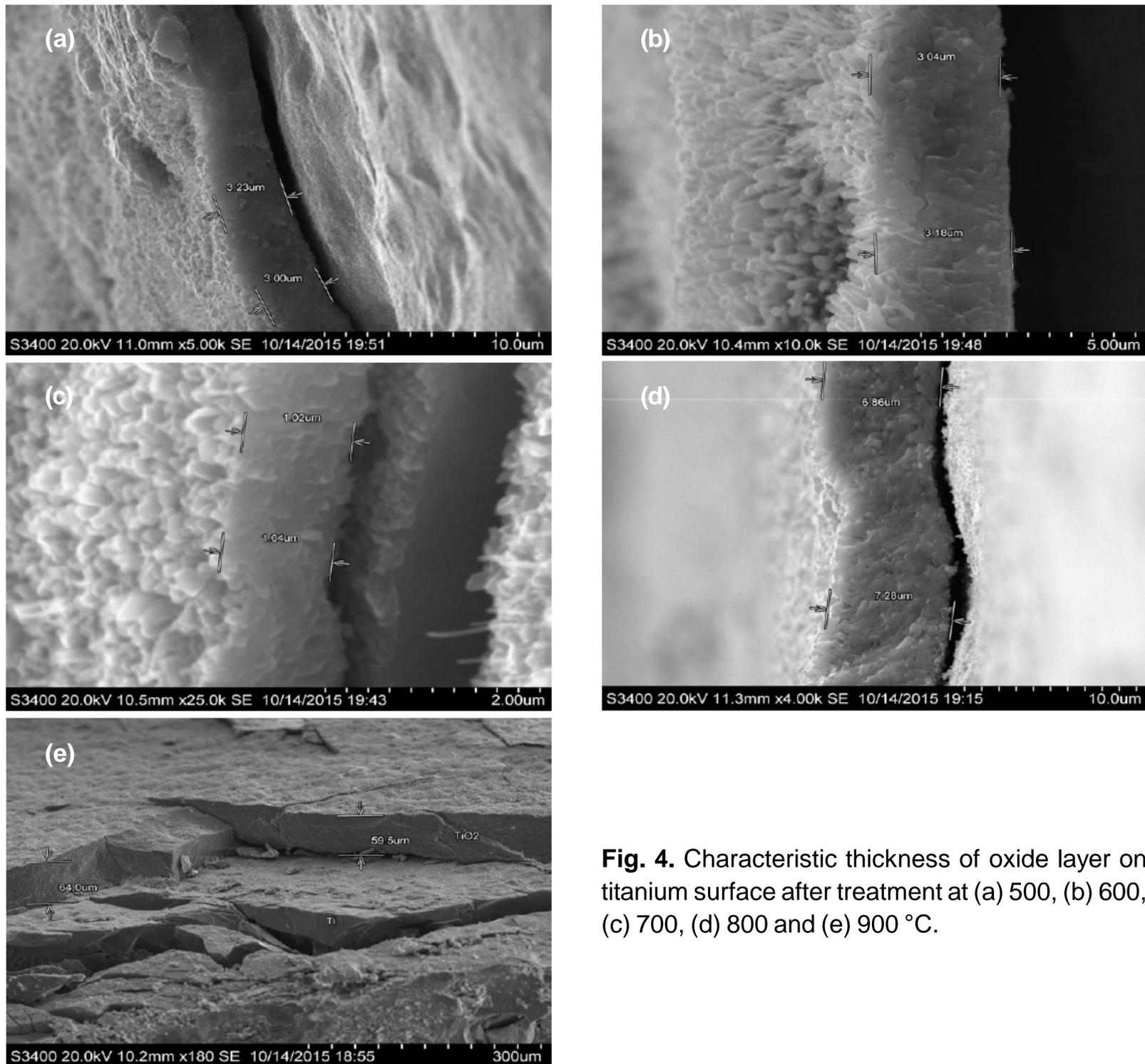


Fig. 4. Characteristic thickness of oxide layer on titanium surface after treatment at (a) 500, (b) 600, (c) 700, (d) 800 and (e) 900 °C.

400 °C is rather low; however, one can consider an onset of titanium surface oxidation here. So, the first oxidation temperature chosen for wafer pretreatment as a first step of YSZ deposition was 400 °C due to minimal losses in the wafer strength due to thermal treatment. The second oxidation temperature tested was 500 °C since it provides well-developed wafer surface. The choice of titanium temperature treatment regimes agree with the data on annealing effect on HTP titanium microhardness, presented in [21].

Titanium wafers with YSZ coatings were studied by XRD analysis in order to identify their phase composition. As an example, XRD patterns for samples with wafers oxidized at 400 and 500 °C coated by $9Y_2O_3-10TiO_2-81ZrO_2$ composition via technique (1) are shown in Fig. 5. The peak at $2\theta = 30^\circ$ in Fig. 5b clearly indicates the presence of cubic zirconia solid solution, i.e. preliminary titanium oxidation at 500 °C results in the deposited layer on the titanium

surface. In contrast to the above case, Fig. 5a that shows XRD data for coating deposited on the titanium wafer oxidized at 400 °C do not show any peaks attributed to YSZ phase. These results contradict SEM data and the results of the hardness tests reported below. So, one can consider that the absence of YSZ peaks in XRD patterns depicted in Fig. 5a is due to the amount of YSZ coating less than that required for XRD determination (~5 wt.% of the whole sample weight). Indeed, as follows from SEM data (see Fig. 1), the thickness of the oxidized titanium layer after the heat treatment at 400 °C is rather low, so, one can expect the low weight content of YSZ coating in the sample. However, SEM data shown in Fig. 6 evidently proves the existence of YSZ coating on titanium surface both for samples oxidized at 400 and 500 °C.

SEM data shown in Figs. 6a and 6b indicate the presence of nanostructured YSZ layer for both samples (titanium oxidized at 400 and 500 °C).

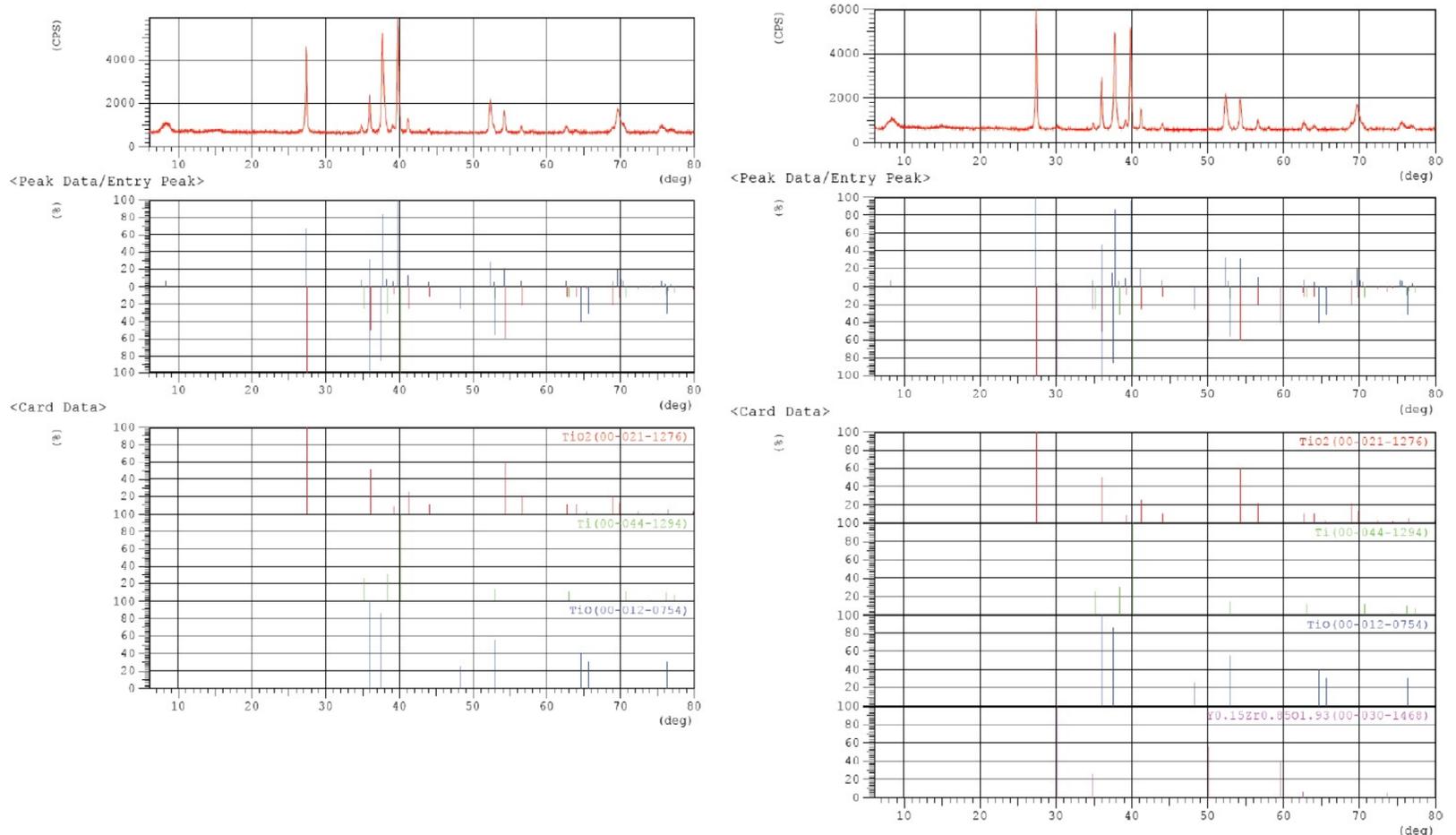


Fig. 5. XRD patterns of titanium covered by $9Y_2O_3$ - $10TiO_2$ - $81ZrO_2$ coating; wafers oxidized at: (a) 400 and (b) 500 °C.

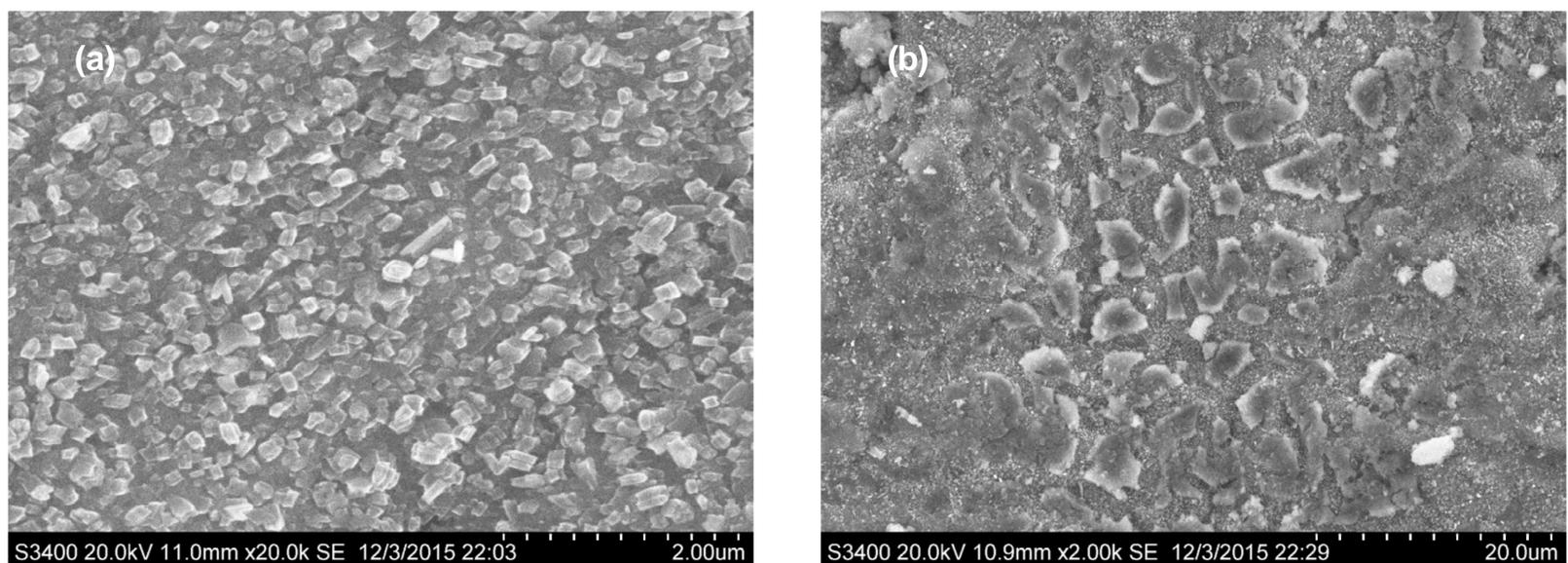


Fig. 6. SEM image of $9Y_2O_3$ - $10TiO_2$ - $81ZrO_2$ layer on titanium oxidized at a) 400 and b) 500 °C.

Herein, nanosized ceramic inclusions with typical linear dimensions less than 100 nm are uniformly distributed on wafer surface, covering not only voids, but also columns. According to EDX data, the deposition using approaches (1) and (2) resulted in stoichiometric YSZ final coating composition with constant Zr-to-Y and Zr-to-O distribution. However, the amount of zirconia-containing phase on the wafer oxidized at 500 °C is shown to be 10 times higher than that in case of 400 °C; this fact supports the assumption stated during XRD data discussion about the integral content of YSZ phase on the wafer oxidized at 400 °C: it is too low to be detected by XRD.

The results of Brinell and Moos hardness measurements of the manufactured samples are listed in Table 2 in comparison with the same data for VT-

0 reference sample. As seen from the table, both Brinell and Moos hardness values of YSZ covered samples increase in comparing to untreated titanium. The value Brinell hardness increases in 20-40 HB units, while Moos hardness increases from 5.5 to 6.5. For the coatings, deposited on titanium oxidized at 500 °C, chosen deposition technique (i.e. reversed co-precipitation or freeze drying of gel) does not significantly affect the resulting hardness value. At the same time, the use of final ceramic composition $9Y_2O_3$ - $10TiO_2$ - $81ZrO_2$ leads to slight increase in hardness – the determined difference between the samples coated with $9Y_2O_3$ - $10TiO_2$ - $81ZrO_2$ and $9Y_2O_3$ - $91ZrO_2$ compositions is about 5%.

Table 2. The results of Brinell and Moos hardness tests for YSZ coated titanium.

№ sample	Description	Brinell hardness, HB (± 7 HB)		Moos hardness	
		oxidation 400 °C, 2 hrs	oxidation 500 °C, 2 hrs	oxidation 400 °C, 2 hrs	oxidation 500 °C, 2 hrs
1	Titanium VT-0 untreated		170		5-5.5
2	Titanium VT-0 oxidized	180	185	5-5.5	5-5.5
3	VT-0, oxidation + reverse co-precipitation, 8Y ₂ O ₃ -9ZrO ₂ , annealing for 5 hours at 550 °C	190	200	6-6.5	6-6.5
4	VT-0, oxidation + reverse co-precipitation, 9Y ₂ O ₃ -10TiO ₂ -8ZrO ₂ , annealing for 5 hours at 550 °C	195	210	6-6.5	6-6.5
5	VT-0, oxidation + freeze-drying 8Y ₂ O ₃ -9ZrO ₂ , annealing for 5 hours at 550 °C	190	195-200	6-6.5	6-6.5
6	BT-0, oxidation + freeze-drying 9Y ₂ O ₃ -10TiO ₂ -8ZrO ₂ , annealing for 5 hours at 550 °C	190	210	6-6.5	6-6.5

To summarize the data discussed, the combination of sol-gel reversed co-precipitation technique and preliminarily titanium oxidation at 500 °C results in cubic zirconia layers production on titanium surface with increased hardness. Potentially, this approach can be used as alternative to magnetron sputtering and coatings production in gas dynamic jet.

4. CONCLUSIONS

Titanium oxidation results in columnar structure formation with linear dimensions of structure components from 100-150 nm at 500 °C up to 800-2000 nm at 900 °C. Thermal treatment at 500 °C leads to TiO₂ layer formation with the thickness of ~3 µm and surface well-developed for further cubic zirconia deposition via sol-gel co-precipitation technique. For all the samples with deposited TiO₂ and cubic zirconia layers, Brinell hardness increases to 10-20% comparing to untreated titanium. The combination of sol-gel synthesis technique and oxidation at 400 and 500 °C can be suggested as possible method for cubic zirconia layers deposition on HPT titanium.

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