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INFLUENCE OF METHODS OF THERMOCHEMICAL TREATMENT ON THE STRUCTURE AND SURFACE PROPERTIES OF TITANIUM

The effect of thermochemical treatment of Ti samples of VT-0 grade, used in particular in the manufacture of containers for storage of radioactive waste, on the structure and surface properties was studied. The following methods were used in the processing with B-medium: in powders, in the coating, and combined with an aqueous electrolyte solution provided the microhardness of 15.24-10.06 GPa within the 20 µm layer. In the 50 µm layer, obtained by treatment in powders, it ranges from 14.13 GPa to 7.95 GPa. The Ti oxides Ti_2O_3, TiO are present in diffusion layer of the samples, along with TiB, Ti_3B_4, and in a smaller quantity TiB_2. In this case, there is the competitive nature of formation of B and O phases. The diffusion layer, which is obtained by plasma treatment in electrolyte, includes nanosized fine dispersed Ti boride phases at grain boundaries. Studies of radiation-absorbing ability of samples show that it depends on the Ti treatment method. Maximum absorbance is observed at the combined method. Production of wear-resistant coatings on Ti, which include Ti-B-, O-Ti-B-containing phases, is a way to raise safety and reliability of nuclear power systems for various purposes.

Keywords: thermochemical treatment, microhardness, diffusion layer, titanium borides, radiation absorbance.

Досліджено вплив хіміко-термічної обробки зразків Ti сплавів марки ВТ-0, що поширена, зокрема, у виробництві контейнерів для зберігання радіоактивних відходів, на структуру і властивості поверхні. Способи їх обробки в середовищі, що містить бор, були такі: у порошках, обмазках і комбінованим з розчинами електроліту, що забезпечував мікротвердість 15,24 -10,06 ГПа в шарі до 20 мкм. Мікротвердість шару глибиною до 50 мкм, отриманого обробкою в порошках, коливається від 14,13 ГПа до 7,95 ГПа. У дифузійному шарі таких зразків поряд з TiB, Ti_3B_4 і, в меншій мірі, TiB_2, присутні оксиди титану Ti_2O_3, TiO. Тут маємо конкурентний характер утворення боридних і оксидних фаз. Електролітна плазма створює дифузійний шар із нанорозмірними дрібнодисперсними фазами боридів Ti по межах зерен. Дослідження поглинання радіації зразками показали, що воно залежить від способу їх обробки. Комбінований спосіб дав максимальну спектральну поглинальну здатність. Отримання зносостійких покриттів Ti, до складу яких входять Ti-B-, O-Ti-B-містячі фази, дає можливість підвищити безпеку та надійність ядерних енергетичних установок різного цільового призначення.

Ключові слова: хіміко-термічна обробка, мікротвердість, дифузійний шар, бориди титану, спектральна поглинальна здатність.

Исследовано влияние химико-термической обработки образцов Ti сплавов марки ВТ-0, используемой, в частности, в производстве контейнеров для хранения радиоактивных отходов, на структуру и свойства поверхности. Способы их обработки в борсодержащей среде были такими: в порошках, обмазках и комбинированный с водным раствором электролита, обеспечивавший микротвердость в 15,24 - 10,06 ГПа в слое до 20 мкм. Микротвердость слоя глубиной до 50 мкм, полученного обработкой в порошках, колеблется от 14,13 ГПа до 7,95 ГПа. В диффузионном слое таких образцов наряду с TiB, Ti_3B_4 и, в меньшей мере, TiB_2, присутствуют оксиды титана Ti_2O_3, TiO. В этом случае имеет место конкурентный характер образования боридной и оксидной фаз. Электролитная плазма создает диффузионный слой с наноразмерными мелкодисперсными фазами боридов Ti у границ зерен. Исследования поглощающей способности радиации образцами показали, что она зависит от способа их обработки. Максимальную спектральную поглощающую способность дал комбинированный способ. Получение износостойких покрытий Ti, в состав которых входят Ti-B-, O-Ti-B-содержащие фазы, даёт возможность повысить безопасность и надежность ядерных энергетических установок различного целевого назначения.

Ключевые слова: химико-термическая обработка, микротвердость, диффузионный слой, бориды титана, спектральная поглощающая способность.

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1. Introduction

Titanium and its alloys have low density, high mechanical properties and specific strength, high corrosion resistance. Titanium alloys without hardening have low wear resistance and a tendency to sticking and scuffing in friction units [1]. To improve the performance properties of titanium and its alloys, there are all known methods from laser [2] to the thermochemical treatment (TT), which increasingly acts as boron saturant [3]. The boriding temperature at all saturation processes is above 1000 °C with soaking duration 4 to 8 hours, and thus the layers obtained are of small thickness 13 μm [4, 5].

In this paper we study the influence of TT of titanium samples of brand mark VT-0, used in the manufacture of containers for radioactive waste storage, on the structure and properties of the surface. The goal of our investigation is to obtain a boron-containing wear-resistant coating on titanium.

2. Experiment

Studies were carried out on titanium samples of VT-0 grade, which were treated with the following methods:

1) by a boron-containing powder in mixture with substances, inhibiting titanium oxidation at a temperature of 970-1000 °C for 3 hours;

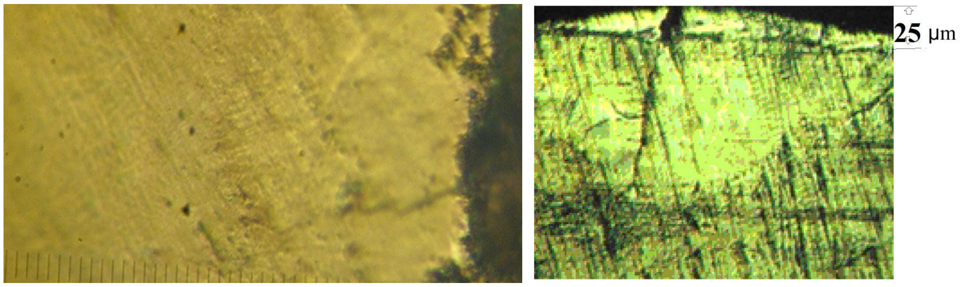
2) by the combined process, including treatment in an aqueous electrolyte solution according to the method [6], followed by treatment with a boron-containing powder mixture at the temperature of 980 °C for 3 hours;

3) in an aqueous solution of boron-containing electrolyte in the mode: voltage U = 80 V, current density j = 2.0-2.7 A/cm^2 in progress, soaking time t = 7-28 min.

The microstructure of treated samples was showed up by etching in 0.5% HF solution. The metallographic analysis of the samples was performed on the microscope "Neophot-21" and microhardness tester “PMT-3” under a load of 50 g. The identification of phase components of the diffusion layer was carried out by X-ray diffraction analysis with diffractometer “DRON-2” in the iron and copper radiation. Relative radiation absorptance of titanium samples, treated with various TT-methods, was evaluated in comparison with that of untreated ones taken per unit.

3. Results and discussion

As a result of the TT, the diffusion layer on the surface of samples is obtained with a microstructure as in Fig. 1.

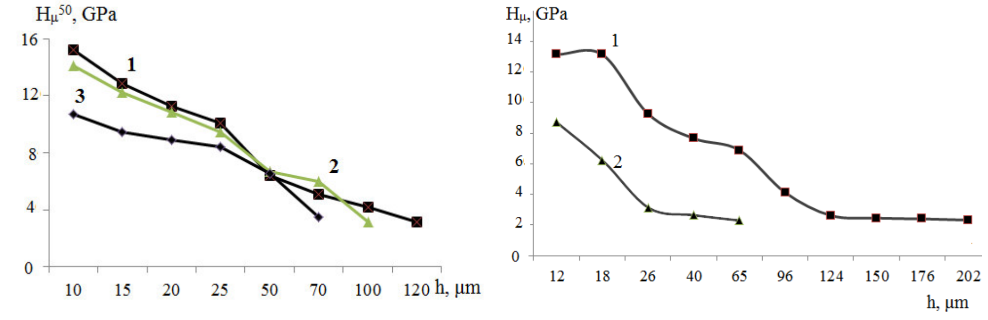


a) b)

Fig. 1 Microstructure of Ti sample:

a) after the TT in the boron-containing medium ×1000;

b) after a plasma treatment in the electrolyte for 28 min., ×800.

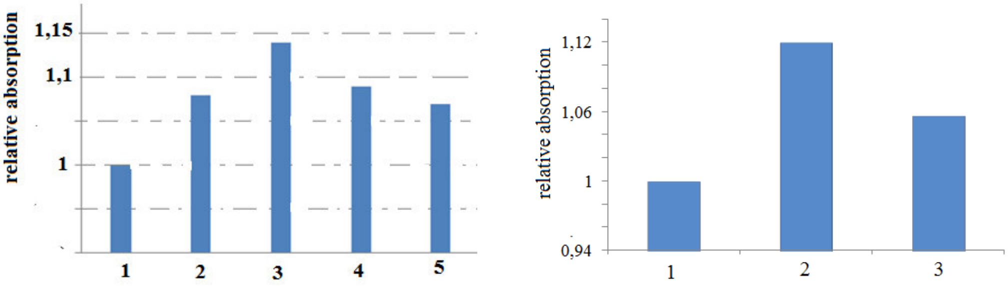


a b

Fig. 2 The depth profile of microhardness for the Ti diffusion layer: a) 1 – after combined treatment in electrolytic plasma and TT followed by coating with amorphous B and Al powder at 1223 K for 3 hours; 2 – treatment in powder medium at T = 1223 K for 3 hours; 3 – TT with coating by amorphous B and Al powder at T = 1223 K for 3 hours; b) electrolyte plasma treatment in the B-containing medium: 1 – at j = 2.3-2.7 A/cm^2, U = 240-280 V, t = 28 min.; 2 – at j = 2-2.4 A/cm^2, U = =240-280 V, t =7 min.

The microhardness of layer of depth up to 50 μm, obtained in the TT with B-containing powders, ranges from 14.13GPa to 7.95GPa (Fig. 2a). At combined treatment the microhardness is slightly higher 15.24-10.06 GPa (Fig 2a.) within a layer depth up to 20 μm. For Ti, at electrolyte plasma treatment (EPT) within 28 and 7 minutes, the microhardness distribution in the layer with thickness 75-80 μm is shown in Fig. 2b. The layer micro–structure includes two phases, one of which is located on the depth of 25 μm from a surface with microhardness of 13.14 GPa, and the other one is on the sample depth up to the 80 μm with microhardness from 6 to 8 GPa depending on the processing mode. We notice that at EPT the probability of formation of oxides is small, while the borides are represented by virtually all known compounds: TiB, Ti_3B_4, TiB_2, $Ti_{1,87}B_{50}$. Uniqueness of the layer, obtained in the electrolyte plasma, is as follows: borides do not form a continuous layer. They are mostly formed at the grain boundaries, in dislocations, microdefects, and have nanoscale size. The result is a precipitation strengthening of Ti surface by boride phase particles. In the case of TT with B-containing powders, we have the competitive nature of formation of boride and oxide phases. With the limitation of oxygen in the sample surface (which is achieved in various ways of hermetic sealing) the growth of boride phase, with B diffusion from saturating medium, slows down and is pushed aside by the growing oxide. If a sample surface has time to form Ti diboride, then boron contained in it in an amount of 28-30 wt. % slowly begins, at temperatures above 1073K, to oxidize to B_2O_3, which prevents the further rapid diboride oxidation. Exactly it gives borides some advantage over the oxides in the process of diffusion. With increasing oxygen on the surface of Ti sample, the oxide at a certain concentration gets preferential growth.

The study of absorptance of Ti, processed in a variety of TT methods, shows that the maximum absorptance is observed for the samples treated with the combined method: in the electrolyte plasma at 45 V, current density 0.13-1.3 A/cm^2 for 22 min followed by TT in coating with amorphous B and Al powder at 1223 K, for 3 hours (Fig.3, a).



a b

Fig. 3 Absorptance of Ti of VT-0 grade: a) 1 – untreated sample; 2 – TT in coating with amorphous B at 1273 K, 5 hours; 3 – EPT in B-containing medium at j = 0.13-1.3 A/cm^2, U = 25-45 V, t = 18min followed by TT in coating with amorphous B at 1223 K, 3 hours; 4 – TT in B carbide powder at 1243 K for 4-5 hours; 5 – thermo–cycling in amorphous B; b) 1 – untreated sample; 2 – EPT in B-containing medium at j = 2.3-2.7 A/cm^2, U = 240-280 V, t = 28 min; 3 – EPT in B-containing medium at j = 2-2.4 A/cm^2, U = 240-280 V, t = = 7 min.

Fig. 3, b shows the absorptance of titanium by samples treated with an aqueous solution of a boron-containing electrolyte at different current densities and treatment times. From the graphs it is seen that the absorptance for a given treatment method depends on the current density and saturation duration.

4. Conclusions

Thus, the depth of layers, hardness, and phase composition of titanium and its absorbance depend on the method of titanium treatment. As a result of research, there are observed more high-quality characteristics of titanium treated by the combined method. The production of wear-resistant coatings on titanium, which include titanium-boron and oxygen-titanium-boron-containing phases, is one of the possible ways of solving urgent problems of safety and reliability of nuclear power systems for various purposes.

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