PHYSICS AND CHEMISTRY OF SOLID STATE
V. 26, No.1 (2025) pp. 78-83
Section: Chemistry

DOI: 10.15330/pcss.26.1.78-83

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ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 26, № 1 (2025) С.78-83
Хімічні науки

PACS: 68.55.-a, 68.47.Gh, 81.40.Ef

ISSN 1729-4428 (Print)
ISSN 2309-8589 (Online)

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Morphology of titanium nanofilms onto sapphire at annealing in vacuum

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A change in the morphology of titanium films on the surface of sapphire was investigated when heated in a vacuum. The coatings interact with the substrate, forming two phases with different adhesion to sapphire. Probably the phase with low adhesion is an intermetallides of the titanium-aluminum system, and the phase with high adhesion is titanium oxide.

Keywords: morphology, nanofilms, sapphire, titanium, surface interaction.

Received 12 June 2024; Accepted 05 February 2025.

Introduction

It is known that thin films of metals deposited to the surface of non-metallic materials show a tendency to defragmentation at temperatures lower than the melting points of these metals [1]. The degree of defragmentation, which can be considered as the ratio of the area of the substrate covered with metal and free from it, as well as the morphology of coatings after annealing depend on the adhesion of the metal to the substrate.

Metals with high affinity to oxygen, such as titanium, zirconium, hafnium, are used as active additions to metal brazing fillers, increasing wetting and adhesion in contact couples. Aluminum oxide materials are widely used in technology, in particular in the joint with metals [2], in the manufacture of joined parts of the exact sizes use the deposition of active metals in the form of thin films, followed by soldering or brazing by inert fillers in vacuum, so it is important to investigate the processes that occur when these films are heated [3]. Some works are devoted to titanium films on alumina substrate [4-7]. In [4] Ti-O and Ti-Al bonds formed when the titanium film on sapphire was annealed at 1523 K, $Ti_3Al[O]$ and Ti_2O phases were revealed. In [5] the titanium film deposited to sapphire interacted with the substrate, at 973 K a solid aluminum solution was formed in titanium, at 1173 K Ti_3Al intermetallides and lower titanium oxides appears. In [6] the interaction of the titanium film with the sapphire substrate is observed too, at 1075 K the coating reacts with sapphire, oxidizing to TiO and reducing aluminum oxide to Al. In [7], the structure of the film and the interface depend on the temperature of titanium on Al_2O_3 deposition and, in turn, affect the adhesion of the film with the substrate. Thus, when the titanium film reacts with alumina, two phases are formed: oxidized titanium and metallic phase, consisting of titanium and aluminum reduced from Al_2O_3. For a better understanding of these processes, it is necessary to study the kinetics of changes in the structure of thin titanium coatings on sapphire during annealing at different temperatures.

So the morphology of thin films of titanium on the surface of aluminum oxide, after annealing in vacuum according to different modes, was investigated. To eliminate the effect of grains boundaries and additives for sintering, aluminum oxide monocrystal (sapphire) was selected as a substrate.

I. Materials and procedure

Sapphire in form of discs 15 mm diameter and 1.5 mm thickness, pure titanium were used. Sapphire were 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 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 vacuum. The vacuum chamber of about 40 litres was pumped out by the BN-2 forevacuum pump and the VA-2-3PR diffusion pump providing vacuum not worse than 2×10^{-3} Pa. A resistance furnace with molibdenum wire heater was used. Annealing temperatures were 1200, 1300, 1400, 1500 and 1600 °C, holding times were 2, 5, 10 and 20 min. For each combination of temperature and holding time, a separate sample was used. The annealed sample cooled together with the furnace in a vacuum.

Than the samples were studied using scanning electron microscopes Neo Scope JCM-5000 and ZEISS EVO SO XVP. The shooting mode was used in secondary electrons with a magnification of ×3000.

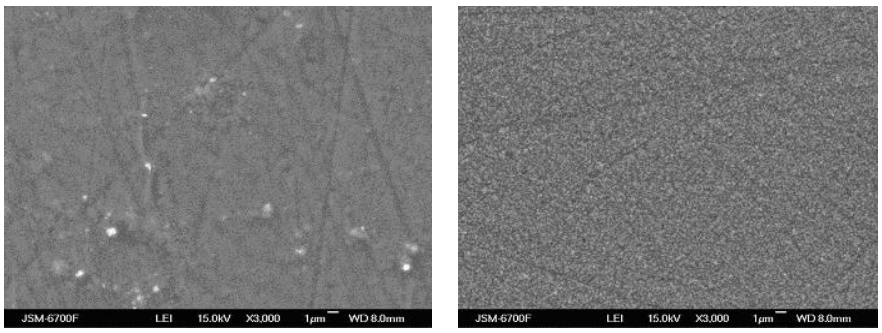
To determine the free of film area of substrate after fragmentation planimetrical method by Adobe Photoshop was used.

II. Results and discussion

On fig. 1 SEM images of the titanium films before annealing (fig. 1 a) and after annealing at 1200 °C for 20 min (fig. 1 b) are represented. As can be seen, the coating becomes inhomogeneous; the beginning of film fragmentation is not observed under these conditions. The probable reason for the lack of fragmentation is the high adhesion of the film to the substrate due to the interaction of titanium with sapphire, since titanium has a high affinity to oxygen.

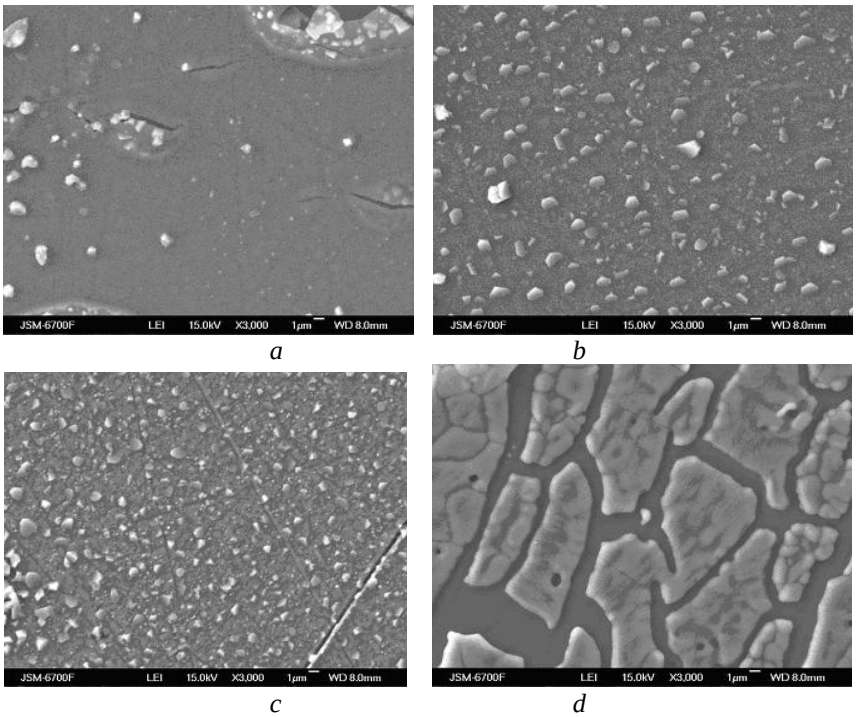
On fig. 2 SEM images of the titanium thin films after annealing at 1300 °C are represented.

After holding 2 min (fig 2 a), cracks appear on the film, and the formation of a new phase in the form of small light islands is also observed. At 5 min holding (fig. 2 b), the islands grow, also new ones of gray color appear. After 10 min (fig. 2 c), the coating becomes very heterogeneous,



a *b*

Fig. 1. SEM image of the titanium nanofilms onto sapphire: a – before annealing; b – after annealing during 20 min at 1200 °C



a *b*

c *d*

Fig. 2. SEM image of the titanium nanofilms onto sapphire after annealing in vacuum at 1300 °C with different holding time: a – 2 min; b – 5 min; c – 10 min; d – 20 min.

most of it turns into new phases of different colors (light and darker), its islands are mainly isolated. The 20 min holding leads to the complete conversion of the film into a new phases, which are present in the form of light areas on the surface of sapphire with sufficiently wide gaps between them, which are likely to be formed due to the heat expansion difference of the coating and the substrate (fig. 2 d).

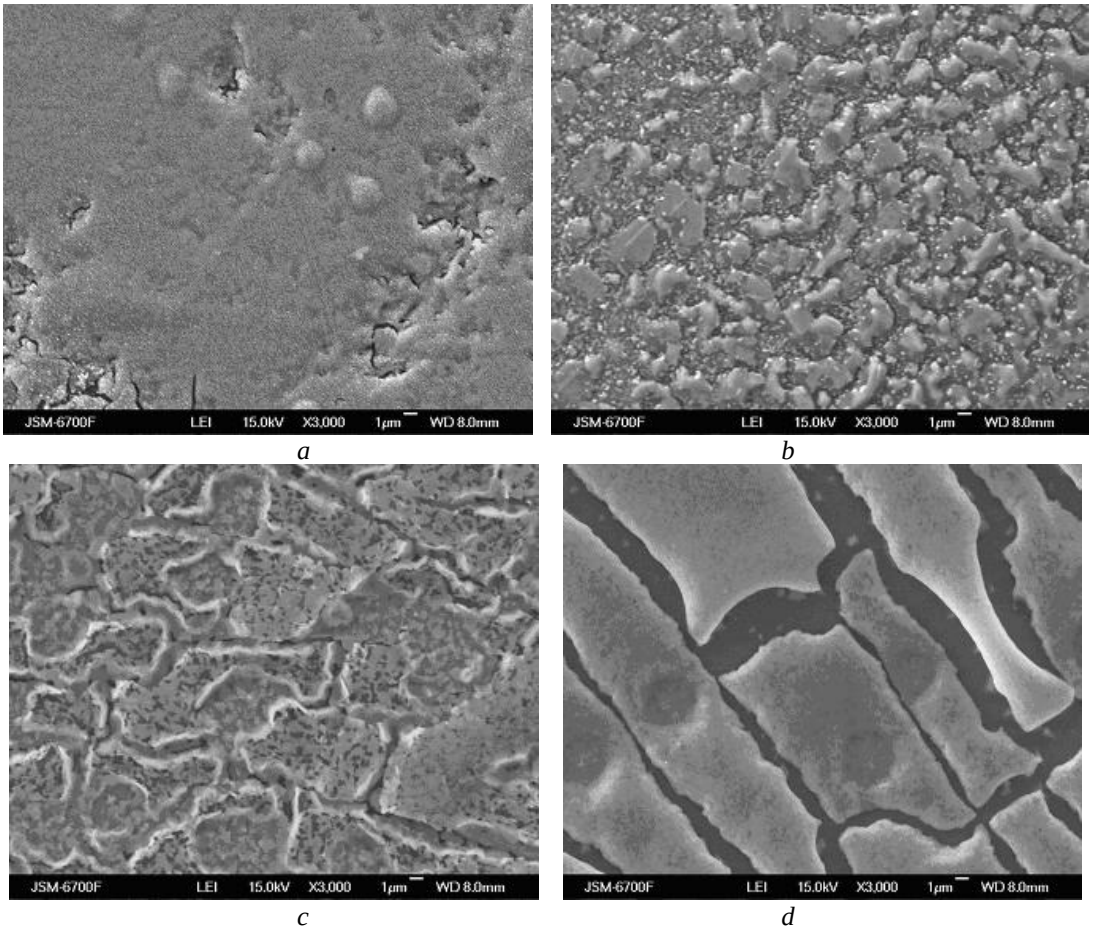
On fig. 3 SEM images of the titanium thin films after annealing at 1400 °C are represented. After the holding of 2 min (fig 3 a), the beginning of the interaction of the coating with the substrate is noticeable, in particular, there are areas consisting of new phases. After 5 min holding (fig 3 b), the coating becomes very heterogeneous and consists of non-symmetric islands of different sizes and color. After 10 min holding (fig 3 c), the aggregation of different phases occurs, in particular, light linear formations that protrude above areas of mostly gray color are noticeable. After 20 min holding (fig 3 d), the coating is an extensive light areas with wide gaps, the edges of the areas are some lighter than the middle.

Annealing at 1500 °C for 2 min (fig. 4 a) leads to the formation of a complex surface structure, which consists of small islands of different colors. After holding for 5 min (fig. 4 b), the coating is a large gray areas of irregular form with narrow intervals of relatively free sapphire surface between them, the edges of the areas are characterized by light color and are slightly higher than the middle. After annealing within 10 min (fig. 4 c), the signs of re-defragmentation of the coating become noticeable, in particular the intervals of the free sapphire surface between its areas become wider and cleaner, in the middle of the areas there is also a free surface, white linear formations become wider and separated from gray areas. Annealing within 20 min (fig. 4 d) leads to even greater defragmentation, in particular, the area of the sapphire surface free from covering increases, the gray phase is divided into the islands, white linear formations also reveal a tendency to aggregate. At the same time, there are signs that the gray phase merges with the substrate, "spreading" on it, in particular, the boundaries between the gray phase and the surface of the sapphire are fuzzy.

At 1600 °C after 2 min holding, the coating splits into small fragments of white or gray color (fig. 5 a), after 5 min, white phase is collecting in linear aggregations, and gray one drains with the surface of sapphire (fig. 5 b), after 10 min is noticeable only a white phase that forms relatively small isolated fragments of incorrect shape (fig. 5 c).

Gibbs energy changes for some reactions between titanium and aluminum oxide were calculated using the resource [8]. The results are presented on fig. 6 in the form of graphs dependence on temperature, the energy of Gibbs is given at one mol of atomic oxygen.

Therefore, the reaction with the formation of $TiAl_3$ and Ti_2O_3 in the system under study is unlikely takes place, since the change in Gibbs's energy is positive for it. It is also unlikely that titanium can restore Al_2O_3 to pure aluminum. At the same time, the probability of other



a *b* *c* *d*

Fig. 3. SEM image of the titanium nanofilms onto sapphire after annealing in vacuum at 1400 °C with different holding time: a – 2 min; b – 5 min; c – 10 min; d – 20 min.

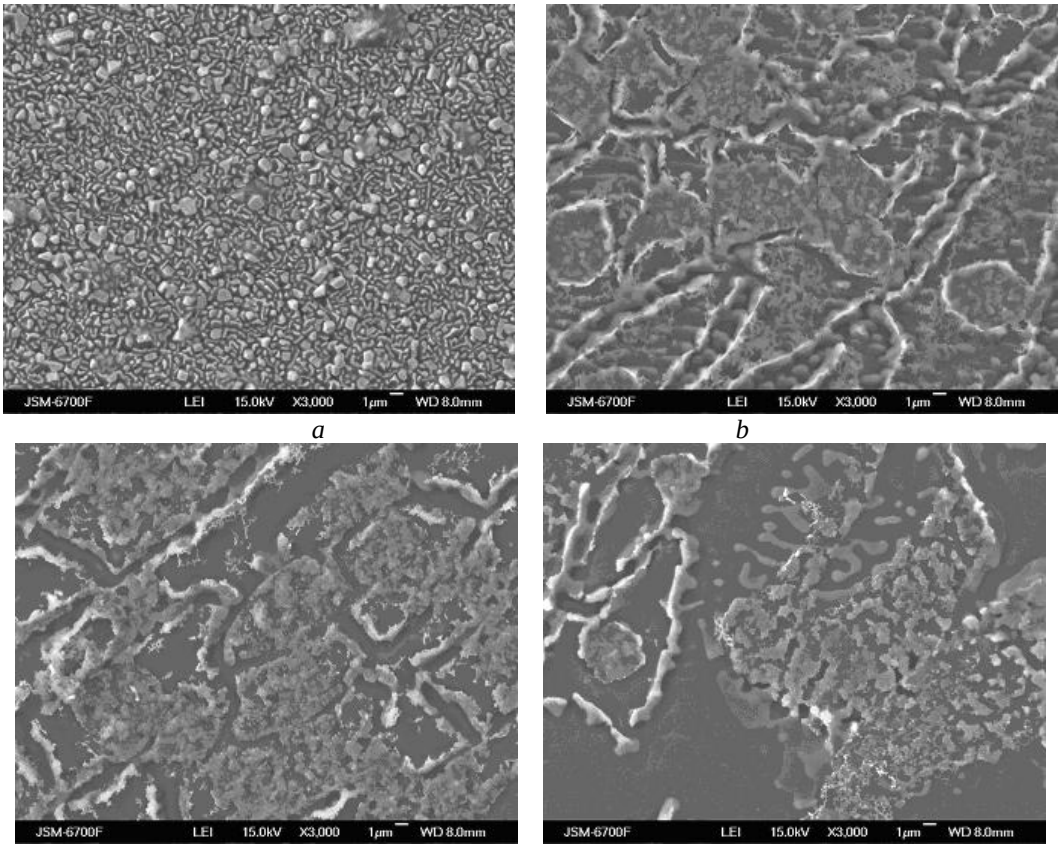


Fig. 4. SEM image of the titanium nanofilms onto sapphire after annealing in vacuum at 1500 °C with different holding time: a – 2 min; b – 5 min; c – 10 min; d – 20 min.

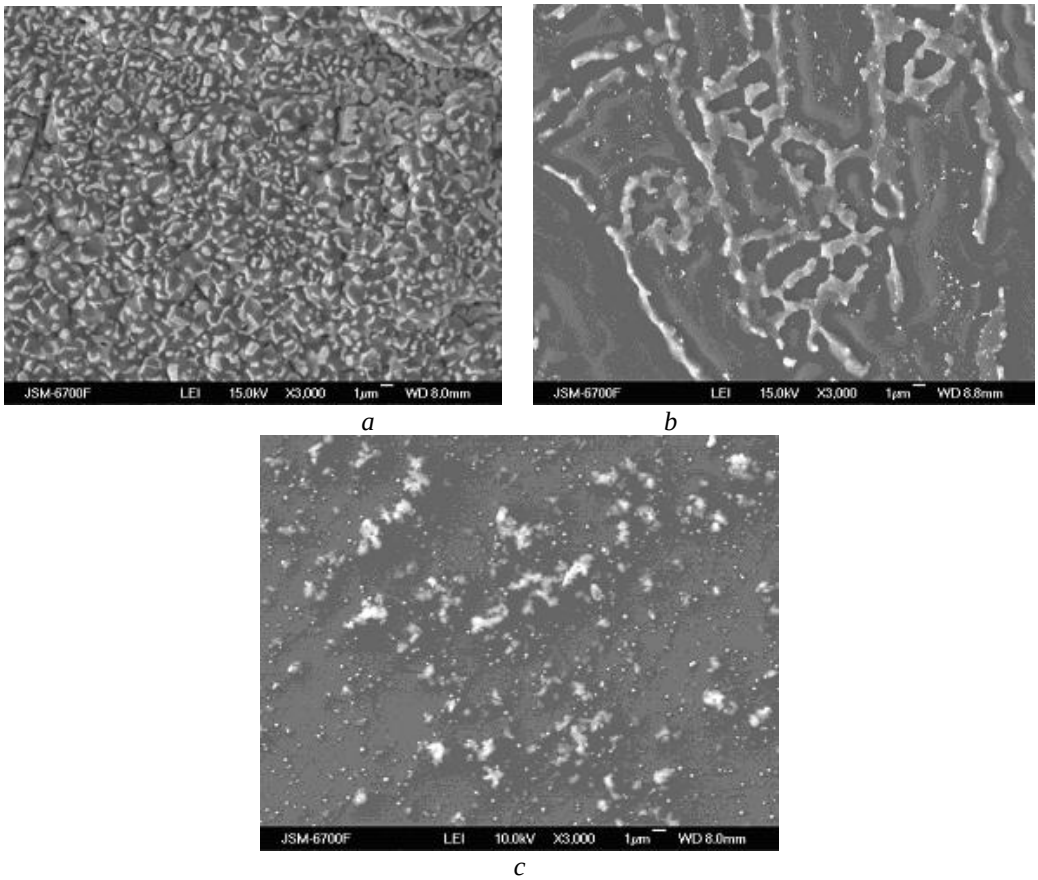


Fig. 5. SEM image of the titanium nanofilms onto sapphire after annealing in vacuum at 1600 °C with different holding time: a – 2 min; b – 5 min; c – 10 min.

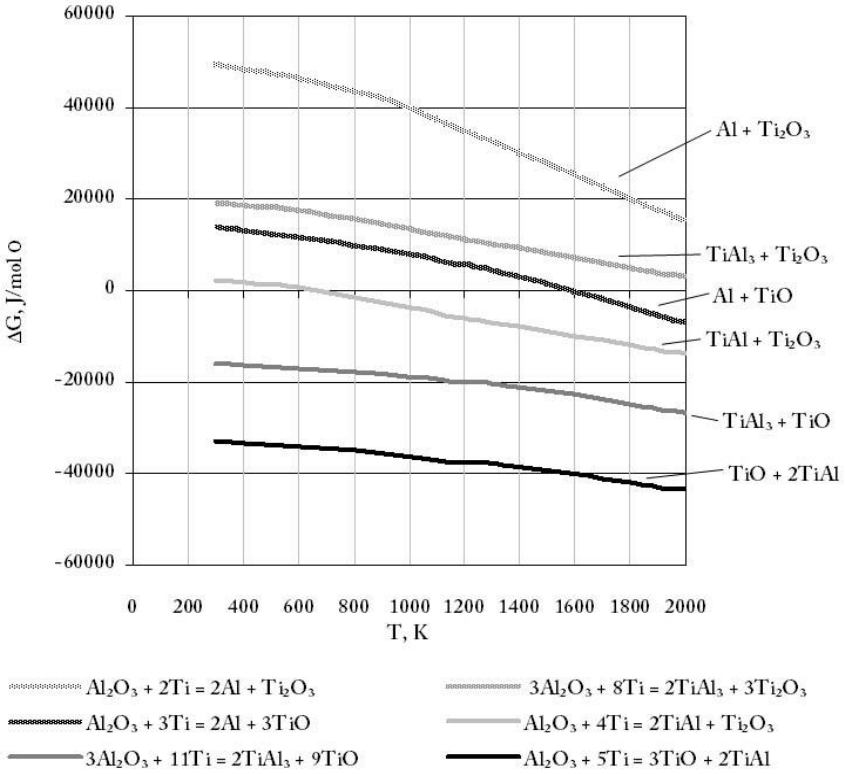


Fig. 6. Dependence of the change in Gibbs energy for some reactions in the Al_2O_3-Ti system.

processes is quite high, especially with the formation of TiAl and TiO.

The phenomena observed when heated in a vacuum of titanium film on sapphire can be explained by give the following considerations. In the interaction of titanium with alumina, including titanium coatings on sapphire [5-7], alumina is reduced to the formation of titanium oxide and intermetallides of the Al-Ti system, i.e. oxide and metal phases. Naturally, the oxide phase reveals much higher adhesion to the oxide substrate than a metal [9]. Therefore, it can be assumed that the destruction of the titanium coating on sapphire in the initial stages of heating is a chemical interaction, the gray phase, which is formed, is the oxidized titanium, and the white phase, respectively, the intermetallide of the Al-Ti system (fig 1, a, b; 2 a; 3 a). With further holding, the metal (white) phase, which does not reveal high adhesion to the substrate, is aggregated first into extensive fragments with relatively narrow intervals between them (fig 2 b, c;3 b, 4 a), then into linear formations (fig 2 d; 3 c, d; 4 b,c; 5 a, b), and then in isolated islands of irregular shape (fig. 5 c), and the oxide (gray) phase with high adhesion to sapphire "spreads" on the substrate (fig. 2 d; 3 d, c; 4 b,c; 5 b) up to merger with it (fig. 5 c).

The process of interaction of the titanium film with the sapphire substrate depends on the temperature, namely, intensifies with its increase. At 1200 °C, the formation of the phase of oxidized titanium and intermetallide with fragmentation of the film is observed (fig. 1 b), the aggregation of intrermetallide and spreading the oxidized titanium do not occur, probably 20 min holding is not enough to reach these stages. At 1300°C, the intermetallide phase and the oxidized titanium become noticeable after 2 min (fig. 2 a), the coating is significantly fragmented after 5 min (fig. 2 b), after 10 min the quantity of phases increases (fig. 2 c), after 20 min, the intermetallide phase is a tendency to aggregate in linear formations, and oxidized titanium to spreading (fig. 2 d). Similar interaction of titanium with sapphire occurs at 1400 °C, but more intensively, the intermetallide phase begins to collect in linear formations after 5 min (fig. 3 b), after 10 min (fig. 3 c) the light linear aggregates become more apparent, and the gray phase is already noticeably spreading on the substrate. At 1500 °C, oxidized titanium begins to spread, and intermetallide is collected in linear formations after 5 min (fig. 4 b), then these effects intensify (fig. 4 c, d). At 1600 °C, intermetallides form linear fragments, and oxidized titanium spreads on sapphire after 5 min (fig. 5 b), and after 10 min the intermetallic phase of the coating is divided into small particles, and oxide is merged with the substrate (fig. 5 c).

The aggregation of intermetallides with an increase in temperature and holding time can be explained by the oxidation of titanium to higher oxides. Obviously, the Ti_2O and TiO are formed first [5], which show adhesion both to the sapphire and, possessing metal-like properties, to the metal phase, providing good “wetting”, and the oxidation of these oxides up to Ti_2O_3 reduces their adhesion to intermetallide, therefore it begins to aggregate.

Thus, overheating of thin titanium films on the sapphire is undesirable, because it leads to the destruction of the coating.

Conclusion

When sapphire with titanium films applied onto its

surface is heated in vacuum, the coating interacts with the substrate, as a result, two phases are formed, a metallic, obviously intermetallides of the Al-Ti system, and oxidized titanium. The metallic phase shows low adhesion to the substrate, therefore aggregates up to the formation of individual particles, while the oxide phase, which has high adhesion to aluminum oxide, is "spreading", on the sapphire surface. The processes intensify with temperature.

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Stesyuk T.V. – researcher.

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О.В. Дуров, Т.В. Стецюк

Морфологія наноплівок титану нанесених на сапфір при відпалі у вакуумі

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Досліджено зміну морфології плівок титану на поверхні сапфіру при нагріванні у вакуумі. Покриття взаємодіють з підкладкою, утворюючи дві фази з різною адгезією до сапфіру. Ймовірно, фаза з низькою адгезією є інтерметалідами системи титан-алюміній, а фаза з високою адгезією – оксид титану.

Ключові слова: морфологія, наноплівки, сапфір, титан, поверхнева взаємодія.