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UDC 621.386.12+53.082

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HYDROGEN CORROSION OF TITANIUM EXPOSED TO IONIZING RADIATION

The work studies the surface of titanium alloys exposed to electron beam having the energy density of 25 J/cm^2 and the power of (3÷6) * 10^4 W/cm^2. Such treatment does not change the structure and phase state of the bulk material. Films that are formed on the surface retains the hydrogen from penetrating into the metal. Electron beam irradiation leads to the enhanced migration of hydrogen in metal and increase of microhardness of titanium surface layer. It was established that irradiation of thin plates of hydrogenated titanium by X-ray photons leads to the formation of pits accompanied by spitting of metal down to the sample destruction.

Keywords: *titanium alloys, hydrogen, strength characteristics, radiation treatment, hydrogen diffusion*

Introduction

Study of hydrogen corrosion conditioned by radiation effects occurring during irradiation of hydrogenated metals is one of the urgent research fields. Studies of the corrosion resistance of films formed on the metal surface and evolution of their microstructure are of great urgency, since they are aimed at the development of new technologies for creation of coatings with specific corrosion properties and characteristics.

It should be noted that the hydrogen diffusion effects accompanying the irradiation process significantly change such films' properties. Exposure to high-intensity beams [1, 2] causes the improvement of performance characteristics of metals such as wear resistance, fatigue resistance under continuous cycle loads, corrosion and erosion resistance. Metal rapidly heated by pulsed beams and cooled afterwards suffers the significant alteration of structure and phase state of sub-surface layers, as well as modification of structure-dependent properties of materials [3, 4]. The effects of the exposure are identifiable both in irradiated and non-exposed areas (the long-range effects are caused by occurrence of elastic waves having the reach exceeding that of the beam particles by several orders). Pulsed electron irradiation (PEI) of low energy still can cause the modification of structure and phase state of materials [5,6]. A large number of works cover different methods for creation of protective coatings [1-3]. Study of hydrogen corrosion conditioned by radiation effects occurring during irradiation of hydrogenated metals is one of the urgent area of research in the field of materials' corrosion. Radiation exposure is accompanied by the formation of surface films having the composition different from that of the material itself, which is conditioned by the diffusion processes occurring in them. Studies of the corrosion resistance of such films and evolution of their microstructure are of great urgency, since they are aimed at the development of new technologies for creation of coatings with specific corrosion properties and characteristics. The study is aimed at investigation of protective coatings formed under irradiation of titanium alloys.

Introduction. Statement of problem

Currently, titanium alloys are the most promising materials in such vital social spheres as medicine, airspace, chemical and nuclear power engineering. Significant improvement of strength characteristics of such alloys can be achieved by formation of nano and submicrocrystalline structures in them, enhancement of their composition, creation of corrosion-resistant coatings, that particularly allow augmentation of the material's resistance to hydrogen embrittlement with the use of various treatment methods such as irradiation by electron and ion beams, plasma treatment, reversible doping by hydrogen [2, 4, 5]. Structure modification shall significantly improve the hydrogen corrosion resistance and drop the hydrogen concentration that corresponds to the transition of the material into brittle state leading to its

destruction. Hydrogen absorbed by products forms brittle hydride phase and dramatically deteriorates the mechanical properties of structural materials [3]. Elimination of material hydrogenation is impossible due to manufacturing and operation technical conditions, i.e. significant content of hydrogen in atmosphere and water medium [4]. Thus, the future of titanium alloys application depends in many respects on their hydrogen embrittlement resistance. E.g., the speed of hydrogen absorption by polycrystalline titanium and its alloys increases with the reduction of crystal grain dimensions, while the surface decreased roughness ensures the improved protection. Identification of such "compound" properties makes the study of hydrogen embrittlement influence on physical and mechanical properties of protective coatings for titanium alloys urgent.

Study materials and methods

The study employed rectangular titanium grade VT-01 samples with the dimensions of 50 x 50 mm and the thickness varying from 0.7 to 10 mm. The irradiation of samples was performed with the use of X-ray photons, continuous and pulsed electron beams (PEB). Treatment of samples was both single and double-sided with the energy densities varying from 12 to 25 J/cm^2. Electron current density was varying from 10 to 50 A/cm^2, electron energy was 18 keV, pulse duration was 50 μs [7]. During the continuous electron irradiation the electron energy reached 30 keV with the current density of 2 μA/cm$_2$. In the case of X-ray irradiation, the samples were treated in air with the use of X-ray system (voltage U = 120 kV, current = 5 mA, tungsten cathode) with the dose value reaching 5×10^4 rad. The study of thermal-stimulated hydrogen egress was performed by placing each of hydrogenated samples into a vacuuming cell. Hydrogen egress from titanium was monitored by time-of-flight mass spectrometer that allows continuous monitoring of the current of mass-spectrum lines. Electrolytic hydrogenation of titanium samples was performed using the Sievert's method [8].

Results

Thickness of the layer affected by the corrosion caused by X-ray photons irradiation increases with the thickness of oxide layer, radiation dose and energy. Furthermore, the hydrogenated titanium with an oxide layer demonstrates egress of hydrogen both from the irradiated and opposite side. This indicates that the energy transfer from electrons and X-ray photons occurs under excitation of the whole hydrogen subsystem of the titanium sample. Corrosion effects evolve in a such way that the irradiation in studied conditions does not lead to the generation of protective films. However, it is worth-mentioning that the surface of studied samples demonstrates removal of organic impurities. The increase of electron energy leads to melting of surface, which in turn causes decreased roughness and increased strength of the material's surface layer. Electron-beam treatment leads to the high-speed melting (10^8–10^{10} K/s) and a consequent crystallization of the surface layer with the thickness of 2–5 μm. In the result of rapid crystallization (about 10^7 K/s) the surface gets a specular gloss. After irradiation, the boundaries of crystal grains are revealed on the surface, size of the grains varying from 2 to 10 μm. The grains comprise irregular folded conformations with acicular structures. The grains are evenly distributed along the surface of alloy. For the irradiation dose value of 15 J/cm^2 the surface includes grains with dimensions up to 2 μm. Increment of the irradiation dose increases the size of grains. E.g. for the dose of 20 J/cm^2 there are no grains with the size less than 5 μm. Increase of the beam energy density (15-24 J/cm^2) leads to gradual increase of the height and span of folds on the sample's surface. Folded relief is non-uniform: there are grains (grain agglomerates) that have no folding. Alongside the large folds, smaller folded structures reveal. PEB irradiation of titanium leads to the sharp drop of material's electron density, which is caused by the formation of surface microstructure and internal stresses that occur in the case of pulsed heating and rapid cooling of titanium alloy. Increase of introduced energy up to 20 J/cm^2 causes the strengthening of material's surface layer in comparison with the initial state. This effect increases the surface roughness and raises the hydrogen absorption during hydrogenation [1].

The surface of titanium irradiated by X-rays demonstrates formation of ragged-edge pores and pits with the dimensions of 10 μm and the evidence of metal spitting (fig. 1). This testifies the presence of accelerated diffusion and egress of hydrogen from the irradiated material.

Irradiation of hydrogenated titanium alloy was performed by narrow continuous beam having the energy of 20 keV and the current of 50 μA, which lead to the intensification of hydrogen diffusion [9]. In such conditions X-ray irradiation with the same energy leads to destruction of titanium, if its thickness is less than 1 mm.

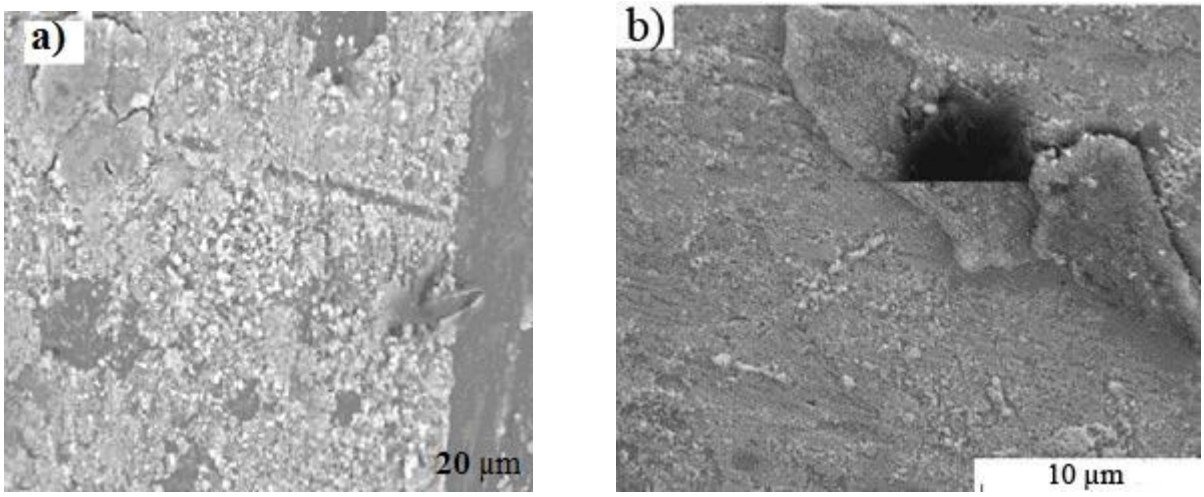

Fig. 1. Images of Ti/TiO_2 samples' surface acquired by electron microscopy: a) initial sample; b) pit of titanium surface with dimensions of 10-12 μm.

The speed of hydrogen absorption depends not only on the hydrogenation temperature, but also on the surface roughness, doping additives composition, etc. Electron-beam treatment increases both the area of commercial titanium samples' surface and the density of defects in a modified surface layer. Increase of the number of defects (primarily, vacancies) facilitates movement of atoms in a solid body and leads to increased diffusion coefficient. It is well-known that the hydrogen solubility in nanocrystalline materials is higher, than for polycrystalline samples of the same composition, which is due to increased proportion of crystal grain boundaries [10, 11]. In addition, the diffusion coefficient in systems with nanocrystalline composition is highly-dependent on the hydrogen concentration and pressure of hydrogenation.

At low hydrogen pressure in Sievert's chamber (0.6 atm) the rate of absorption for initial titanium is significantly lower, than for nanostructured one, which conditions the high resulting concentration of hydrogen in irradiated samples. Electron beam treatment with the energy density of 18 J/cm^2 leads to decrease of hydrogen amount in commercial titanium grade VT1-0. At the same time, its hydrogen sorption capability grows [7]. Hydrogenation at the pressure of 0.6 atm and the temperature of 300° C leads to increased hydrogen content in nanostructured VT1-0 samples more than 40-fold. At the hydrogenation temperature of 650° C after preliminary surface nanostructurization, the hydrogen content in VT1-0 samples increases about 600-fold, while for the untreated material it is only 20-fold. Under intense hydrogenation (for 180 minutes, 2 atm, 550 and 600° C) the resulting concentration of hydrogen in the initial and nanostructured material becomes the same. In the case of pressure increased up to 2 atm the thin nanostructured layer stops playing the core role for the hydrogen flow that penetrates into a metal. The VT1-0 samples exposed to surface nanostructurization and subsequent hydrogenation with the increase of hydrogen content up to 165 ppm after 30 minutes of hydrogenation at the temperature of 300° C and the pressure of 0.6 atm do not suffer the generation of a hydride phase. Increment of hydrogen concentration higher than 610 ppm leads to formation of laminar titanium hydride in the sample's bulk metal [7].

However, electrolytic saturation of titanium samples in 1M H_2SO_4 during the period from 4 to 20 hours with the current of 10 mA leads to the formation of hydrogenous TiH_2 and $TiH_{1.5}$ phases of titanium. Amount of hydrogen introduced into titanium increases proportionally with the time of saturation and electrolysis current density varying from 50 to 2000 mA/cm^2.

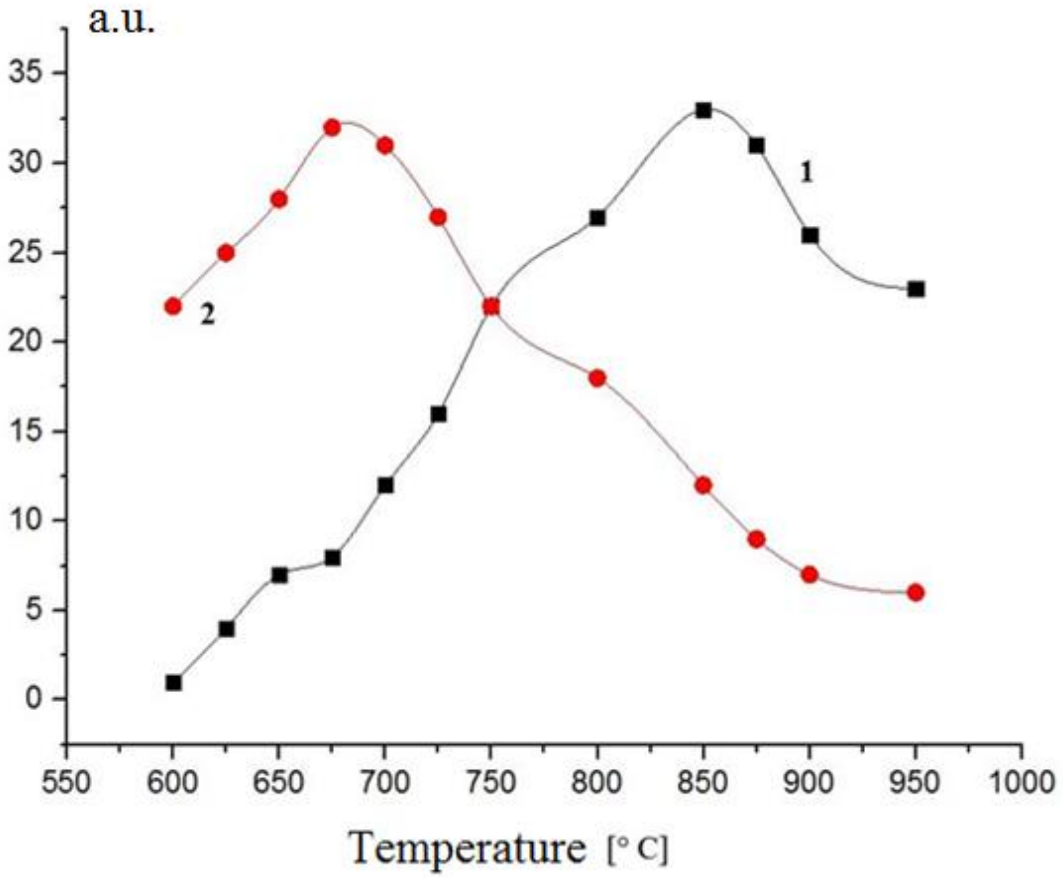

Fig. 2. Thermally induced egress of hydrogen (in arbitrary units) from titanium samples during linear heating with the rate of 0.4 K/s under irradiation by electron beam (E = 20 keV, I = 50 μA): 1 - sample treated by pulsed beam; 2 - electrolytically saturated.

Increase of the temperature up to 600° C leads to the total destruction of titanium dihydride [12]. In this connection, the study covered hydrogen egress from titanium treated by PEB under linear heating and simultaneous irradiation by electron beam (fig. 2). It was taken into account that heating to 200° C leads to complete dissociation of all hydride phases in titanium, in the case the hydrogenation was performed electrolytically. Apparently, the peculiarity of the method lies in the fact that hydrogen subsystem formation is complemented by formation and preservation of the submicrocrystalline and grain-subgrain structures of titanium, i.e. in most cases, hydrogen ingress and egress is accompanied by the creation of the aforesaid structures. Titanium alloy suffer the formation of nanostructured and submicrocrystalline structures with the dimensions of grain-subgrain structure of about 200 nm. Uniqueness of the physical and mechanical properties is conditioned by small size of a grain (10-500 nm) and large span of internal interface regions, i.e. crystal grain boundaries. Excitation of hydrogen by vacuum heating in the temperature range of 873-973 K causes recrystallization and growth of crystal grains in metals with submicrocrystalline structure, grains having the dimensions of 0.5-1 μm. This causes a nonresonant thermal dissipation of hydrogen. Irradiation of metals by electron beams (with

energies of dozens of keV and current densities not exceeding 100 mA/cm^2 results in a significant shift to low-temperature region of the largest value on the plot representing the dependence of hydrogen egress intensity from metals on temperature in comparison to conventional heating of samples [13]. For instance, the maximum intensity of outgassing during the linear heating of VT1-0 titanium without electron beam exposure corresponds to the temperature of 700° C, without beam exposure the temperature is 300° C. Thus, selection of ionization radiation beam parameters can enable excitation of hydrogen subsystem in metal, while preserving its structure and elimination of hydrogen-corrosion effects.

Conclusion

The surface of titanium alloys treated by electron beam (PEB) having the energy density of 25 J/cm^2 and the power of (3÷6) 10^4 W/cm^2 comprises films that inhibit penetration of hydrogen into bulk metal and eliminate corrosion of a material. Titanium hydride that is formed during the hydrogenation is easily decomposed by heating to 230° C (for electrolytic saturation). This changes the structure and phase state of the bulk material. However, implementation of PEB does not change the structure and phase state even in the presence of titanium hydrides. It was demonstrated that electron beam irradiation leads to the enhanced migration of hydrogen in metal and increase of microhardness of titanium surface layer. Irradiation of titanium by X-ray photons leads to the formation of pits with spitting of metal and destruction of hydrogenated titanium sample having the thickness of 1 mm.

The study was performed with the financial support of State program entitled as “Nauka” in the frame of research project No. 1524, subject 0.1325. 2014

Authors are grateful to Professor A.V. Panin for provision of titanium samples that were used for analysis and for the fruitful discussion of the obtained results.

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