

# PROTECTION OF TITANIUM AGAINST HYDROGEN EMBRITTLEMENT

## ЗАЩИТА ТИТАНА ОТ ВОДОРОДНОЙ ХРУПКОСТИ

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**Abstract:** *The protective coatings of  $Al_2O_3$  and AlN on iodide titanium in initial state and after annealing in a hydrogen atmosphere were investigated by scanning electron microscopy. It was found that the coatings protect titanium from the interaction with hydrogen at a pressure of 0.6 MPa up to 650 °C. It was shown that at 700 °C and pressure 0.6 MPa cracking of the protective coatings occurred, and the process of active absorption of hydrogen started.*

**KEYWORDS:** IODIDE TITANIUM, COATING, OXIDE, NITRIDE, EMBRITTLEMENT, SORPTION, HYDROGEN CAPACITY.

### 1. Introduction

The nature of the hydrogen embrittlement of metals is determined by the content of hydrogen, the interaction of metals and alloys with hydrogen, the state of hydrogen in the metal, the magnitude of applied stresses (external or internal), and the scheme of the stressed state. Hydrogen can affect the initiation and propagation of cracks, or both these stages of fracture. This variety of factors leads to the absence of a single mechanism of hydrogen embrittlement of metals, and even for the same material the existing mechanism of hydrogen embrittlement can alter with the change of the above factors [1].

According to the authors of [2,3], the degradation of the physical and mechanical properties of metals in the presence of hydrogen is a complex process. In their analysis of hydrogen embrittlement, they propose to distinguish between primary and secondary factors. The primary factors include hydrogen sources, the processes of transporting hydrogen atoms from the source to the surface of material, their adsorption, absorption and diffusion into the bulk of metal, where they then contribute to the formation of hydrides, decohesion, interaction of hydrogen atoms with dislocations. The secondary factors include various impurities, surface hydrides and oxide films, the magnitude of stress [4].

In [5] the feasibility of separating the direct and indirect effects of hydrogen with respect to titanium and its alloys was substantiated. The direct effect of hydrogen is manifested in its direct effect on the mechanisms of initiation and propagation of cracks, and the indirect effect is related to the structural changes caused by hydrogen (change in the type of structure, size and morphology of the phases). In the cases where titanium or its alloys are in the atmosphere of hydrogen-containing gases during operation or manufacture of semi-finished products, certain measures should be taken to prevent the penetration of hydrogen into the bulk material. In this case, possible ways of combating hydrogen embrittlement may be: (i) protective coatings; (ii) alloying with aim to reduce the rate of interaction of the metal with the hydrogen-containing atmosphere and to increase the maximum acceptable concentrations of hydrogen; (iii) regular vacuum annealing of the products.

Protective coatings are widely used in industry, and their use gives great economic effect. The methods of their application are very diverse: electrolytic deposition of metals and alloys, vacuum evaporation with subsequent condensation on the cathode substrate, gas transport method, ion implantation, chemical-thermal treatment, etc. The compositions of protective coatings are also very diverse: oxides, borides, nitrides, carbides, silicides [6,7].

Thin films of aluminum oxide are widely used as protective barrier layers to reduce the permeability of hydrogen due to their excellent properties, especially in terms of chemical, thermal, abrasion and corrosion resistance. According to the results of studies carried out in [8], it was found that the hydrogen permeability through the  $Al_2O_3$  film with a thickness of ~ 500 nm under hydrogen pressure within 2-50 kPa and at 1200-1450 °C was two orders of magnitude lower than that for uncoated metals (vanadium, niobium, molybdenum, and uranium).

In [9,10] it was concluded that  $Al_2O_3$  film is a good barrier against hydrogen penetration into metal, especially during operation under low pressures. It was shown that, regardless of the method of application of film, the coating thickness above ~ 40  $\mu$ m did not further affect the permeability of hydrogen and the protective properties of  $Al_2O_3$  film.

However, in [11] it was determined that the protective film prevented the penetration of hydrogen into titanium when the holding time of the  $Al_2O_3$  / Ti system in a hydrogen atmosphere did not exceed 3 hours at 400°C and a pressure of 0.2 MPa, and after 4 hours there was a sharp increase in the amount of hydrogen absorbed. This was explained by the fact that the coefficients of thermal expansion of metals and the coating are very different. This leads to the development of high thermal stresses in the coating, which results to the formation of defects and cracks, as well as to delamination, and consequently to a decrease in the resistance to hydrogen penetration.

Thus, we consider it appropriate to establish the protective characteristics of coatings  $Al_2O_3$  and AlN on iodide titanium under more severe operating conditions (hydrogen pressure of 0.6 MPa and temperature above 600°C).

### 2. Materials and methods

The samples were fabricated from iodide titanium (99.95%) which was melted in a laboratory electric arc furnace with a non-consumable tungsten electrode in a cooled copper crucible by a six-fold melting in a purified argon atmosphere. After melting the samples were annealed in a vacuum of  $1.3 \times 10^{-2}$  Pa at 1100 °C for 15 h, then they were ground to obtain a cubic shape with an edge size of 10 mm.

The protective coatings were applied in a hybrid helicon-arc ion-plasma reactor using an aluminum cathode at the arc current  $I_d = 40$  A, the reaction time 10 minutes, and the gas pressure (oxygen or nitrogen) in the reactor 2.7 Pa. The coatings were applied in several stages, to protect all sides of the cubic samples.

Metallographic examinations were performed with a scanning electron microscope VEGA3 TESCAN equipped with EDX detector XFlash610M (Bruker).

The interaction of the metal with hydrogen was studied by the Sieverts method at IVGM-2M unit [12] at room temperature and upon heating at a rate of  $0.125^{\circ}\text{C/s}$  and isothermal holding at  $T = 700^{\circ}\text{C}$  and absolute pressure  $\sim 0.6\text{ MPa}$ . The amount of hydrogen absorbed was calculated from the change in pressure in a closed volume, and was determined by weighing samples on VLR 20 scales with an accuracy of  $1.5 \times 10^{-5}\text{ g}$ .

### 3. Results and discussion

After plasma sputtering the  $\text{Al}_2\text{O}_3$  and AlN films comprised of  $\sim 40\%$  Al,  $\sim 58\%$  O,  $\sim 1.5\%$  Ti and  $\sim 52\%$  Al  $\sim 12\%$  O,  $\sim 35\%$  N,  $1.4\%$  Ti, respectively (Fig. 1).

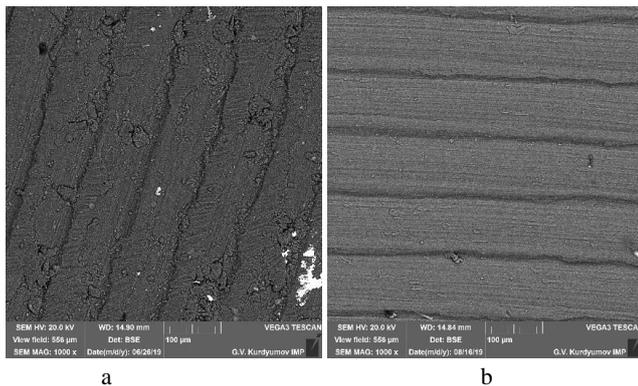


Fig. 1. Surface layer after plasma sputtering of  $\text{Al}_2\text{O}_3$  (a) and AlN (b) on titanium.

The temperature and pressure conditions of the hydrogenation processes were chosen to be much more severe than the conditions under which titanium and its alloys are usually operated. The temperature of isothermal holding ( $450^{\circ}\text{C}$ ) exceeds the temperature of the beginning of active hydrogenation of the material unprotected by coating.

The hydrogenation of the uncoated sample (iodide titanium) was carried out only to a concentration of  $1.7\text{ wt.}\%$  ( $\sim 45\text{ at.}\%$ ), which at the hydrogenation temperature of  $450 \pm 10^{\circ}\text{C}$  corresponded to the formation of  $\beta$ -phase, and at room temperature  $\alpha_s + \gamma$  state, where  $\alpha_s$  is saturated solid solution in  $\alpha$ -Ti, and  $\gamma$ -titanium dihydride with HCC lattice. The limitation of hydrogenation to a given concentration which was achieved approximately in 3.5 h. (Fig. 2) ensured the integrity of the sample.

For the coated samples the temperature of  $450^{\circ}\text{C}$  was insufficient to provoke the initiation of the hydrogenation process. Therefore, the heating was continued, and hydrogen absorption was registered at  $700^{\circ}\text{C}$ . The temperatures of the onset of active absorption of hydrogen by an uncoated sample and the samples with the applied protective coatings are shown in Fig. 3.

The analysis of the influence of coatings on the processes of hydrogen absorption by bulk material should be considered from two positions: the hydrogen permeability of surface film and the catalytic influence of the surface on the processes of hydrogen dissociation.

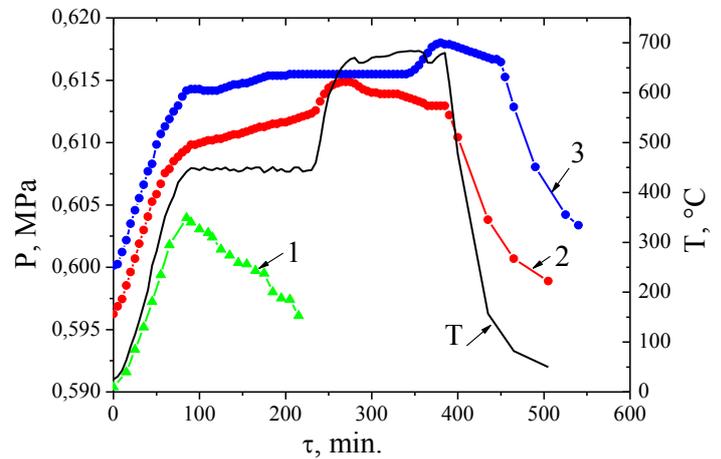


Fig. 2. Change of hydrogen pressure in a closed volume during hydrogenation of the samples: 1 – initial (iodide titanium); 2 – with  $\text{Al}_2\text{O}_3$  surface film; 3 – with AlN surface film.

Metallic materials absorb hydrogen only in atomic state which forms in its own (hydrogen) environment starting from  $1700^{\circ}\text{C}$ . On the metal surface hydrogen dissociates at lower temperatures. The temperature at which hydrogen dissociation begins is determined by the catalytic capacity of the surface, which can be estimated by the duration of incubation period at isothermal holding in hydrogen or by the onset of active absorption of hydrogen upon heating. In our case, the catalytic ability of the surface was evaluated by the temperature of onset of active absorption of hydrogen during heating (Fig. 3), from which it follows that the highest catalytic ability is inherent to the surface of initial (uncoated) sample. Plasma sputtering led to a decrease in the catalytic capacity, the value of which depended on the chemical composition of coating. The values of reduction of the surface catalytic ability can be arranged as follows: Ti (iodide)  $\rightarrow$  Ti, ( $\text{Al}_2\text{O}_3$ )  $\rightarrow$  Ti, (AlN).

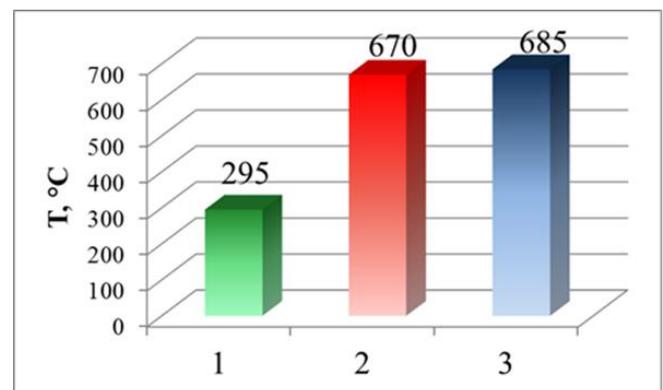
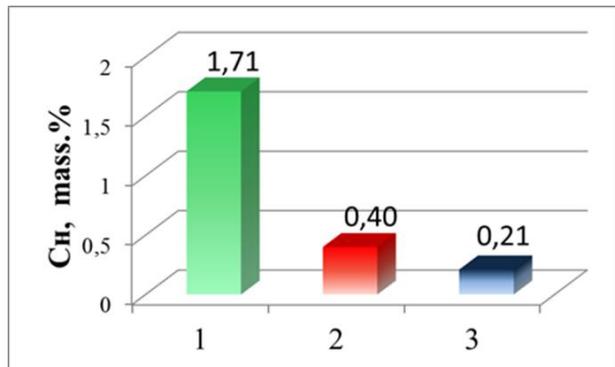


Fig. 3. Temperatures of the beginning of active absorption of hydrogen by samples: 1 – initial state (uncoated iodide titanium); 2 – coated by  $\text{Al}_2\text{O}_3$ ; 3 – coated by AlN.

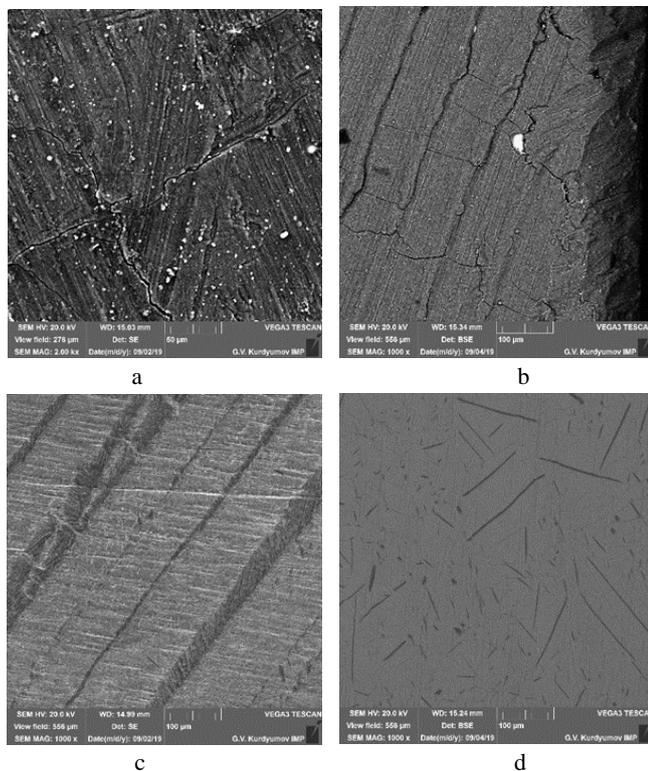
Hydrogen permeability is characterized by the degree of damage of protective layer in the process of active hydrogenation, and the amount of hydrogen absorbed (Fig. 4). Based on the values of  $C_H$ , the degree of permeability of surface can be arranged by analogy with a decrease in catalytic capacity of the samples.



**Fig. 4.** Concentration of absorbed hydrogen in samples: 1 – initial (uncoated iodide titanium); 2 – coated by  $\text{Al}_2\text{O}_3$ ; 3 – coated by AlN.

Analysis of the structures of surfaces of the samples after exposure at  $700^\circ\text{C}$  for 2 hours in an aggressive hydrogen medium indicates that they absorbed significant amount of hydrogen. However, under such conditions it was not possible to avoid the damage of protective films, and for the  $\text{Al}_2\text{O}_3$  coating it was much more significant than for AlN (Figs. 5a, b), which is also determined by the amount of hydrogen absorbed.

The structures of bulk material after hydrogenation (Figs. 5c, d) confirm that hydride forms in titanium in the process of hydrogen absorption. Hydride precipitates in the form of plates oriented along certain crystallographic directions within grains or along grain boundaries. The nature of hydride precipitation depends on the initial state of surface, the grain size, and the content of hydrogen. With increasing hydrogen content, the volume of compact precipitates along grain boundaries is increasing.



**Fig. 5.** Surface and volume structure of samples coated with  $\text{Al}_2\text{O}_3$  (a,c) and AlN (b,d) after hydrogenation.

#### 4. Conclusions

1. Plasma sputtering of  $\text{Al}_2\text{O}_3$  and AlN leads to a decrease in both the permeability of surface and its catalytic ability, the value of which depends on the chemical composition of the protective coating. The values of permeability and catalytic capacity reduce in the following range: Ti (uncoated iodide titanium)  $\rightarrow$  Ti, ( $\text{Al}_2\text{O}_3$ )  $\rightarrow$  Ti, (AlN).
2. When covered by  $\text{Al}_2\text{O}_3$  or AlN coating deposited by plasma spraying, titanium is able to withstand aggressive hydrogen media at  $700^\circ\text{C}$  and pressure of 0.6 MPa.

#### 5. References

1. C.D. Beachem, New model for hydrogen assisted cracking (hydrogen embrittlement). *Metall. Trans. A*, **3**: 1972, p. 437-451.
2. H.G. Nelson, Hydrogen embrittlement. *Treatise on Materials Science and Technology*, **25**: 1983, p. 275-359.  
<https://doi.org/10.1016/B978-0-12-341825-8.50014-3>
3. J. P. Hirth, Effects of hydrogen on the properties of iron and steel *Metall. Trans. A*, **11A**: 1980, p. 861-890.  
<https://doi.org/10.1007/BF02654700>
4. N.N. Sergeev, A.N. Sergeev, S.N. Kutepov, A.E. Gvozdev, E.V. Ageev, Analysis of theoretical concepts on the mechanisms of hydrogen cracking of metals and alloys *Izvestiya Yugo-Zapadnogo gosudarstvennogo universiteta*, **21**, No.3: 2017, p. 6-33 (in Russian).  
<https://doi.org/10.21869/2223-1560-2017-21-3-6-33>
5. P. Cotterill, Hydrogen embrittlement of metals. Moscow, Metallurgizdat., 1963, 117 p. (in Russian).
6. B.A. Kolachev, Hydrogen embrittlement of metals. Moscow, Metallurgizdat., 1985. 216 p. (in Russian).
7. A. Iulianelli, T. Longo, S. Liguori, P.K. Seelam, R.L. Keiski, A. Basile, Oxidative steam reforming of ethanol over Ru- $\text{Al}_2\text{O}_3$  catalyst in a dense Pd-Ag membrane reactor to produce hydrogen for PEM fuel cells. *Int. J. Hydrogen Energy*, **34**, No.21: 2009, p. 8958-8963.  
<https://doi.org/10.1016/j.ijhydene.2009.07.063>
8. A.V. Gapontsev, V.V. Kondratiev, Hydrogen diffusion in disordered metals and alloys *Physics-Uspexhi*, **173**, No.10: 2003, p. 1107-1129.  
<http://dx.doi.org/10.1070/PU2003v046n10ABEH001660>
9. K.S. Forcey, D.K. Ross, C.H. Wu, The formation of hydrogen permeation barriers on steels by aluminizing. *J. Nucl. Mater.* **182**: 1991, p. 36-51.  
[https://doi.org/10.1016/0022-3115\(91\)90413-2](https://doi.org/10.1016/0022-3115(91)90413-2)
10. E. Serra, H. Glasbrenner, A. Perujo, Hot-dip aluminium deposit as a permeation barrier for MANET steel. *Fusion Eng. Des.*, **41**, No.1-4: 1998, p. 149-155.  
[https://doi.org/10.1016/S0920-3796\(98\)00224-5](https://doi.org/10.1016/S0920-3796(98)00224-5)
11. A. Perujo, K.S. Forcey, T. Sample, Reduction of deuterium permeation through DIN 1.4914 stainless steel (MANET) by plasma-spray deposited aluminum. *J. Nucl. Mater.* **207**: 1993, p. 86-91.  
[https://doi.org/10.1016/0022-3115\(93\)90249-X](https://doi.org/10.1016/0022-3115(93)90249-X)
12. G.F. Kobzenko, A.A. Shkola, Reactor for the studying of metal-gas reaction *Materials diagnostics*, **56**: 1990, p. 41-45 (in Russian).