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# Morphology of titanium, zirconium and hafnium nanofilms deposited onto zirconia ceramic at annealing in vacuum

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The morphology of titanium, zirconium, and hafnium nanofilms deposited onto zirconia after annealing in vacuum at 1400, 1500, and 1600 °C was studied. Nanofilms show a tendency to fragmentation; for titanium it begins at 1400 °C, for zirconium and hafnium at 1500 °C. At further heating, titanium nanofilm coagulates, while zirconium and hafnium nanofilms interact with the oxygen of the substrate. Tendencies for the formation of swellings on films prior to fragmentation and a certain role of grain boundaries in the cases of titanium and hafnium were noted.

**Key words:** morphology, nanofilms, zirconia, titanium, zirconium, hafnium.

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## Introduction

Metal nanofilms deposited onto nonmetallic surface can fragment when heated in vacuum to temperatures much lower than the melting temperature of the film metal, and the higher the adhesion in the contact pair, the less the tendency to island formation [1]. Metals with high affinity to oxygen, such as titanium, zirconium and hafnium show high adhesion to solid oxides surfaces, in particular to zirconia [2]. As the affinities of these metals for oxygen are different, the morphology of thin films of these metals on zirconia after annealing should also be different. So, studying of the fragmentation of these films is of interest from a scientific point of view considering peculiar properties of zirconia, in particular possibility of non-stoichiometric phases with oxygen deficit formation, that can affect the oxide-metal interaction [3], and for technologies in which nano-dimensional metal objects are in contact with solid electrolytes, in particular in the manufacture and operation of high-temperature electrochemical devices, electronic devices, catalysts, etc.

## I. Materials and procedure

Ceramic based on zirconia stabilized with 3 at. % $Y_2O_3$, pure titanium, zirconium, and hafnium were used. $ZrO_2$-ceramic were machined to plates 4×4×1 mm, polished with 0.7-0.3 μm diamond powder, cleaned in acetone, and annealed on air at 1000°C during 1 h. 100 nm thickness titanium, zirconium, and hafnium films were applied by electron-beam sputtering during 10 min onto the surface of substrates. During the film deposition, samples were heated up to no more than 100°C. The coating thickness was measured with a special quartz resonator located in a vacuum chamber of electron beam apparatus ELU-2 along with samples. The quality of the deposited films was monitored by metallographic microscope XJL-17.

The samples were annealed in a vacuum not worse than $2\times10^{-3}$ Pa at different temperatures with varying holding times.

The annealed samples were studied using scanning electron microscopes Neo Scope JCM-5000 and ZEISS EVO SO XVP. To determine the free of film area of substrate after fragmentation planimetrical method by Adobe Photoshop was used.

## II. Results and discussion

On fig. 1 SEM images of the titanium films after annealing at 1400°C are represented.

As one can see, a fragmentation of the film occurs at these conditions: after 2 min (fig. 1 a) the film is relatively uniform, there are signs of film swelling due to delamination. After 5 min holding extensive tears form on the film (fig. 1 b). 10 min holding (fig. 1 c) corresponds to the initial stage of fragmentation, the metal "flows out" from the substrate, and an open ceramic surface appears. At 20 min holding (fig. 1 d) the film coagulates with formation of small unconnected islands.

On fig. 2 SEM images of the titanium thin films after annealing at 1500°C are represented.

After 2 min at 1500°C (fig. 2 a) the film loose the smoothness, some signs of delamination appear. After 5 min (fig. 2 b) the delamination becomes more obvious, cracks appear, the film starts to destroy. After 10 min (fig. 2 c) titanium starts to coagulate, and the film divides into sections, the surface between which is the metal-free zones of uniform width. Perhaps these areas correspond to grain boundaries emerging on the surface of the ceramic [4] in this case the absence of titanium on them may be due to the intense diffusion of oxygen precisely along the grain boundaries. Inside the sections the film coagulates too forming interconnected islands of irregular shape. After 20 min (fig. 2 d) titanium is coagulating in large fragments of irregular shape.

On fig. 3 SEM images of the titanium thin films after annealing at 1600°C are represented.

As one can see, at 2 min holding at 1600°C (fig. 3 a) the film starts to coagulate: becomes rough and porous, some cracks appear. After 5 min (fig. 3 b) the picture is similar to that for 10 min holding at 1500°C (fig. 2 c): sections with partially fragmented film and metal-free zones of uniform width between them. After 10 min (fig. 3 c) the picture is similar to that for 5 min, coagulation is somewhat more noticeable. After 20 min (fig. 3 d) titanium collected into separate drops of regular shape.

On fig. 4 kinetic curves of titanium nanofilm onto zirconia coagulation for different temperatures is represented in the form of diagrams as dependences of the area of the metal-covered ceramic surface on the holding time.

So the titanium film fragmentation accelerates with temperature increasing. It should also be noted that the adhesion of the titanium film to $ZrO_2$ is quite low, as evidenced by the delamination of the film at the initial stages of fragmentation and coagulation of titanium into spherical islands.

The fact that at certain stages of annealing, the titanium-free areas are formed near the boundaries of $ZrO_2$ grains on the substrate surface can be explained as follows. Due to the high mobility of anions, $ZrO_2$ can lose oxygen when heated forming non-stoichiometric phases [5], and metals exhibit adhesion precisely to zirconia with a significant oxygen deficiency ($ZrO_{2-x}$) [3].

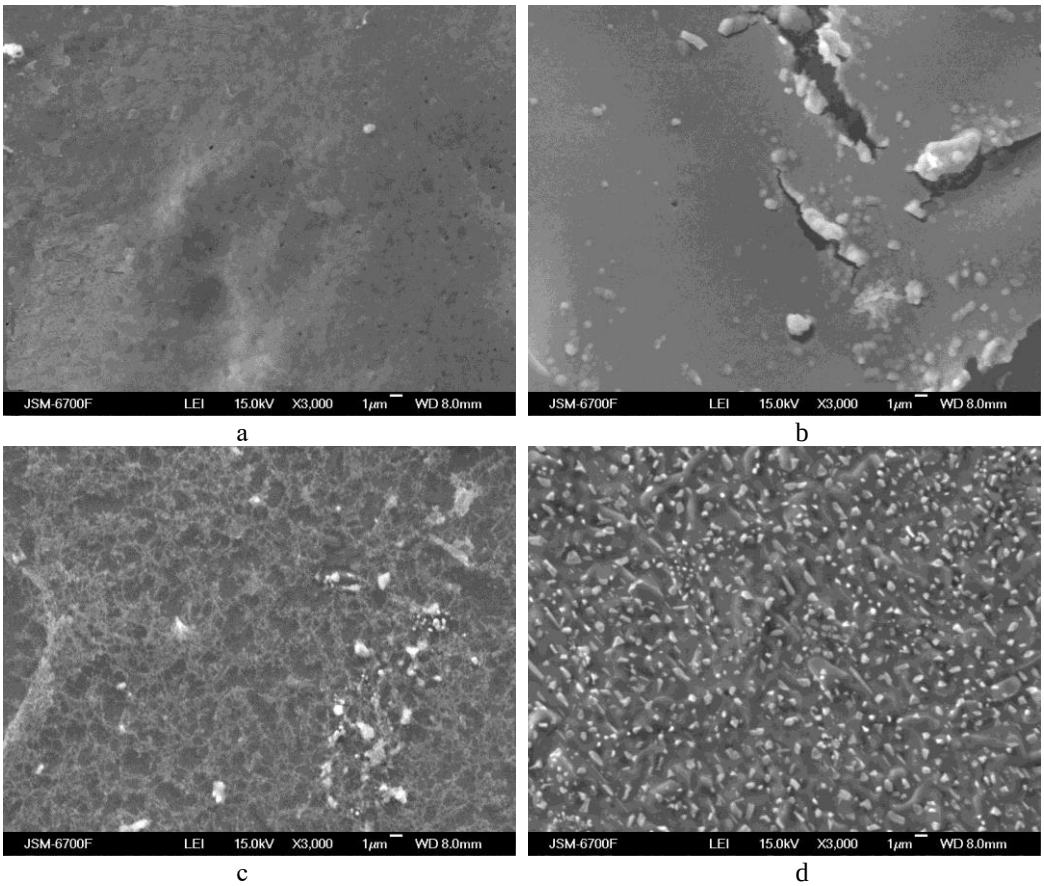



**Fig. 1.** SEM image of the titanium nanofilms onto $ZrO_2$-ceramic after annealing in vacuum at 1400°C with different holding time: a – 2 min; b – 5 min; c – 10 min; d – 20 min.

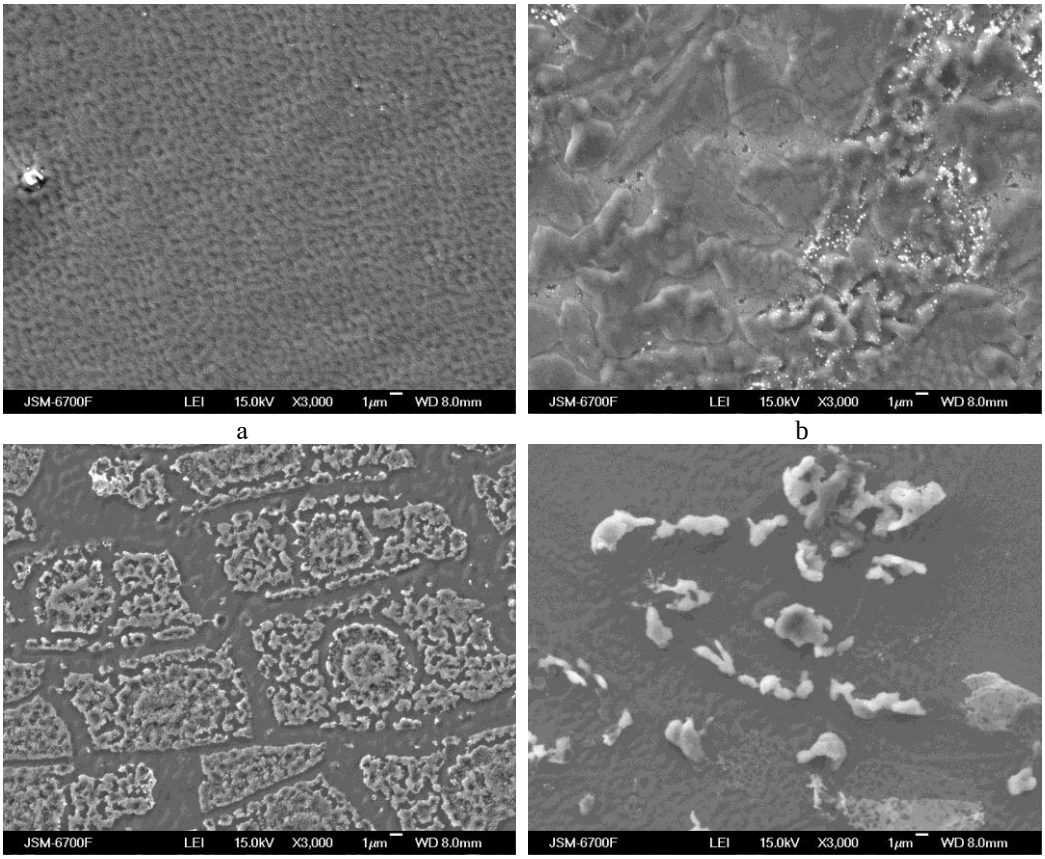



**Fig. 2.** SEM image of the titanium nanofilms on the $ZrO_2$-ceramic after annealing in vacuum at 1500°C with different holding time: a – 2 min; b – 5 min; c – 10 min; d – 20 min.

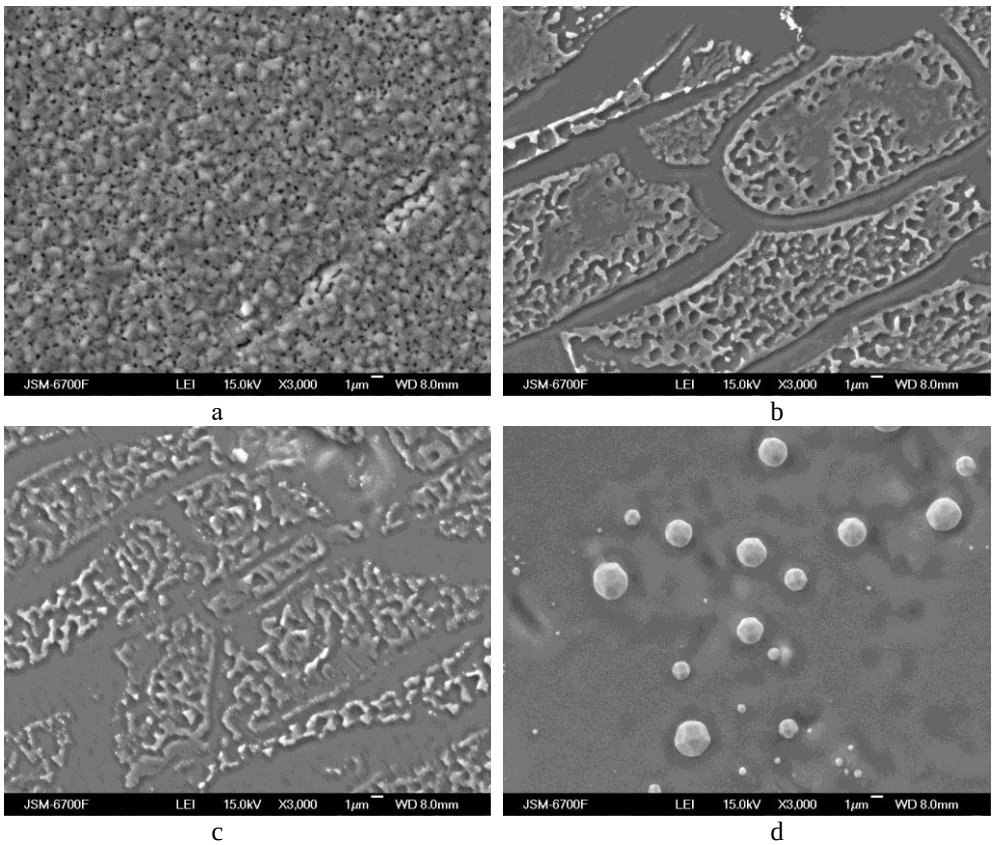



**Fig. 3.** SEM images of the titanium nanofilms on the $ZrO_2$-ceramic after annealing in vacuum at 1600°C with different holding time: a – 2 min; b – 5 min; c – 10 min; d – 20 min.

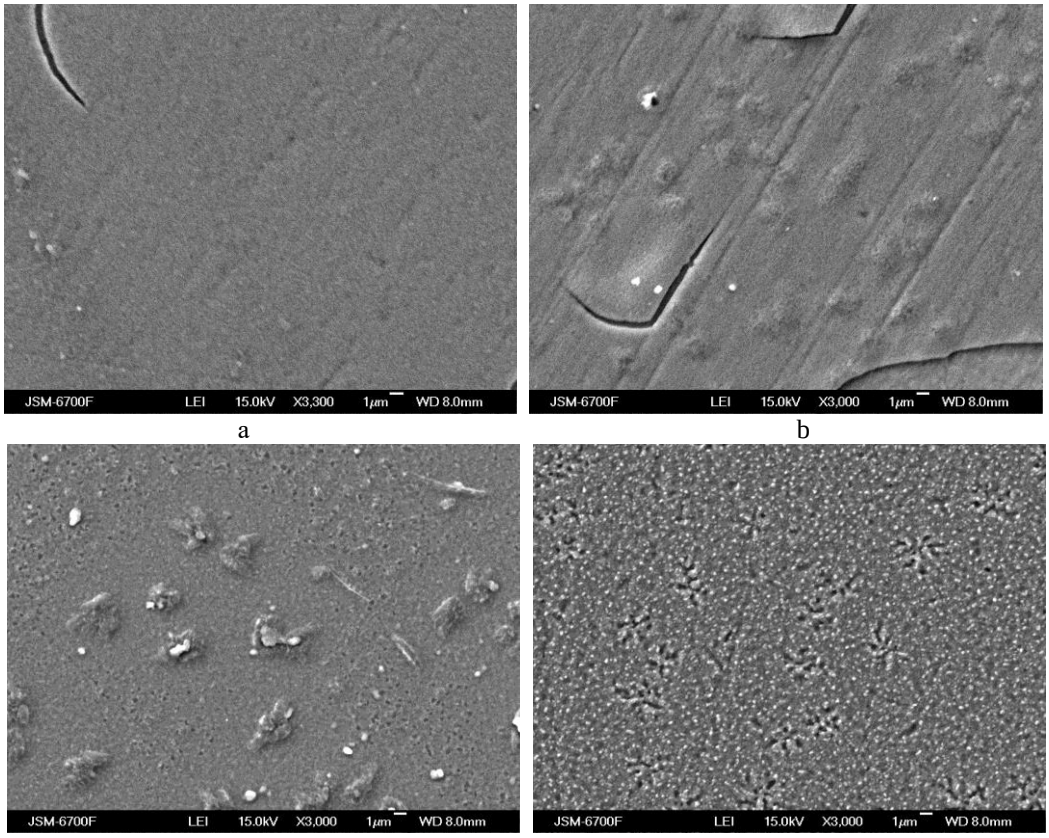



**Fig. 5.** SEM image of the zirconium nanofilms on the $ZrO_2$-ceramic after annealing in vacuum at 1400°C with different holding time: a – 2 min; b – 5 min; c – 10 min; d – 20 min.

Under the conditions of these experiments, the surface layers of the substrate lose oxygen both due to heating and due to interaction with the titanium film (which is typical for contact of dioxide with active metals [2]), so the adhesion of the metal film to the zirconia substrate increases. However, the mobility of anions along grain boundaries is significantly higher than in the bulk of grains [6, 7], so the stoichiometry of zirconia near these boundaries is quickly restored due to the diffusion of oxygen from the depths of the ceramic, the adhesion of titanium to such a surface decreases, and metal "flows away" from it.

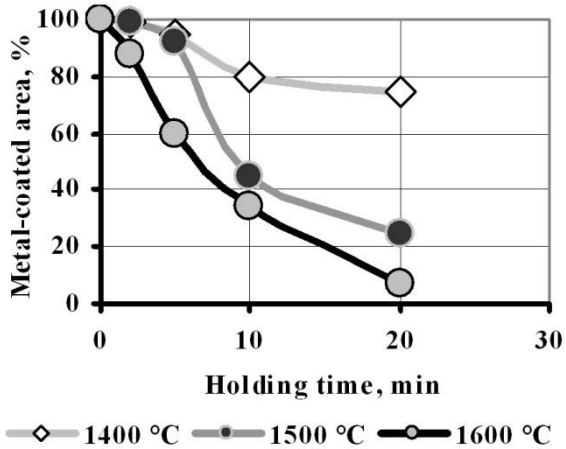



**Fig. 4.** Kinetics of the titanium nanofilms onto zirconia coagulation.

On fig. 5 SEM images of the zirconium thin films after annealing at 1400°C are represented.

After holding for 2 min at 1400°C the zirconium film onto $ZrO_2$-ceramic remains homogeneous (fig. 5 a), although some cracks appears, small fragments of the film break off. After 5 min numerous swellings are formed, apparently due to the release of oxygen from the substrate (fig. 5 b). However, after 10 min holding the number of swellings noticeably decreases, although on some of them cracks are visible (fig. 5 c). The irregular shape of the swellings may indicate that they are decreasing, possibly due to the interaction of oxygen released by the substrate with metallic zirconium. Holding for 20 min leads to the transformation of the film into a non-uniform porous coating, at the same time, the swellings disappear (fig. 5 d).

On fig. 6 SEM images of the zirconium thin films after annealing at 1500°C are represented.

As one can see after 2 min holding the film is relatively uniform (fig. 6 a), small fragments of the film break off, possibly due to thermal stresses generated during heating. After 5 min holding (fig. 6 b), the film is still fairly homogeneous, with small depressions appearing. After 10 min (fig. 6 c), very numerous swellings appear on the film and even merge with each other. After 20 min (fig. 6 d), the swellings disappear, small isolated depressions merge into extended ones, that is, the film fragments; the formation of isolated islands does not occur, it indicates relatively high adhesion of the film to the substrate.

On fig. 7 SEM images of the zirconium thin films after annealing at 1600°C are represented.

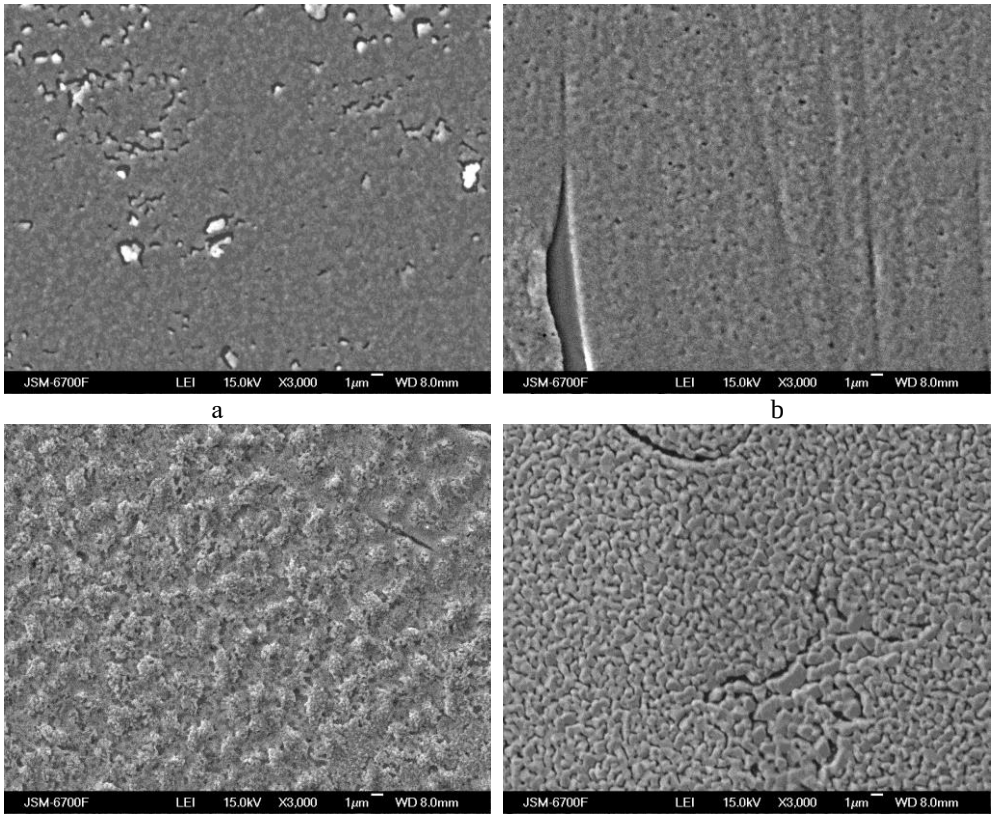



**Fig. 6.** SEM images of the zirconium nanofilms onto $ZrO_2$-ceramic after annealing in vacuum at 1500°C with different holding time: a – 2 min; b – 5 min; c – 10 min; d – 20 min.

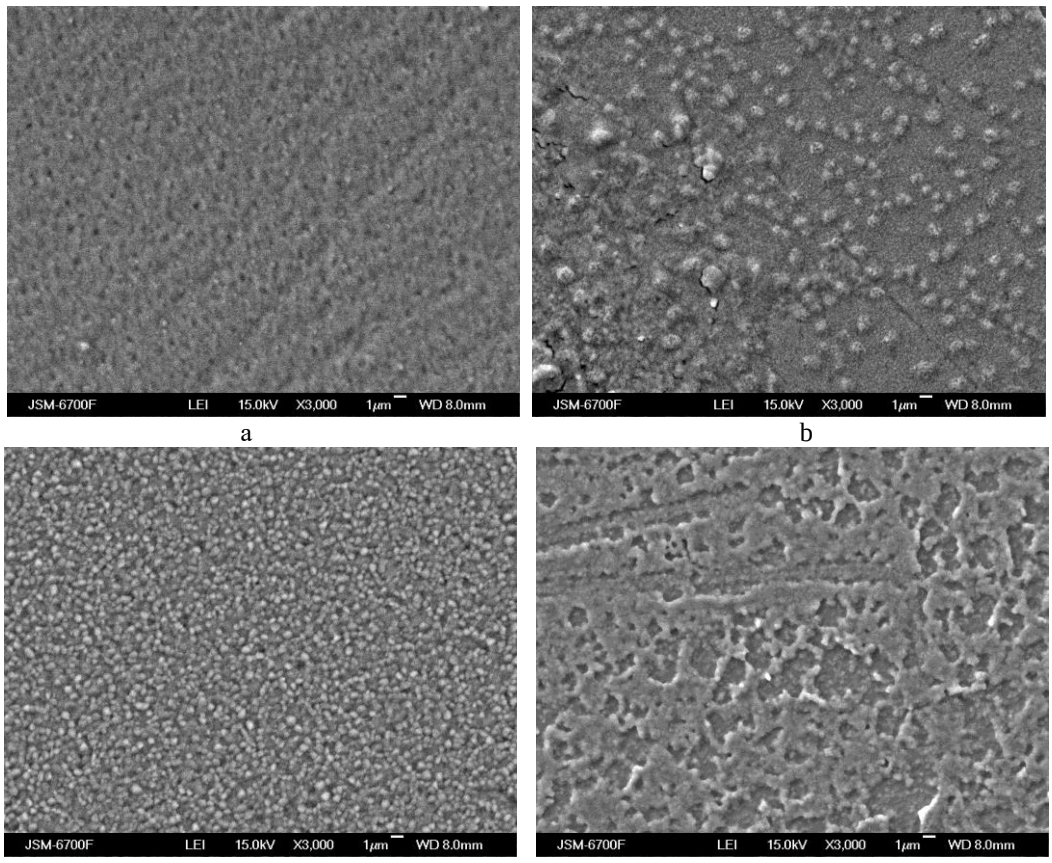



**Fig. 7.** SEM images of the zirconium nanofilms onto the $ZrO_2$-ceramic after annealing in vacuum at 1600°C with different holding time: a – 2 min; b – 5 min; c – 10 min; d – 20 min.

After 2 min holding (fig. 7 a) the film is relatively uniform, after 5 min (fig. 7 b) numerous small swellings appear. After 10 min holding (fig. 7 c) the swellings disappear, the film transforms into a rough coating consist on small fragments. After 20 min (fig. 7 d) these fragments merge, although not isolated islands are formed, but, on the contrary, a covering is a metal layer with isolated extensive openings. Probably due to interaction with zirconium, the substrate oxide becomes non-stoichiometric, as a result of which the adhesion of the metal to it increases. It is also possible that the zirconium in the film is oxidized to dioxide, completing the structure of the substrate, which is why openings are formed on the film.

On fig. 8 kinetic curves of zirconium nanofilm onto zirconia coagulation for different temperatures is represented in the form of diagrams as dependences of the area of the metal-covered ceramic surface on the holding time.

On fig. 9 SEM images of the hafnium thin films after annealing at 1400°C are represented.

After annealing at 1400°C for 2 min (fig. 9 a), the film remains homogeneous. After 5 min (fig. 9 b), individual symmetrical swellings formed; after 10 min (fig. 9 c), small ones were added to them, and it should be noted that grain boundaries clearly appeared in the form of thin dark lines, which probably represent breaks in the film. It is interesting to note that the formation of swellings is not observed near the grain boundaries, perhaps oxygen, which caused the swelling to form, escaped through breaks in the film. After 20 min (fig. 9 d), small blisters spread over the entire surface of the film.

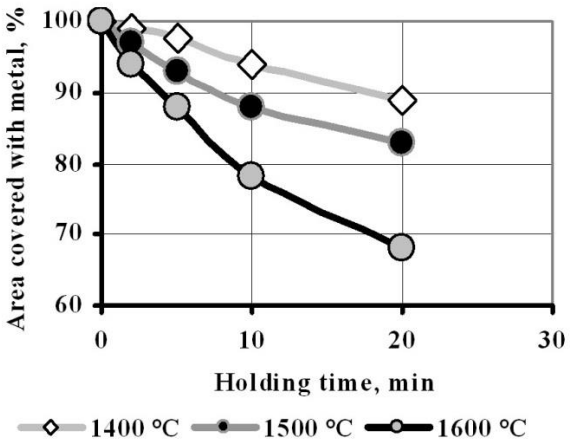
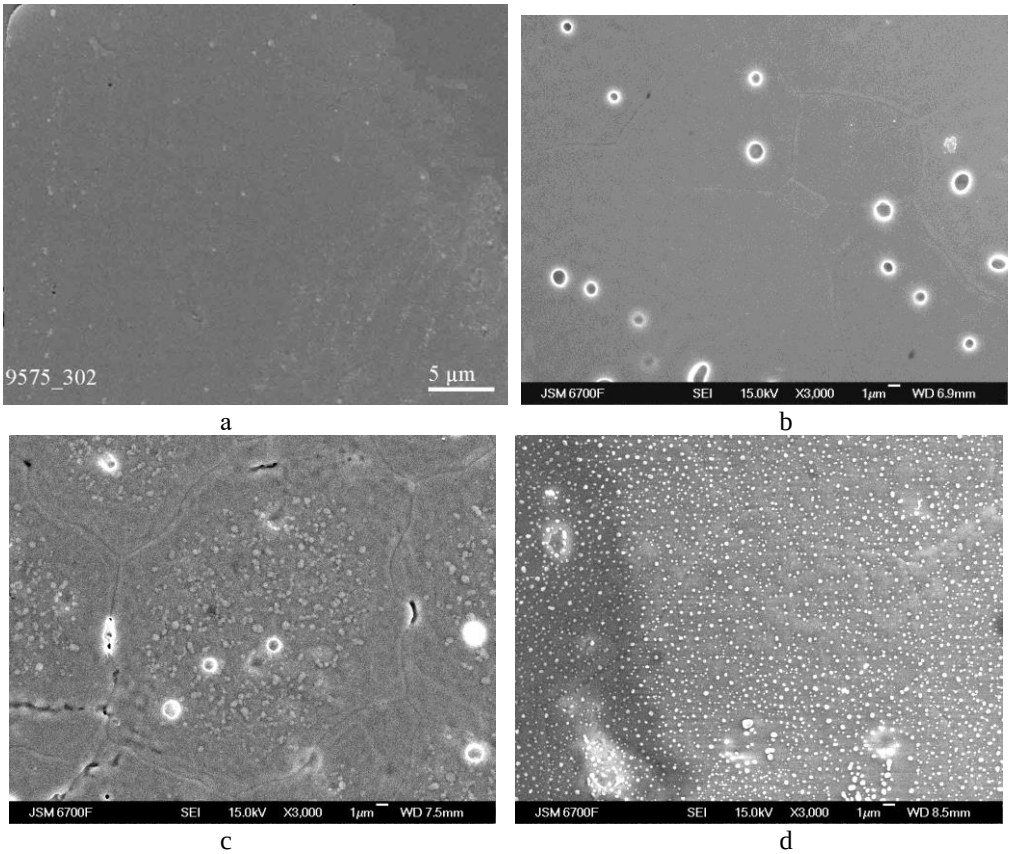



**Fig. 8.** Kinetics of the zirconium nanofilms onto zirconia coagulation.

On fig. 10 SEM images of the hafnium thin films after annealing at 1500°C are represented.

After 2 min holding (fig. 10 a), numerous cracks form on the surface of the film, probably due to thermal stress; after 5 min (fig. 10 b), the cracks become wider, small swellings also appear, usually far from the cracks, some swellings burst. Further holding for up to 10 min (fig. 10 c) does not lead to significant changes in the film morphology. After holding for 20 min (fig. 10 d), pores form in place of the swellings, the film divides into closely spaced islands, it can be considered the beginning of fragmentation.




a b c d

**Fig. 9.** SEM images of the hafnium nanofilms onto the $ZrO_2$-ceramic after annealing in vacuum at 1400°C with different holding time: a – 2 min; b – 5 min; c – 10 min; d – 20 min.

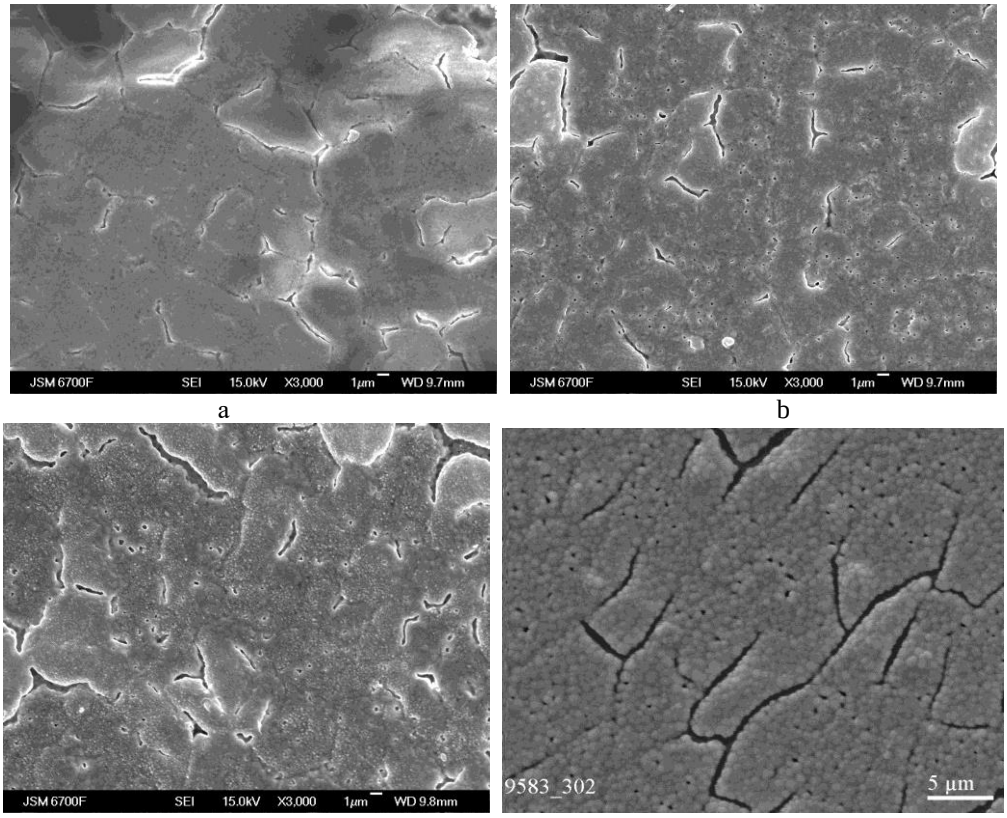



**Fig. 10.** SEM image of the hafnium nanofilms onto the $ZrO_2$-ceramic after annealing in vacuum at 1500°C with different holding time: a – 2 min; b – 5 min; c – 10 min; d – 20 min.

On fig. 11,a SEM images of the hafnium thin film after holding at 1600 °C during 2 min is represented.

As one can see the film collapsed and delaminated from the surface of the substrate over a significant area; oxidation of hafnium to its oxide apparently occurred.

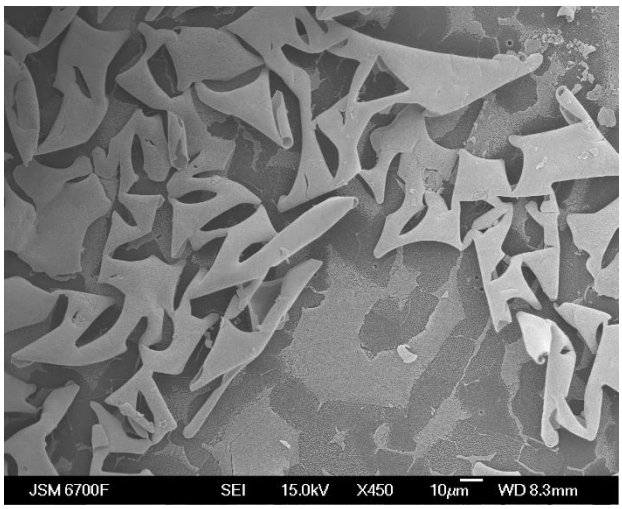



**Fig. 11.** SEM image of the hafnium nanofilm onto the $ZrO_2$-ceramic after holding during 2 min at 1600°C in vacuum.

On fig. 12 kinetic curves of hafnium nanofilm onto zirconia coagulation for different temperatures is represented in the form of diagrams as dependences of the area of the metal-covered ceramic surface on the holding time.

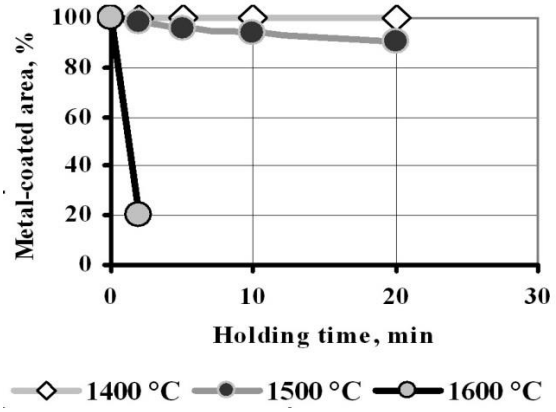



**Fig. 12.** Kinetics of the hafnium thin films coagulation on zirconia.

So the tendency to fragmentation decreases in the range titanium - zirconium - hafnium. For titanium, the first signs of fragmentation are observed at 1400°C and 10 min holding time, for zirconium and hafnium at 1500°C and 20 min holding. This may be related to the melting temperatures of metals, since fragmentation temperatures depend on them [1]. However, at further heating, titanium continues to fragment, while in the cases of zirconium and hafnium, fragmentation stops due to the interaction of the films with the substrate. The interaction obviously represents the oxidation of films deposited on the metal with oxygen from the substrate. The affinity of the studied metals to oxygen was assessed as the change in the Gibbs energy in the reactions of interaction of these metals to atomic oxygen with the formation of their higher oxides

($TiO_2$, $ZrO_2$, $HfO_2$), which was calculated using the resource [8]. Graphs of the dependence of the change in the Gibbs energy in these reactions on temperature are presented on fig. 13.

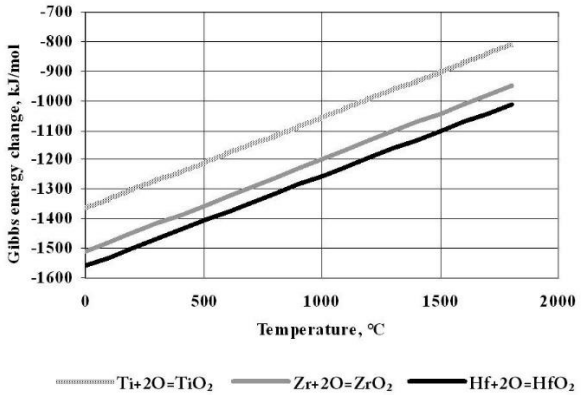



**Fig. 13.** Gibbs energy change for reactions of titanium, zirconium and hafnium to oxygen.

So the affinity of zirconium and hafnium for oxygen is higher than that of titanium, which explains the different behavior of the films during annealing.

It should also be noted that before fragmentation begins, swellings form on the films, the size of which decreases in the titanium-zirconium-hafnium series. This is probably due to the mechanical properties of the films.

## Conclusion

The effect of annealing in vacuum on the morphology of titanium, zirconium, and hafnium nanofilms deposited onto the surface of a $ZrO_2$-ceramic was studied. Films tend to fragment; in the case of titanium, fragmentation begins at lower temperatures than in the cases of zirconium and hafnium. At the same time, titanium can coagulate completely, and zirconium or hafnium interacts with the oxygen of the substrate, which prevents fragmentation. These features are explained by the difference in the oxygen affinity of the studied metals.

Before fragmentation, swellings are formed on all studied films, the size of which probably depends on the mechanical properties of the coating.

For titanium and hafnium, the grain boundaries emerging on the surface of the substrate play a certain role.

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***Stetsyuk T.V.*** – researcher.

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О.В. Дуров, Т.В. Стецюк

# Морфологія наноплівок титану, цирконію та гафнію нанесених на оксидноцирконієву кераміку при відпалі у вакуумі

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Досліджено морфологію наноплівок титану, цирконію та гафнію, нанесених на діоксид цирконію після відпалу у вакуумі при 1400, 1500 та 1600°С. Наноплівки виявляють схильність до фрагментації; для титану вона починається при 1400°С, для цирконію і гафнію при 1500°С. При подальшому нагріванні наноплівки титану коагулюють, а наноплівки цирконію та гафнію взаємодіють з киснем підкладки. Відмічено тенденції до утворення здуття на плівках перед фрагментацією та певну роль меж зерен у випадках титану та гафнію.

**Ключові слова:** морфологія, наноплівки, діоксид цирконію, титан, цирконій, гафній.