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Process parameters influence on formation of oxides in coatings during pulsed laser deposition of titanium on inner surface of tubes

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Abstract. This study concerns droplet phase influence and process parameters influence (laser radiation power, oblique deposition, residual oxygen pressure, etc.) on morphology and composition of the coating and formation of oxides in the coating during pulsed laser deposition of Titanium on inner surface of tubes. It is shown that droplets in the coating in the presence of residual oxygen significantly affect the composition of Ti-coatings.

Pulsed laser deposition (PLD) is widely used for the deposition of films of various materials and functional purposes [1, 2]. This is due to a number of advantages of PLD over other methods, such as the possibility of spraying both single- and multicomponent films, stoichiometric transfer into the film of the composition of the target material, simplicity of the scheme, deposition at lower substrate temperatures, etc. [1].

However, the PLD method has a significant disadvantage – when the target is ablated (with the laser radiation power density significant for practical applications), droplets and solid microparticles along with ions and atoms are generated to the deposited flow, which substantially degrade the properties of the coatings. To obtain high-quality thin films, it is necessary to avoid precipitation of such particles on them. Many methods of filtering these particles have been developed for deposition on open surfaces. However, it is very difficult to do this while spraying inside small cavities, for example long, small diameter pipes [3–5] (with a rare exception, when drops precipitate specifically to solve specific problems, as was done in [3, 6] during coating deposition on the internal walls of chambers).

This can be achieved by significantly reducing the intensity of laser radiation to values not much exceeding the evaporation threshold (above 25·10⁶ W/cm²) [7], but this results in an extremely low productivity of the PLD method. In [8], the drop phase was reduced by the additional evaporation with second laser, which complicates the scheme.

When depositing nano-sized Ti films, residual oxygen in the sputtering chamber has a significant effect on the process of their formation. Recently, it’s influence on the properties and composition of nano-films has been investigated in the interests of a wide range of applications ranging from solving plasmonics problems [9] to increasing the physico-mechanical properties of metals and alloys [10], carried out at a residual oxygen partial pressure of 5·10⁻⁹ and 2·10⁻⁵ Pa, respectively.
In this paper, we continued the investigation of the PLD coating process on the walls of long (~1 m) small diameter pipes (~10 mm). Sputtering occurred in the quasi-closed volume of the pipe, the pressure of the residual gases in which was \( 10^{-3} \) Pa. Due to the complexity of controlling the processes inside the pipe, the experiments were carried out under conditions simulating the deposition process in the pipe, but in an open space.

A laser stand was used for the experiments [11]. Ablation was carried out with the help of a Gaussian beam laser LTI-215 (M) on yttrium-aluminum garnet activated by neodymium, with pulsed pumping and modulated \( Q \), at room temperature of the substrate. The parameters of the laser radiation are as follows: wavelength \( \lambda = 1064 \) nm with a maximum pulse energy of \( I = 180 \) mJ, pulse duration \( \tau = 10 \) ns, repetition rate \( f = 30 \) Hz, the radiation divergence \( \gamma = 5 \) mrad. Laser radiation was focused on the target by a lens with a focal length \( F = 100 \) mm. The size of the laser mark on the target was 0.8 mm, then the power density of the laser radiation on the target was \( W = 5 \times 10^9 \) W/cm\(^2\). Thus, in order to find out more clearly the effect of droplets on the presence of residual oxygen in films during investigation of deposition regimes with high productivity, an ablation regime with a knowingly large generation of droplets in the deposited stream was used.

As a target, the rod end was used with a diameter of 10 mm, cut at an angles of 60 and 70° from the axis (thus, the axis of the plasma plume had the same angle from the normal to the substrate). As a substrate were used plates 1 mm thick. Target material: Ti alloy (Al \( \sim 7 \% \), Si \( \sim 0.5 \% \)), and substrates – polished steel SUS 304. Irradiation time \( \sim 30 \) and 5 min. The distance from the spot on the target (the axis of the rod) to the substrate was 10 mm. Target’s and substrate’s surfaces were chemically cleaned and placed in a working chamber, which was evacuated by turbomolecular and rotary pumps.

Analysis of the chemical composition of the applied coatings was carried out using the Rutherford backscattering method (RBS) \( \text{He}^+ \) with energy of \( E \approx 1 \) MeV on the ion-beam complex “Sokol-3” of IPTM RAS. Morphology and elemental composition studies were also performed with the FEI Quanta 600 FEG scanning electron microscope with the EDAX Trident energy dispersive system, as well as the KLA Tencor MicroXAM-100 optical profilometer.

Figure 1 shows the RBS spectra measured at points outside the droplets on Ti films deposited on SUS 304 steel at different times. Analysis of both spectra showed the amount of oxygen in the film sufficient to form oxides of TiO\(_2\) and TiO\(_{1.5}\).

![Figure 1. RBS spectra of Ti-film on SUS 304 steel, deposition time: (a) – 30 min, (b) – 5 min. Impact angle – 60°.](image-url)
However, at a pressure of $10^{-3}$ Pa, the amount of residual oxygen on the wall and in the volume of the pipe is small and, therefore, to ensure that the amounts of titanium and oxygen in the film correspond to these oxides compositions, the titanium flux onto the substrate (without droplets) seems to be very low despite the high intensity of laser radiation. Such situation possibly takes place due to the fact that most of the ablated material is in droplets (see figure 2). In figure 3 large droplets (more than 30 μm) are visible, which spread over the surface due to the oblique angle deposition. Droplets, among other things, significantly worsen the morphology of the film (see figure 4). Thus, we see that the presence of droplets has a complex effect on the composition and properties of the films and on the areas outside the droplets.

![Figure 2](image1.png)

**Figure 2.** The general form and composition of the films shown in figure 1: (a) and (b), respectively.

In our opinion, several factors affect the composition of the film in areas outside the drops. First, as mentioned above, this is a small fraction of the atomic particles in the flow relative to the total ablated titanium mass. This, in turn, significantly increases the relative oxygen content of the film. The smaller relative content of oxygen in the drops is explained by the large mass of droplets. Oxygen can get into the drops only during the flight of a drop in the liquid state, and also as a result of adsorption and diffusion into the drop after its solidification on the substrate. The latter is confirmed by figure 4, which shows a drop with a very developed surface and the highest atomic concentration of oxygen.

Secondly, a lower oxygen value in the film at 5 min irradiation is associated with higher ablation efficiency in the initial period, which then decreases due to the formation of a crater on the target [12]. Thirdly, the inclined deposition of particles on the substrate influences. As is known, in this case there is an effect of shading, which leads to the growth of inclined columns on the surface.

The RBS analysis also showed a significant depletion of Fe (up to 50%) of the substrate layer under the coating, which may be due to the mass transfer of titanium into the substrate material by diffusion along the grain boundaries and a decrease in the relative titanium content in the film. This diffusion is quite effective in columnar structures. In addition, certain additional oxidation of the film surface can occur after the air is introduced into the chamber.
To reduce the observed effect, it is necessary to take traditional measures to reduce the amount of droplets in the deposition flow, and also to reduce the partial pressure of residual oxygen by improving the ultimate vacuum in the working chamber and substantially warming up the pipe or cleaning its inner wall with hollow cathode glow discharge plasma [11].

Figure 3. Spreading of large drops.

Figure 4. The section of the profilogram of the film shown in figure 1(a).

It should be noted that up to 12% of nitrogen was detected in some drops. Apparently, it was captured by a drop when flying away from the target. In the future, it is planned to continue studying the interaction of droplets with residual gases, including during ablating the target inside the tube.

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