The study of hydrogenated titanium coatings

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Abstract. The paper considers use of a titanium coating as a sorbent of hydrogen isotopes in targets for neutron generators. The results of microsection analyses of coatings applied by the method of magnetron deposition with the various initial temperatures of a substrate are presented.

Thin-film metal coatings find wide application in various fields including nuclear technology. Neutron generators forming monoenergetic neutron flux [1] are used in geology for radioactive well logging, for elemental and isotopic analysis of materials, for neutron therapy in medicine, for scientific investigations, and for detection of explosives and drugs.

Deuterium or tritium targets are parts of neutron generators. The targets represent a substrate of copper, molybdenum, tungsten and other materials covered with a layer of a sorbent metal. As effective hydrogen sorbent and its isotopes the metals of group IV from the periodic table of elements are used as well as metals of the groups of scandium and lanthanum. The important factor to achieve the resource characteristics of targets, is the strong-bond between the substrate and the applied layer of sorbent. With this purpose it is necessary to minimize gas impurities (N₂, O₂, CO, CO₂ and others), since gas molecules are absorbed on the surface of the coated metal, dissolve in it or form compounds that results in decreasing of sorbent absorbing capacity and in some cases is followed by cracking and breakaway of a sorbing layer.

Targets of neutron generators, in which a substrate is made of copper, and titanium is used as a sorbent are the most spread. Titanium has relatively high sorption ability: one gram of titanium can absorb up to ~460 cm³ hydrogen isotopes. Titanium hydrides are stable at the temperatures up to 300–400°C and resistive to atmospheric effects. However, it is necessary to notice that during the process of titanium hydrogenation its density decreases. When atomic ratio H/Ti is equal to 2, hydride density is less than that of titanium by ~12%. This decrease results in stresses of a sorbent, cracking and breakaway of a substrate. To minimize a risk of such effects, it is better to perform saturation up to the atomic ratio H/Ti≈ 1.7. The equilibrium pressure over TiH₁.₇ will be lower than over TiH₂.₅ [2]. This is the important factor especially when working with tritium targets. It should be noted that when working with tritium, the most significant requirement is to provide radiation safety [3]. Tritium targets for neutron generators are open radioactive sources. In this connection, it is inadmissible to separate metal tritide from a substrate both in the process of storing and operation. From the point of view of environmental safety, it is important to minimize or completely prevent propagation of radionuclides and decrease amount of radioactive wastes [4].
When developing methods that provide reasonable characteristics of a sorbing coating after hydrogenation, the titanium coating applied on a copper substrate was analyzed. Titanium coating was applied in two ways:

- «Cold method» – a titanium layer is applied on a copper substrate with the initial temperature equal to the room temperature;
- «Hot method» – a titanium layer is applied on a copper substrate with the initial temperature 350ºС.

Later, the titanium coating was hydrogenated by deuterium up to the atomic ratio D/Ti = 1.7.

Microstructural analysis of hydrogenated coating was made using specially prepared sections. For this purpose the prepared samples were filled with epoxide compound. The sections were prepared in such a way that the investigated surface was at the minimum possible angle $\alpha$ to the coating surface (figure 1). As a result, the size of the investigated section of the titanium layer increased practically by two orders comparatively “right” sections ($\alpha = 90^\circ$).

![Investigated surface](image1)

**Figure 1.** Layout of the investigated surface.

The optical microscope Axiovert 25 with the maximum optical power up to a factor of 1000 allowed us to control uniformity of titanium (hydride) coating with the nominal thickness 5 µm with the accuracy up to ±0,1 µm over the entire length of the section.

The structure of the titanium coating was analyzed after etching in the agent of the following composition: 2 ml of nitric acid, 2 ml of hydrofluoric acid, 96 ml of water.

The structure of the copper substrate was analyzes after etching in hot Krupp agent (50 ml of hydrochloric acid, 50 ml of water, 5 ml of nitric acid).

The initial temperature of a copper substrate when applying a titanium layer influenced the substrate surface conditions (figure 2).

![Image of microstructure](image2)

**Figure 2.** Microstructure of the boundary of the copper substrate and hydrogenated titanium layer.

In the titanium layer (the darker color) adjacent to the copper substrate and applied by the cold method, there could be seen the inner microcracks 0.3 µm thick (figure 2(b)). When applying the hot method (figure 2(a)), microcracks were not found. Qualitatively, this fact can be explained the
following way. The most probable reasons of microcracks are thermal stresses in the titanium layer. When applying a titanium layer, titanium particles as a result of collision with a substrate surface are heated themselves and heat the surface of a copper substrate. Since the substrate mass and copper heat conductivity are significantly higher than those of the titanium layer, the substrate surface temperature will be lower than the temperature of the adjacent titanium layer that results in temperature drop in the contact zone and in the following generation of thermal stresses. If the level of these stresses exceeds critical values, microcracks are formed. Since the value of thermal stresses depends directly on the value of temperature drop, the increase of initial substrate temperature will decrease the value of these stresses and decrease probability of microcracks formation. It should be noted that ductile materials to which annealed copper refers are not sensitive to thermal stresses as a rule.

When applying a titanium layer, the initial temperature of the copper substrate influences also the state of the substrate surface. If a coating is applied by a cold method, a contact line between a substrate and a titanium layer is fluent (see figure 2(b)). If a coating is applied by a hot method, a contact line is stepped, i.e., the surface of the copper substrate is rough (see figure 2(a)). Rough substrate surface enables a better adhesion of a substrate and a titanium layer. Formation of a rough surface of a copper substrate using a hot method is connected probably with specific features of mechanical effect of titanium particles on the surface of a heated substrate. With the increased temperature, the strength properties of copper significantly decrease (copper ultimate strength decreases from 24 to 16 kgs/mm$^2$ under increase of temperature from room temperature to 350°C). In addition, it should be noted that using the hot method of applying there must be formed a stronger adhesion between a coating and a substrate surface because of two reasons:

– When heating the substrate, the process of mutual diffusion between precipitating titanium particles and the copper substrate surface becomes evident;
– The temperature of substrate heating (350°C) is close to Tammann temperature (0.4–0.5 of copper melting temperature (1083.4°C)) which characterizes the temperature range when materials begin sintering.

Besides, when heating a substrate the surface is additionally cleaned from retained gas-producing impurities, and organic impurities are annealed which enables better adhesion between a coating and a substrate.

The microstructural analysis has shown that with applying titanium coating to the copper substrate heated up to 350°C, adhesion between the coating and substrate is better as opposed to the process without additional substrate heating. This advantage remains after hydrogenation of titanium coating. The results of this study were used in the further process of target fabrication for neutron generators.

References
[1] Gorlovoy GD and Stepanenko VA 1965 Tritievie izluchateli (M., Atomizdat)
[2] Sofyina V V, Azarkh Z M, Gavrilov P I, Yurieva N D et al. 1993 Issledovaniye sistemy titan-vodorod Preprint 29-93 VNIIEF
[3] Federal Law Ob obrashenii s radioaktivnymi otkhodami i o vnesenii izmeneniy v otdelnye zakonodatelnye akty Rossiyskoy Federatsii 190-FZ 11.07.2011
[4] Kazakovskiy N T and Korolev V A 2018 IOP Conference Series: Materials Science and Engineering 387