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Complex Approach to Protecting Titanium Constructions from Hydrogen Embrittlement

T. V. Pryadko, V. A. Dekhtyarenko, V. I. Bondarchuk,
M. A. Vasilyev, and S. M. Voloshko*

*G. V. Kurdyumov Institute for Metal Physics, N.A.S. of Ukraine,
36 Academician Vernadsky Blvd.,
UA-03142 Kyiv, Ukraine*
**National Technical University of Ukraine
'Igor Sikorsky Kyiv Polytechnic Institute',
37 Peremohy Ave.,
UA-03056 Kyiv, Ukraine*

The research is aimed at studying the complex effect of alloying and protective coating on the resistance of titanium to embrittlement in a hydrogen environment. When determining the alloying complex, elements are selected that reduce the rate of interaction of titanium with the hydrogen-containing medium and increase the maximum allowable hydrogen concentrations. The AlN coating applied by helicon-arc ion-plasma sputtering is chosen as the barrier layer. The dynamics of hydrogen accumulation is studied by the Sievers' method in the mode of heating and isothermal exposure at hydrogen pressure of 0.6 MPa and temperature of $(700 \pm 10)^\circ\text{C}$. As proved, the proposed protective coating has a high resistance in aggressive hydrogen environments at temperatures up to 700°C , significantly reduces the catalytic ability of the surface, and has an order of magnitude lower permeability to hydrogen. Additional doping with aluminium and molybdenum further reduces the amount of absorbed hydrogen by 30%.

Key words: titanium, hydrogen embrittlement, alloying, protective coating, catalytic ability, surface layer permeability.

Дослідження спрямовано на вивчення комплексного впливу легування та

Corresponding author: Volodymyr Anatoliyovych Dekhtyarenko
E-mail: Devova@i.ua

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захисного покриття на стійкість титану до окрихчування у водневому середовищі. При визначенні легувального комплексу обрано елементи, що зменшують швидкість взаємодії титану з водневмісним середовищем та підвищують максимально допустимі концентрації Гідрогену. В якості бар'єрного шару обрано покриття AlN, нанесене методом гелікон-дугового йоно-плазмового напорошення. Динаміку накопичення Гідрогену вивчали за методом Сівертса у режимі нагрівання та ізотермічної витримки за тиску водню 0,6 МПа і температури $(700 \pm 10)^\circ\text{C}$. Доведено, що запропоноване захисне покриття має високу стійкість в агресивному водневому середовищі за температур до 700°C , у значній мірі знижує каталітичну здатність поверхні та має на порядок нижчу проникність для Гідрогену. Додаткове легування Алюмінієм та Молібденом знижує кількість сорбованого Гідрогену додатково на 30%.

Ключові слова: титан, воднєве окрихчування, легування, захисне покриття, каталітична здатність, проникність поверхневого шару.

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1. INTRODUCTION

The main condition for the brittle fracture of a solid under the influence of hydrogen is the absorption of the gas to concentrations that cause significant changes in volume and, as a consequence, the emergence of internal stresses locally exceeding the stresses required for the destruction of the material. When titanium or Ti-based alloys operate in an hydrogen-containing environment, measures should be taken to prevent the penetration of hydrogen into the volume of the material.

One of the ways to combat the hydrogen brittleness of titanium and its alloys is to prevent hydrogenation during technological processes. This is not always possible, especially for alloys highly prone to hydrogen embrittlement [1, 2]. In [3] it is shown that when a titanium part is in a hydrogen-containing medium, microcracks and craters up to 10 μm in size appear on its surface in two hours.

In order to evaluate the likelihood of hydrogen embrittlement of titanium and its alloys in certain cases, one needs to know the minimum concentrations of hydrogen that lead to destruction of the material. Currently, the maximum allowable concentrations of hydrogen have been set for most industrial alloys [4, 5]. If the hydrogen content in semi-finished and finished products exceeds the maximum allowable values, it can be removed by vacuum annealing, but it is a long and costly operation. Also, hydrogen embrittlement can be avoided by reducing the design stresses to a level below which it does not develop, but this is hardly an appropriate way, as it leads to an increase in the weight of parts. The latter is clearly unacceptable for aircraft and missiles.

The penetration of hydrogen into metals is limited by processes oc-

curing on the surface (in the near-surface region), and the intensity of these processes is determined by the catalytic ability of the surface and its 'transparency' for the diffusion of hydrogen into the bulk material. In this case, possible ways to combat hydrogen embrittlement may be deposition of protective coatings that prevent hydrogenation. This approach is widely used in industry, and the use of protective coatings has a great economic effect. They are produced by various techniques: electrolytic deposition of metals and alloys, vacuum evaporation with subsequent condensation on the cathode substrate, the method of gas transport reactions, ion implantation, chemical-thermal treatment, etc. The composition of coatings is also very diverse: oxides, borides, nitrides, carbides, silicides [6–12]. Besides, many researchers are inclined to believe that it is more promising not to apply a certain coating, but to modify the surface, for example, using a pulsed carbon ion accelerator [13], or by means of high-energy methods, namely laser irradiation in various gas environments [14].

Another way to combat the hydrogen brittleness of titanium is alloying which reduces the rate of interaction of the metal with the hydrogen-containing medium and increases the maximum allowable concentrations of hydrogen. For titanium, the protective alloying elements are Al, Fe, Mo, Ni [1]. In particular, aluminium increases the solubility of hydrogen in the α -phase and complicates the formation of hydride phase. Therefore, increasing the aluminium content in α -Ti is an effective way to reduce its susceptibility to hydrogen embrittlement. Hydride embrittlement in pure titanium develops when the hydrogen content exceeds 0.01% wt., and in the alloy BT5 (Ti + 5% Al)—0.035% wt. [15].

Thus, to reduce the risk of hydrogen damage of constructions, it is necessary to deepen the knowledge of the dynamics of hydrogen accumulation. Our research is aimed at studying the complex effect of alloying and protective coating on the resistance of titanium to embrittlement in a hydrogen environment.

2. EXPERIMENTAL DETAILS

To solve these problems, samples of cubic shape with a rib size of 10 mm are made from molten iodide titanium (Ti-I (TY48-4-282-72), purity 99.95) and alloy Ti + 6.69% Al + 0.81% Mo. These alloying elements are chosen basing on the following considerations: they are often part of titanium alloys, under the conditions of research they almost do not interact with hydrogen; they increase the maximum allowable concentrations of hydrogen.

AlN coating is chosen as a barrier layer basing on the information that aluminium nitride is stable in an atmosphere of hydrogen and carbon dioxide up to 980°C, and the applied coating leads to a decrease in

the rate of hydrogen absorption by BT6 alloy from $4.3 \cdot 10^{-5}\%$ wt./min to $1.5 \cdot 10^{-5}\%$ wt./min [16].

The deposition of a layer of aluminium nitride on the investigated samples in a hybrid helicon arc ion-plasma reactor provided pre-cleaning of the sample surface for 15 minutes with a high-energy helicon discharge with a power of 430 W from all unwanted inclusions that can interfere adhesion. Then the ion-plasma component of the cathode material is transferred to the surface of the sample in an atmosphere of nitrogen (at a pressure of $2.7 \cdot 10^{-6}$ MPa) with the help of a plasma-arc accelerator. To achieve uniform application of the aluminium nitride film, the sample is rotated in horizontal plane. The deposition time is 10 minutes. After deposition the sample is cooled in a chamber in a nitrogen atmosphere.

For layer-by-layer analysis, the method of mass spectrometry of secondary ions is used [17]. The current of single-charged positive secondary ions of the corresponding isotopes of chemical elements (including hydrogen) is measured at a mass spectrometer MS-7201M. The targets are bombarded by Ar^+ ions with an energy of 4 keV in a wide range of irradiation doses ($D = 10^{14} - 10^{19}$ ions·cm⁻²), ion gun discharge current is 0.3 mA, the current of the primary beam on the target is 10 μA (current density 1.5 $\mu\text{A}/\text{mm}^2$). The initial pressure in the working chamber of the spectrometer is $P = 2.5 \cdot 10^{-6}$ Pa. The registration of mass spectra and processing of the results are performed using SpectrumRecorder software (ver. 1.7). The intensity of the secondary ions is registered and is given below in pulses. The average scan rate of the mass spectra is 50 sps/min. After spattering of the primary oxide film from the target surface, the intensities of the secondary ions of all isotopes reached stable values which are used for further analysis of the physicochemical state of the target surface.

Metallographic examinations are performed with a scanning electron microscope VEGA3 TESCAN equipped with an EDX detector XFlash610M (Bruker). The interaction of the metal with hydrogen is studied by the Sieverts' method at IVGM-2M unit [18] at room temperature and upon heating at a rate of 0.125°C/s and isothermal holding at $T = 700^\circ\text{C}$ and absolute pressure ~ 0.6 MPa. The amount of hydrogen absorbed is calculated from the change in pressure in a closed volume, and is determined by weighing samples on VLR 20 scales with an accuracy of $1.5 \cdot 10^{-5}$ g.

3. RESULTS AND DISCUSSION

A protective layer of AlN with a thickness of ~ 2 μm is applied to all faces of a cubic sample, which allowed to completely protect the volume of the sample from direct contact with the hydrogen medium. According to the energy-disperse analysis after spattering, a protective film

formed on the surface of titanium; the chemical composition of this film is given in Table 1, and its appearance is shown in Fig. 1. The chemical compositions of the layer of aluminium nitride deposited on different substrates are comparable; the difference is in a slightly higher oxygen content and lower titanium content in our case.

To ensure a reasonable time for the experiment, the temperature–pressure conditions of the hydrogenation processes are chosen to be much more severe than the conditions under which titanium and titanium-based alloys are usually used.

The hydrogenation of initial samples is performed only up to a concentration of 1.7% wt. (~45 at.%)—at the hydrogenation temperature of $(450 \pm 10)^\circ\text{C}$ it corresponds to the β -phase field, and at room temperature to $\alpha_p + \gamma$ state, where α_p is supersaturated solid solution in α -Ti, and γ is titanium dihydride with f.c.c. structure. Limiting the absorption process to this concentration (it is enough ~3.5 hours to achieve it, Fig. 2) ensured the integrity of the samples.

For samples with a protective coating, a temperature of 450°C and

TABLE 1. Chemical composition of coatings applied to titanium and its alloy.

Basis	Chemical composition, at. %			
	Al	O	N	Ti
Ti	~56	~7	~35	~2
Ti–Al–Mo	~54	~10	~35.5	~0.5

Fig. 1. Surface layer of AlN at magnification: $\times 150$ (a), $\times 1000$ (b).

Fig. 2. Change of hydrogen pressure in a closed volume during hydrogenation of samples: 1—original, with an AlN surface layer deposited: 2—on titanium, 3—on the alloy, 4—temperature change in the reactor [9].

exposure time 6 hours is insufficient to initiate the hydrogenation process. Therefore, the heating is continued, and at a temperature of $\sim 700^{\circ}\text{C}$, the characteristic for absorption changes of pressure with temperature in a closed volume are registered (Fig. 2).

The rate of formation of the surface hydride layer or the initial rate of hydrogen absorption (Fig. 3) is determined by the total effect of the

Fig. 3. Initial and average rates of hydrogenation of samples: 1—initial, with an AlN surface layer deposited: 2—on titanium, 3—on the alloy.

catalytic ability of the surface and the permeability of the surface layer. These processes are comparable, that indicates the same nature of the protective factors that slow down the absorption of hydrogen, regardless of the substrate used.

With a further increase in the thickness of the formed hydride, the amount of hydrogen flow through it decreases, because its concentration in this layer, reaching the maximum value for the β -phase, changes little, and the path length increases. As a result of the drop in the total hydrogen flow, there is a decrease in the absorption rate. This is fully consistent with the data presented in [2], according to which, as soon as a solid hydride layer is formed on the surface of the material, the rate of hydrogen absorption is significantly reduced and subsequently controlled by the rate of hydrogen transport through the surface hydride layer.

The catalytic ability of the surface is determined by the temperature at which the dissociation of hydrogen molecules starts. With the chosen research method, this temperature is identical to the temperature of the beginning of active hydrogen uptake when heated, which implies that the highest catalytic ability is inherent in the surface of the initial sample, while coatings significantly decrease it (Fig. 4).

The transfer of hydrogen through the barrier layers is also reduced. The amount of absorbed hydrogen by the samples with protective films after exposure at hydrogen atmosphere with pressure of 0.6 MPa for 6 hours at 450°C or 2 hours at 700°C is an order of magnitude lower than the corresponding value for the unprotected sample which is hydrogenated at much milder conditions (Fig. 5). It should also be noted that

Fig. 4. Temperatures of the beginning of active hydrogen absorption for samples: 1—initial, with an AlN surface layer deposited; 2—on titanium, 3—on the alloy [9].

Fig. 5. The concentration of absorbed hydrogen in samples: 1—initial, with an AlN surface layer deposited: 2—on titanium, 3—on the alloy [9].

the amount of hydrogen absorbed by titanium with AlN coating exceeds by 30% the same figure for the alloy Ti + 6.69% Al + 0.81% Mo with a coating of almost the same chemical composition.

The analysis of the distribution profile of the emission intensity of secondary ions in the protective layer AlN deposited on titanium and alloy (Fig. 6) allows assuming that the positive effect of alloying is manifested not only in increasing the maximum allowable hydrogen concentration, but already at the stage of the deposition of protective layer. Under the conditions of helicon arc ion-plasma deposition of aluminium nitride, as well as during heating up to 700°C in a hydrogen atmosphere, the alloying elements diffuse into the deposited layer, as

Fig. 6. The time distribution profile of intensity of emission of secondary ions in AlN protective layer deposited: on titanium (a), on the alloy (b).

evidenced by the presence of titanium. If the substrate is an alloy, then the diffusion of aluminium inhibits the diffusion of titanium.

As a result, a slight variation in the chemical composition of the protective layers leads to a significant change in the distribution of hydrogen in their volume. In the case of the Ti substrate, there is a uniform distribution of all components along the depth of the layer. When the alloy is used as substrate, the intensity of hydrogen emissions is an

Fig. 7. The structure of the surface and volume of samples with AlN surface layer deposited on titanium (*a, c*) and on alloy (*b, d*).

order of magnitude lower under the same conditions. If we assume that the emission intensity is proportional to the amount of absorbed hydrogen and the latter is sufficient for the β -phase hydride TiH_{2-x} to form on the surface, then at a depth of 80 nm (corresponding to the sputtering duration of 40 minutes) one can expect only the formation of TiN monohydride. That is, the permeability of hydrogen through the protective AlN film deposited on titanium exceeds the corresponding value for the alloy. This is explained by higher content of oxygen and lower amount of titanium which has high affinity to hydrogen.

Not the last factor determining hydrogen permeability is the degree of destruction of the protective layer in the process of active hydrogenation. Analysis of the surface structures of the samples after exposure to aggressive hydrogen environment at 700°C for 2 hours indicates a fairly high stability (Fig. 7); nevertheless, partial destruction of the protective layer occurred. This result coincides with the data [14] according to which the surfaces modified by laser radiation also destroyed under milder conditions.

Given that the hydride needles extend into the volume of the samples in the zones with damaged protective layers, the extrapolation of hydrogenation rate of the protected samples to the hydrogen concentration in the initial sample (1.7% wt.) is incorrect, and further research is required to explain much longer stability of the proposed protective surface layers.

4. CONCLUSIONS

1. The study of kinetic parameters of physicochemical interaction with hydrogen of annealed titanium and samples with AlN protective coating proved high stability of this barrier layer in aggressive hydrogen environment under conditions much more severe than those in which titanium parts are usually applied.
2. The rate of hydrogen absorption for titanium with AlN protective coating is four times lower compared to unprotected samples. This is due to the lower intrinsic hydrogen permeability of the barrier layer and its much lower catalytic capacity.
3. The amount of hydrogen absorbed by the samples with protective layer at 700°C is an order of magnitude lower than the corresponding value for the unprotected sample which is hydrogenated under much milder conditions.
4. The positive effect of alloying is manifested not only in increasing the maximum allowable concentration of hydrogen. Under the conditions of helicon arc ion-plasma deposition of aluminium nitride, as well as during high-temperature the exposure of the samples in the hydrogen atmosphere, the alloying elements diffuse into the coating, and if alloy is taken as a substrate, aluminium diffusion inhibits titanium

diffusion. Therefore, the permeability of hydrogen through the AlN protective layer deposited on titanium by 30% exceeds the corresponding value for the coating deposited on Ti + 6.69% Al + 0.81% Mo alloy, which is explained by higher content of oxygen and lower amount of titanium.

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