

NANOSTRUCTURED YTTRIUM STABILIZED ZIRCONIA COATINGS ON HPT TITANIUM – NANOSTRUCTURE AND PHASE COMPOSITION ANALYSIS

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Abstract. Yttrium stabilized zirconia coatings were deposited on titanium (hardened by high pressure torsion) by magnetron sputtering. The produced coating was compared with that deposited on polished Mo wafer. The results of XRD, X-ray fluorescence probe, and electron microscopy analysis provides an opportunity to study the phase composition and the structure of both coatings. The effect of wafer pretreatment on coating quality and microstructure is discussed, and the procedure of HPT titanium pre-treatment for magnetron sputtering is suggested.

1. INTRODUCTION

A lot of modern hi-tech applications require a new type of composite materials – nanostructured coatings based on stabilized zirconia (SZ) [1]. In particular, such coating on tantalum and titanium are considered as promising bone implants in general and maxillofacial surgery, as well as in dentistry. Physical, chemical, and mechanical properties of titanium covered by SZ are described in detail in reviews [2,3]. Coupling these data with the results of the original works [4-7], one can conclude that such composites possess high strength (up to 650 MPa for hot-pressed samples manufactured from nanosized precursors) and excellent biocompatibility. In addition, the possibility of wide color range is provided, this feature is very important for dentistry.

Magnetron sputtering is one of the effective approaches for the manufacturing of complex oxide coating on titanium. In particular, magnetron sputtering of biocompatible calcium-phosphate coatings for dentistry applications is well studied [8,9]. This method provides uniform coating of high density; in addition, the bonding strength of such coating is rather high. However, some problems mainly due to evaporation and deposition behavior of complex oxide systems were mentioned. The attempts to apply magnetron sputtering to produce stabilized zirconia coatings were reported in [10]. High purity of the produced coating, the absence of pores in them along with the above mentioned high uniform density were confirmed.

The present paper describes the magnetron sputtering of nanostructured yttrium stabilized zirconia

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(YSZ) coating on reinforced titanium that was subjected to high pressure torsion (HPT titanium) during an annealing, see [11] for the details on microstructure and mechanical properties. Synthesis of the YSZ target for magnetron sputtering providing the opportunity to deposit nanostructured fluorite-like modification was reported in our previous paper [12]. The approach includes sol-gel reverse precipitation of nanosized YSZ precursor powders with further freeze-drying. It was shown that the applied method provides high precursor powder dispersity and low agglomeration level in a wide temperature range. The use of such precursor powders makes possible fabrication of YSZ ceramics free of inorganic binders; this ceramics meets the requirements for the magnetron sputtering source material.

As follows from the above reference data, the pretreatment of titanium is critical for successful magnetron sputtering of both Ca-P and YSZ coatings. The conventional approach to get acceptable bonding strength along with high quality of the surface is partial titanium oxidation. However, this method was unacceptable for HPT titanium since it could negatively affect the surface layer mechanical properties, some considerations dealing with biocompatibility of partly oxidized HPT titanium also prevented us from this pathway. So, the main task of the work was the development of the procedure of HPT titanium preparation for YSZ magnetron sputtering; molybdenum wafer was used as a reference material. Indeed, HPT titanium treatment is rather difficult due its hardness, while molybdenum could be easily polished up to excellent wafer surface quality.

2. EXPERIMENTAL

HPT titanium, see [11] and commercial Mo foils as a reference were used as wafers for coating deposition. YSZ target synthesized according the procedure reported in [12] was used for magnetron sputtering.

Magnetron sputtering was performed using ASPIRA (ISOVAC Co., Byelorussia) installation designed for ion-beam and magnetron sputtering; the installation includes RF magnetron with power supply (Stolberg HF GmbH, Germany) and built-in ion cleaning source. Surface cleaning and sputtering itself were carried out in argon ambience, the Ar flow here was 700-900 mL/min. The surface ion cleaning regime was: residual pressure - $2.5 \cdot 10^{-5}$ Pa; magnetron voltage - 1500 V, current - 70 mA, the cleaning duration was 400 sec. Magnetron sputtering was performed at 0.1 Pa under 600 V magne-

tron voltage and 1 kW power; the process lasts for 300 min.

The structure of the deposited coatings was studied by electron microscopy (Supra Zeiss 55-V), phase composition was checked by XRD analysis (SHIMADZU XRD-600 with Cu-K $_{\alpha}$ irradiation at $\lambda = 1.54 \text{ \AA}$ at room temperature, surface composition and typical dimensions of the surface objects were determined by X-ray fluorescent probe (INCA Microanalysis systems).

2.1. HPT titanium surface preparation

As it was mentioned in Section 1, the preparation of the metal surface to coating deposition is one of the key points providing high quality of the coating. Since the reference metal wafer (commercial Mo) surface was polished up to $N=2$ (the ISO surface roughness scale is used hereinafter), no additional mechanical surface treatment was applied. This wafer was thoroughly degreased by ethanol, washed by distilled water and then dried at 110 °C in a drying cabinet. On the contrary, the initial surface of HPT titanium (in this case, the samples were cylinders) was rather rough, so, the additional surface grinding was performed up to $N\sim 5$. As it was mentioned in [11], HPT titanium possesses high mechanical properties, in contrast to molybdenum, its mechanical treatment is rather laborious. A number of experiments were carried out to find the optimal conditions of HPT titanium surface treatment. It was shown that surface improvement higher than $N=5$ does not significantly affect the coating quality, while rougher wafer surface manifests itself as a source of macrodefects in the coating. This fact can be seen from Fig. 1 that demonstrates microphotos of YSZ coatings on the HPT titanium surface grinded to different surface roughness. Fig. 1a presents the typical microphoto of YZ coating deposited on HPT titanium with the surface roughness of 6. As seen from this figure, there are a number of macrodefects on the surface with typical linear dimensions of 30-60 μm , usually, such defects can be noticed even at visual observation. The increase in HPT surface quality up to $N=5$, Fig. 1b, increases the coating quality. In this case, the coating surface is not completely smooth, however, the surface irregularities in this case are likely due to the coating growth processes. In addition, it should be noted that the average size of such irregularities is lower. As a comparison, Fig. 1c shows the microphoto of the coating deposited on polished molybdenum wafer. As seen from this figure, polishing up to $N=2$ significantly increases the coating quality. Note that Fig.

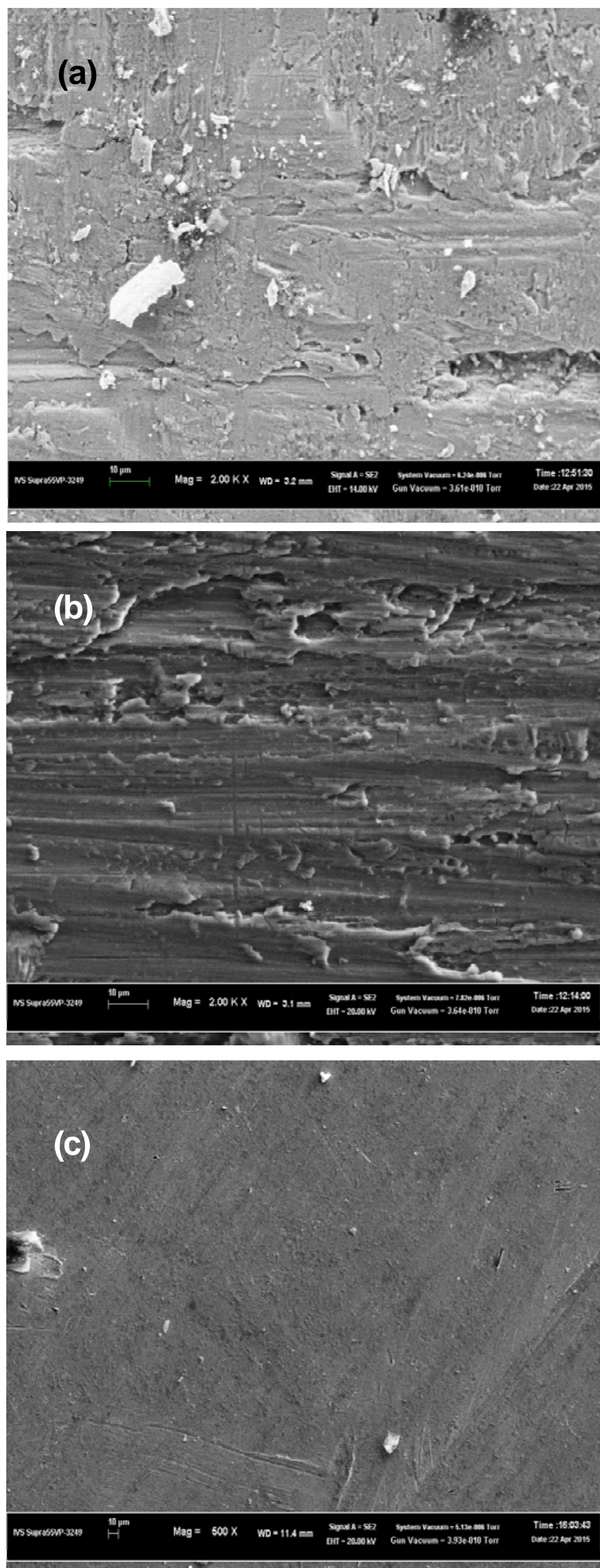


Fig. 1. Microphotos comparing the YSZ coating quality resulting from initial wafer surface roughness: (a) typical photo for the coating on HPT titanium with surface roughness of $N=6$; (b) HPT titanium surface of $N=5$; (c) reference Mo wafer with $N=2$.

1b is a typical image for YSZ coatings deposited on HPT titanium with $N=4-5$; the increase of surface roughness up to $N=3$ is quite laborious, while the difference in coating quality for $N=4$ and $N=5$ is fairly small. For this reason, the surface roughness of $N=5$ was chosen for further experiments.

Similar to Mo wafer, titanium cylinders were degreased by ethanol, washed by distilled water and dried at $110\text{ }^{\circ}\text{C}$ in a drying cabinet before magnetron sputtering.

3. RESULTS AND DISCUSSION

Yttrium stabilized zirconia coating were deposited on HPT titanium and on reference molybdenum wafer using magnetron sputtering, see Section 2. In both cases, the coating thickness was $\sim 6\text{ }\mu\text{m}$. Both coatings were studied by XRD analysis in order to identify the modification of YSZ phase. As was previously shown in [12], fluorite-like zirconia is a preferable phase instead of low-symmetry tetragonal and monoclinic phases, see also [2,3] for more detail. It should be noted that the analysis of XRD patterns was rather complicated since the wafer input in peak intensity was dominant.

For this reason, the coating was scraped from titanium wafer and pounded into a powder, Fig. 2 demonstrates typical XRD data for both for coatings deposited on HPT titanium and polished Mo wafer. As seen from the figure, the deposited coating on both wafers is amorphous (glassy-like) phase. However, it should be mentioned that the XRD patterns depicted in Fig. 2 are quite similar to those registered for zirconia-based precursors used for the YSZ target synthesis, see [13] for more details. So, we believe that the deposited coating is the zirconia-based amorphous phase; this statement will be proved later during the discussion of the X-ray fluorescence probe data. Additional XRD analysis of the YSZ target after magnetron sputtering was per-

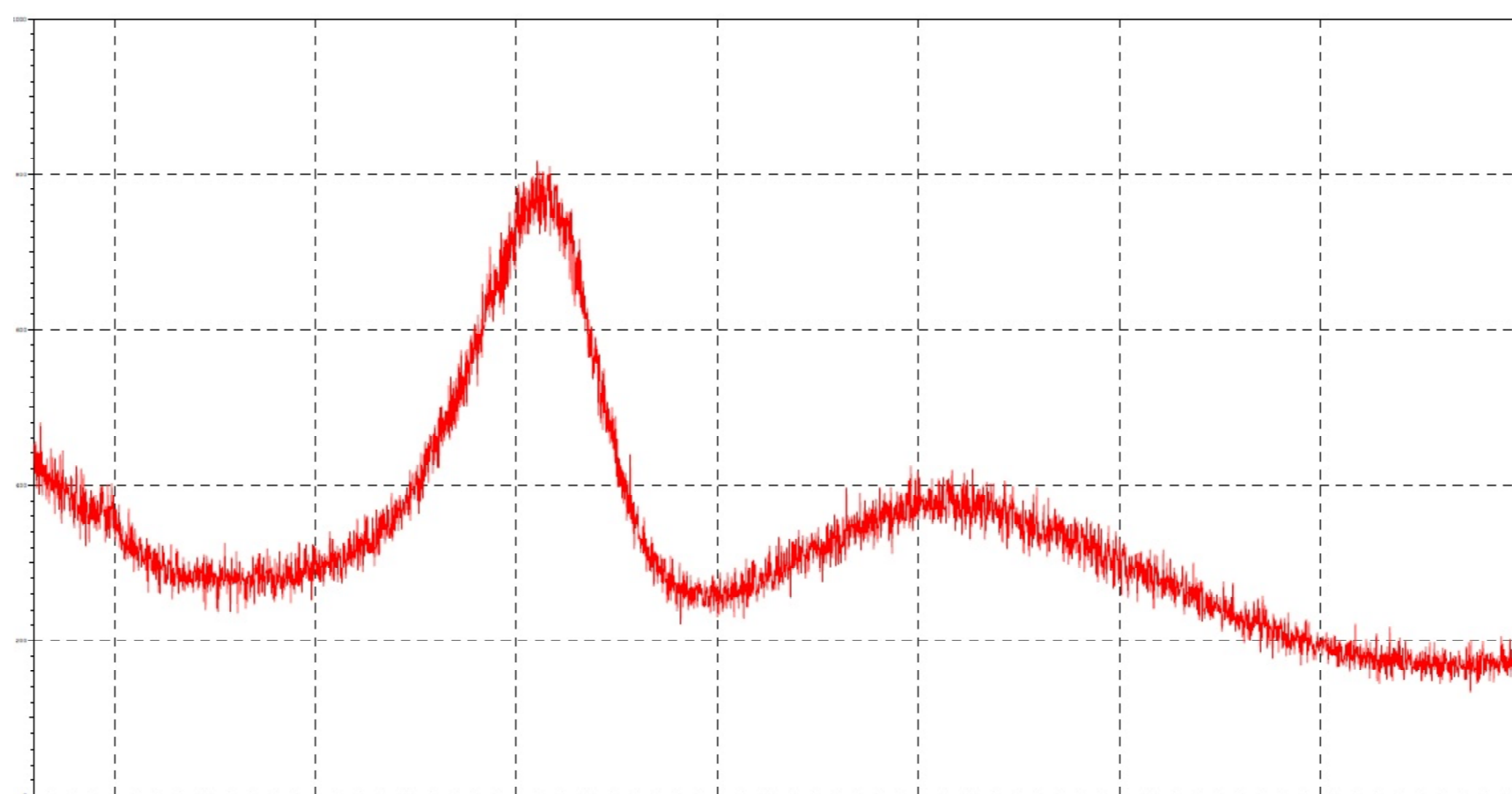


Fig. 2. XRD patterns for YSZ coating scraped from HPT titanium coating.

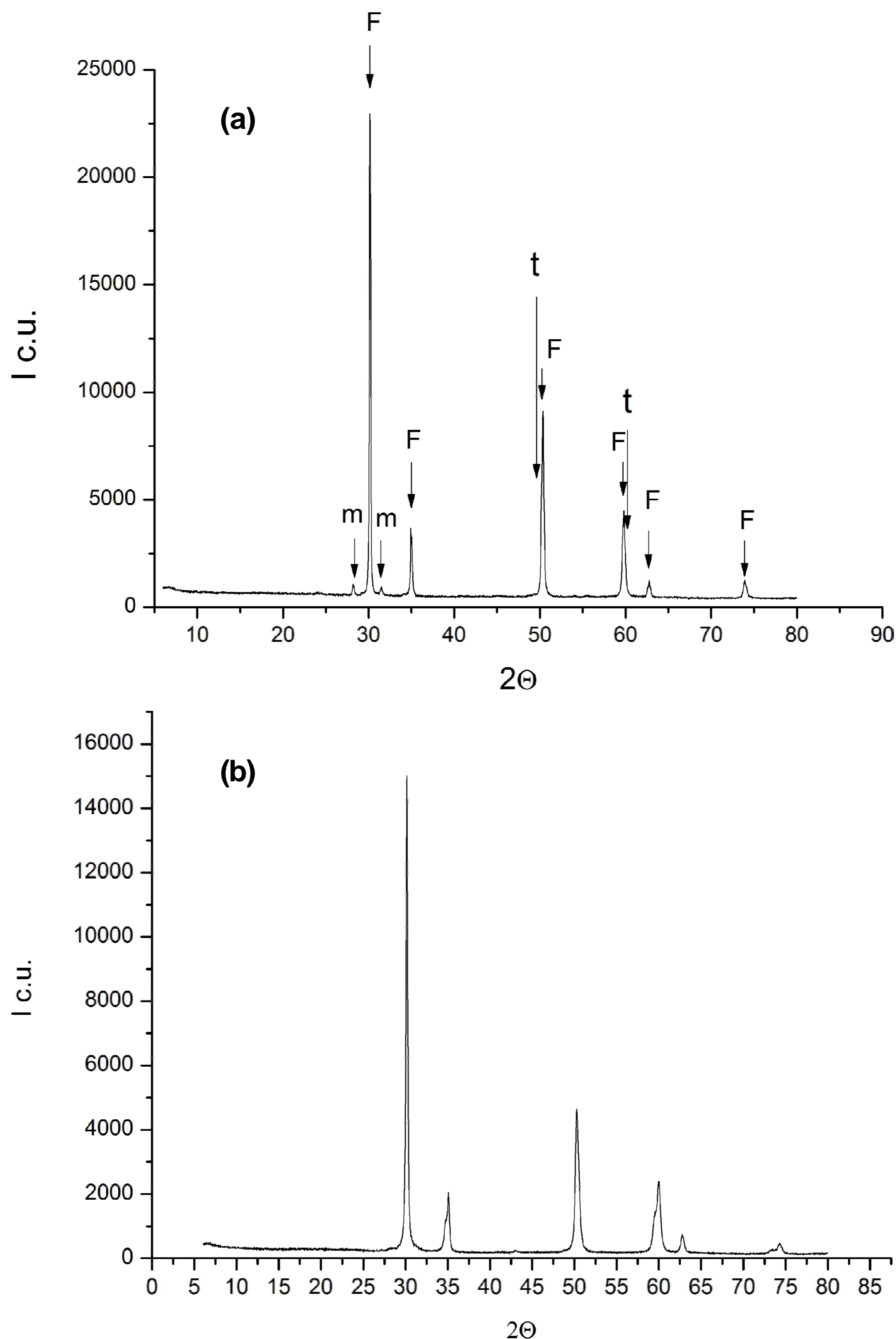


Fig. 3. XRD patterns: (a) for YSZ target surface layer scraped from the target after the magnetron sputtering, F- fluorite-like phase, t – tetragonal phase, and m – monoclinic one; (b) – target bulk.

formed, the surface layer scraped from the target bulk and target bulk itself were studied. Fig. 3a demonstrates XRD patterns of the surface layer. It can be seen from the figure that the surface layer of the YSZ target after magnetron sputtering is a mixture of mixture of fluorite-like, tetragonal, and monoclinic phases; fluorite-like phase seems to be a dominant one. However, this assumption is based on indirect data on XRD peaks intensity only. On the contrary, Fig. 3b, XRD patterns of the target bulk indicate the presence of the fluorite phase only. This fact can be attributed to well-known difference in the zirconium and yttrium oxide volatilities, see, e.g. [14]. Since the yttrium oxide removal is preferable, the surface layer of the target after the sputtering is partly depleted in yttrium oxide that is the stabilizing com-

ponent for zirconia fluorite-like phase. As a result, phases with low symmetry, i.e. tetragonal and monoclinic, are formed.

Table 1 presents the comparison of X-ray fluorescence probe data for pure HPT titanium surface with the composition detected for coated cylinder. The analysis of the X-ray fluorescence probe proves that the sputtered coatings are YSZ phase, a number of selected spectra both for coated and uncoated wafer are given. Considering the presented data, one should take into account that some minor components (Fe, Ni, Cl, Mn, etc.) with the maximal input less than 0.5 at.% detected due to holder material, ambience specifics, etc. are excluded from the listed data for simplicity. For this reason, the sum of the components can insignificantly deviate from 100.

Table 1. Surface composition according X-ray fluorescence probe data (at.%, recalculated regarding for carbon elimination).

Pure HTP titanium surface spectrum	Pure HTP titanium surface spectrum		YSZ coated titanium spectrum	YSZ coated titanium spectrum					
	Ti	O		Ti	O	Y	Zr	Zr/Y ratio	Zr/O ratio
1	100.00	0.00	1a	4.87	41.08	1.54	52.51	34.21	1.28
2	98.24	1.76	2a	2.44	43.81	1.35	52.40	38.85	1.20
3	97.17	2.83	3a	22.11	44.41	0.86	32.62	38.04	0.73
4	100.00	0.00	4a	9.55	39.32	1.33	49.80	37.37	1.27
5	92.68	7.32	5a	5.93	43.83	0.93	49.31	52.79	1.12
Max	100.00	7.32	Max	22.11	44.41	1.54	52.51	52.79	1.28
Min	92.68	0.00	Min	2.44	39.32	0.86	32.62	34.21	0.73

The presence of carbon in both cases (with the average content of about 8-11 at.%) was attributed as being due to construction of the probe. Since the carbon content was detected in all spectra, it was also excluded from the table and the data on composition were recalculated regarding for the elimination of carbon input. Oxygen in the spectra of individual HPT titanium is possibly an adsorbed one or the result of residual atmosphere. It can be seen that individual Ti is a dominant component in the spectra of pure HPT titanium, while its content is much less in case of coated sample. Oxygen content is small in case of uncoated samples (less than 7%) and increases up to minimum 39% in case of coating, obviously, it is due to oxygen presence in ZrO_2 and Y_2O_3 . Zirconium and yttrium are detected in the spectra of coated samples, in most cases Zr is a dominant element. One can see that measured Zr to Y ratio in most cases ranges from 34 to 38, the maximal value of ~53 in spectrum #5a is suggested to be due to extreme content of detected carbon. Similar tendency can be seen for Zr/O ratio – for spectra ## 1a, 2a, 4a, and 5a it lies in the range 1.12-1.28, the deviation in case of spectrum #4a can be explained by high Ti content. It looks like that the coating is somehow depleted in yttrium as compared to pure YSZ phase. This fact contradicts the above XRD data on preferable yttrium oxide removal from the target surface, see Fig. 3. Nevertheless, magnetron sputtering does not provide the inheritance of the target modification on the wafer; deposition here is a complex process affected by a lot of parameters. However, the above mentioned depletion in yttrium indicates the pathway for further modification of the deposition process in order to improve the Zr-to Y ratio. On the other hand, X-ray fluorescence probe data determines the composition of a minor “point” of the surface; for this reason the above considerations on the limited spec-

tra are only qualitative. However, these data prove the presence of YSZ coating on HPT titanium, we can also assume the uniform Zr-to-Y and Zr-to-O distributions in this coating.

Fig. 4 presents the microstructure of the deposited coatings. Images 4a and 4c shows the structure of the coatings deposited on HPT titanium and Figs. 4b and 4d shows the reference coating on Mo at the same magnification. As seen from the figure, two phases are present in both samples: the first is nanosized crystalline phase which is included in a glassy-like phase. Typical sizes of the crystalline objects according to microscopy data are shown in Fig. 5 for the coating on HPT titanium, it could be seen that typical linear dimensions of crystalline objects here are 50-150 nm. Thus, we can state that the deposited coatings are nanostructured, the glassy-like matrix of the coating is additionally stabilized nanosized YSZ crystals. It should be mentioned that the effect of surface treatment manifests itself even at nanosized level. Indeed, the size of nanocrystalline objects in coatings deposited on polished Mo foil is lower than that for HPT titanium (see Figs. 4a and 4b); their distribution in the matrix of the coating deposited on Mo wafer is more uniform (see Figs. 4c and 4d). However, the general structure of the coating – nanocrystalline objects included in glassy-like matrix is typical for both cases.

4. CONCLUSIONS

Yttrium stabilized zirconia coatings were deposited on titanium hardened by high pressure torsion grinded to $N=5$ at ISO roughness scale using magnetron sputtering. The coating quality and its microstructure were compared with the reference sample deposited on polished Mo wafer. XRD analysis proves that, in both cases, the coatings are

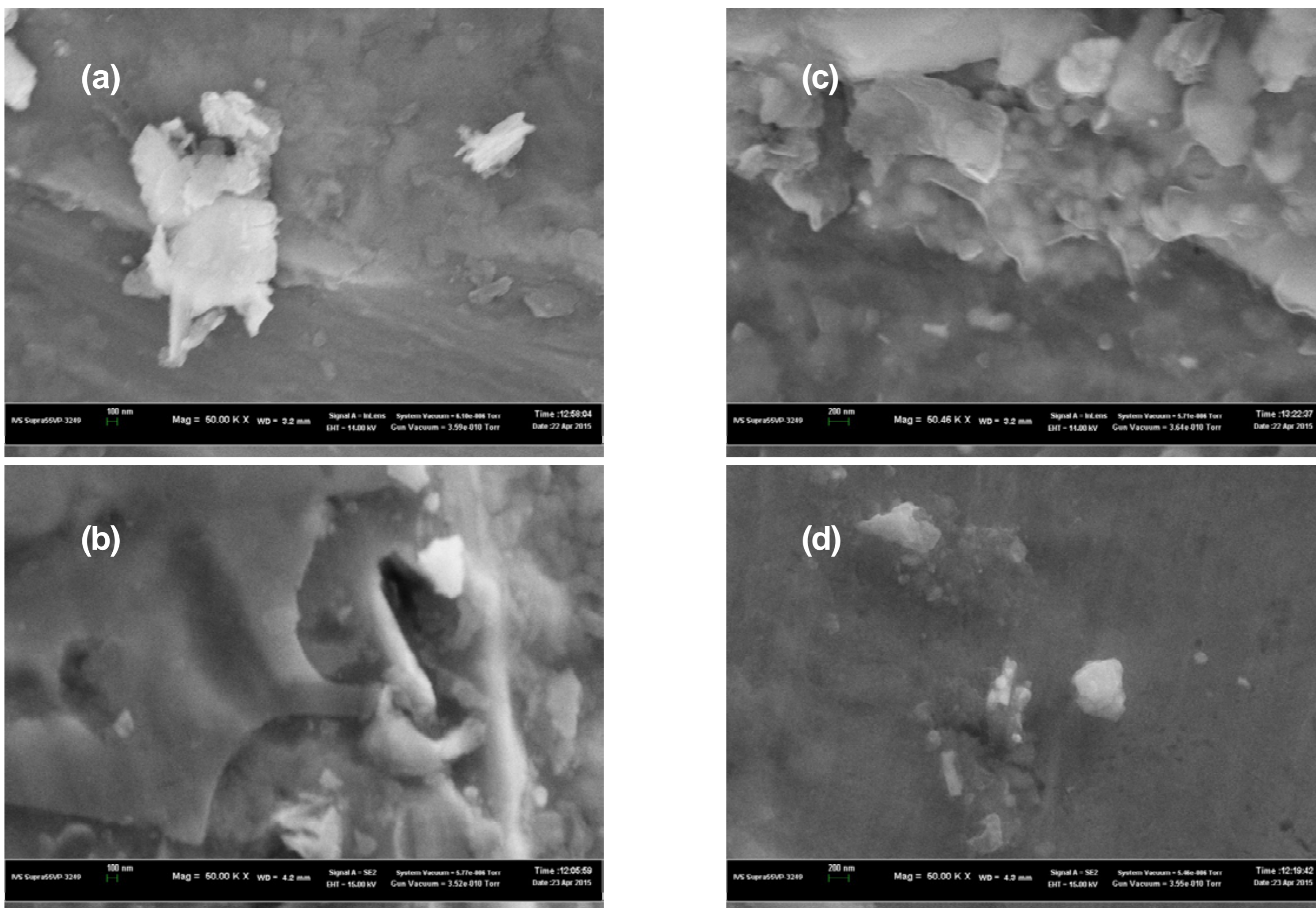


Fig. 4. Microstructure of the YSZ coatings according electron microscopy: (a) and (c) – on HPT titanium, 100 and 200 nm scale, respectively; (b) and (d) – on Mo wafer, 100 and 200 nm scale, respectively.

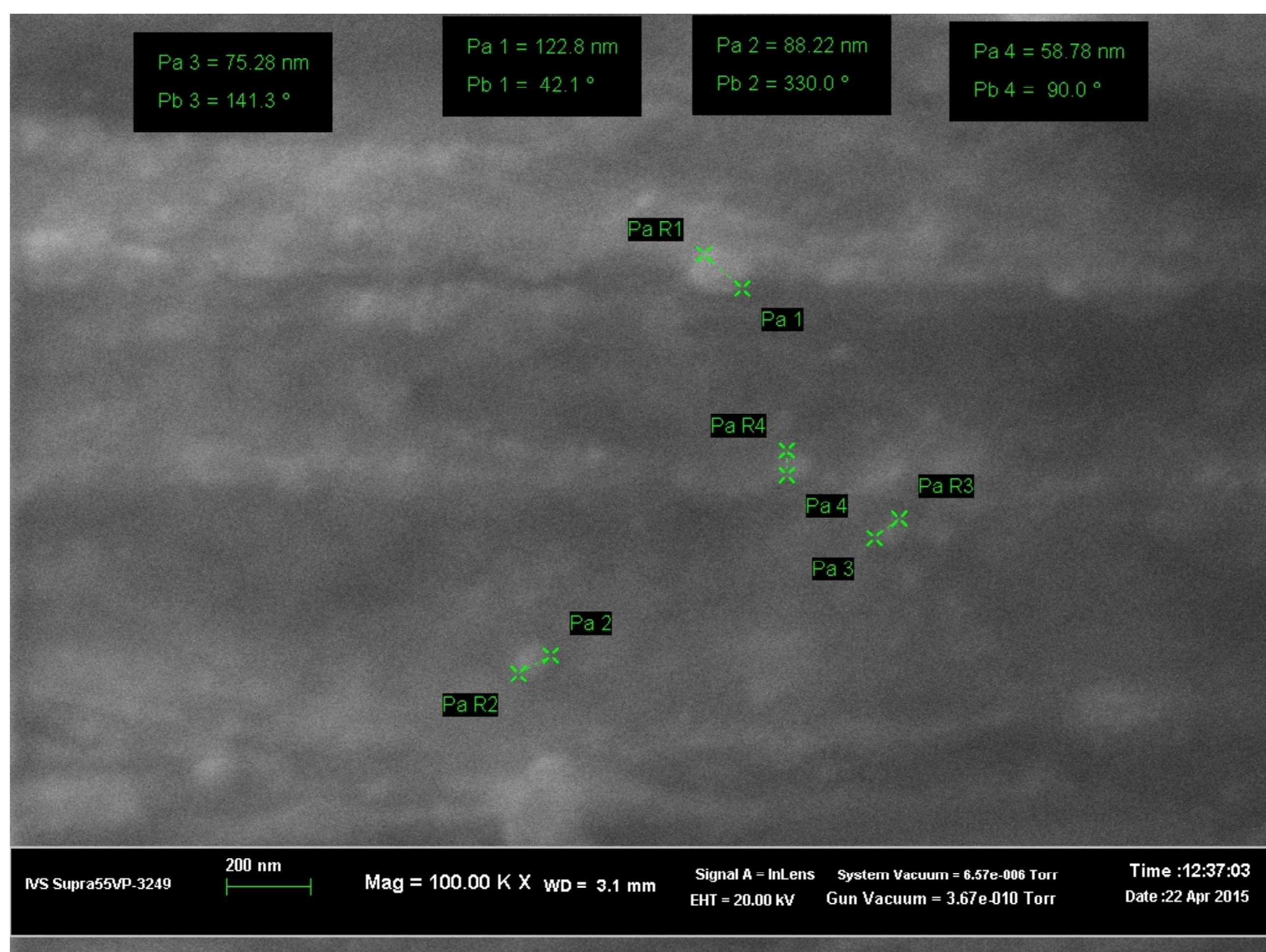


Fig. 5. Typical size of crystalline phase inclusions in YSZ coating on HPT titanium.

amorphous zirconia phase, X-ray fluorescence probe data give an opportunity to suggest that this coating is an YSZ composition with uniform Zr and Y distribution. The data obtained by electron microscopy showed that both coatings are glassy-like matrix stabilized and hardened with nanosized crystalline inclusions. It was shown that the wafer sur-

face roughness affects coating surface quality and microstructure; the approach for HPT titanium pre-treatment for magnetron sputtering is suggested.

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