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HYDROGEN EMBRITTLEMENT OF TITANIUM: PHENOMENA AND MAIN WAYS OF PREVENTION

This work deals with the issue of the deterioration of the mechanical properties of metallic materials (on an example of Ti) in the presence of hydrogen (hydrogen embrittlement). Three main forms of fracture caused by the presence of hydrogen in metallic materials are distinguished. The first one is the damage in internal pores and cracks, which appear when bubbles of gaseous hydrogen are trapped during melt solidification or hydrogen diffusion through the metal lattice. The second one is associated with hydrogen that forms hydrides and changes the type of crystal lattice of the metal. The third one includes other types of fracture associated with hydrogen in the bulk material under long-term static loads. The main methods of preventing the interaction of metallic materials with hydrogen are determined as follow: (i) alloying that reduces the rate of interaction of the metal material with hydrogen, (ii) surface modification by methods of high-energy impact, (iii) application of protective coatings, and (iv) heat treatment of final products.

Keywords: titanium, hydrogen embrittlement, protective coatings, surface modification, structure, hydride.

1. Introduction

According to the literature [1], hydrogen has unique physicochemical properties, and it is widely distributed in the world. Hydrogen can diffuse at a high rate in solids and is active in most materials and compounds. It has unique properties as an alloying element, not only dissolving in crystal lattices and forming new phases but also being almost completely removed from materials with changing thermal and barometrical conditions. Today, these features of hydrogen are the basis of many technologies for materials processing, which allow controlling their structure, and physical and mechanical properties. The ability of hydrogen to inversely interact with materials (*i.e.*, to temporarily saturate them to certain concentrations and then easily leave) was used as a basis for the development of hydrogen storage materials, widely known examples of which are solid compounds — metal hydrides. Despite all the positive aspects of hydrogen listed in Ref. [1], this work considers the negative impact of hydrogen on the mechanical properties of metallic materials.

According to Ref. [2], the degradation of the mechanical properties of cast irons and steels caused by hydrogen was discovered for the first time in the second half of the 19th century (hydrogen embrittlement). Later, this phenomenon was confirmed for all other metallic materials. As noted in Ref. [3], hydrogen embrittlement is a common, dangerous and poorly studied cause of fracture of many metallic materials. In practice, various types of failure of industrial components associated with the presence and localization of hydrogen have been observed in metallic materials. Many efforts have been made to understand the effect of hydrogen on materials, which has led to the appearance of a huge number of theoretical models and works [4]. However, a completely developed and practically applied physical model for predicting and preventing hydrogen embrittlement still does not exist in industry. The determination of the correlation between the strength of metallic materials and their susceptibility to hydrogen embrittlement was the first step in the research on the nature of this phenomenon [5].

The penetration of hydrogen into metallic materials is controlled by phenomena occurring on the surface. The surface layer, without exceptions, differs in its properties from the bulk material; in the ideal case, this difference consists in the presence of open uncompensated bonds (catalytic effect), which determine the kinetics of interaction of hydrogen with a material at the initial stages [6]. In real materials, the surface layer contains many defects caused by mechanical processing, as well as a significant amount of adsorbed air impurities, which form various types of compounds with metal at elevated temperatures. These layers play a significant and in some cases crucial role in the interaction of hydrogen with materials that have a rough surface. As has been shown in many

studies [7−10], material processing by various methods allows the creation of layers that differ from the bulk material not only in terms of crystal structure (defects) and electronic state but also in chemical composition, due to the redistribution of components contained in the volume. Such passivation of the surface can protect the volume of the material from the diffusion of hydrogen, and so prevent the deterioration of its properties (brittleness) [11−13].

As noted in Refs. [9, 10], surface modification can crucially change the process of interaction with hydrogen. The active interaction with hydrogen begins at much higher temperatures and proceeds much more slowly. The authors of Ref. [9] noted that the role of the surface layer in the hydrogen absorption into the bulk material should be considered from two viewpoints: the hydrogen permeability of the layer, and the catalytic effect of the modified surface on the hydrogen dissociation. In this case, the rate of formation of the surface hydride layer or the initial rate of hydrogen absorption is determined by the combined effect of the catalytic activity of the surface and the permeability of the surface layer.

Hydrogen is absorbed by metals only in the atomic state, which forms in its own (hydrogen) environment starting from 1700 °C. On the surface of metallic materials, hydrogen molecules dissociate at lower temperatures. The temperature at which the dissociation of hydrogen molecules begins is determined by the surface catalytic ability. The catalytic capacity can be estimated by the incubation period during isothermal exposure in hydrogen atmosphere or the temperature of the beginning of active absorption of hydrogen under heating [9, 10]. The incubation period is the time between the moment of contact of the metallic material with hydrogen and the beginning of the interaction [9, 10]. The authors noted that the highest catalytic ability is inherent in the surface of the original sample. The surface modification reduces its catalytic ability.

2. The Phenomenon of Hydrogen Embrittlement of Metals

The hydrogen embrittlement of metals is determined by hydrogen content, the nature of the interaction of metallic materials with hydrogen, the state of hydrogen in the metal, the applied stresses (external or internal), and the scheme of loading [14, 15]. Hydrogen can affect both the initiation of cracks and their propagation [13]. Such a variety of factors leads to the fact that there is no single mechanism of hydrogen embrittlement of metals, and this mechanism can alternate when the above factors change even for one material. Several mechanisms can act simultaneously.

In addition, according to Ref. [1], the interaction of metallic materials with hydrogen is quite complex and can be divided into four main stages. In the first stage, molecular hydrogen contacts with the metal surface. Then the accumulation of hydrogen molecules on the surface and their

dissociation (physical adsorption, dissociation, and chemical adsorption (chemisorption) of hydrogen molecules) occur. In the third stage, atomic hydrogen redistributes throughout the volume of the metal. In the last stage, H atoms are orderly arranged in the interstitial sites of the metal lattice with the gradual formation of a chemical compound.

Absorption of hydrogen by a material usually refers to the transition of hydrogen from the gaseous state to the crystal lattice. The term 'absorbed hydrogen' refers to all absorbed hydrogen, which is both in a solid solution and in a chemical compound. Hydrogen capacity is the maximum amount of hydrogen that a given metal can absorb. In Ref. [6], based on the results of Ref. [11], it was stated that there are no certain forces, which cause hydrogen adsorption. However, it was claimed that the adsorption of hydrogen molecules by the metal surface occurs due to the forces of attraction between molecular hydrogen and the surface atoms of the adsorbent. Hydrogen molecules can be adsorbed by the metal surface due to physical or chemical adsorption. The authors of Ref. [6] claim that physical adsorption is based on the van der Waals interaction between molecular hydrogen and adsorbent atoms; during this process, a hydrogen molecule simultaneously interacts with several adsorbent atoms. The potential energy of a hydrogen molecule has a minimum at a distance of approximately one radius of the adsorbent molecule (0.2 nm) [16]. The energy of physical adsorption is usually negative, and its value does not exceed 20 kJ/mole H (–0.2 eV). For many metals, the energy of physical adsorption is close to –5 kJ/mole H (–0.05 eV) [16], so significant physical adsorption takes place only at low temperatures (<273 K) [14]. According to Ref. [17], hydrogen atoms that diffuse into the metal volume have a lower chemical potential of interaction with hydrogen traps, which results in the formation of molecular hydrogen. As the critical concentration of hydrogen in the defective structure of the metal is reached, the hydrogen pressure continues to increase and reaches about several thousand MPa, which leads to an increase in the number of microdefects and their subsequent coalescence. Since this pressure exceeds the yield strength of the material, the crack can propagate even in the absence of external applied stress.

According to the authors of Refs. [18–20], the degradation of physical and mechanical properties of metals in the presence of hydrogen is a complex process. They propose to distinguish between primary and secondary factors when analysing hydrogen embrittlement. The primary ones include hydrogen sources, the transportation of hydrogen atoms from the sources to the surface of the material, and their adsorption, absorption, and diffusion into the volume of the metal. After diffusion into the volume, hydrogen atoms contribute to the formation of hydrides, decohesion, the interaction with dislocations, initiation and propagation of cracks, and formation of pores filled with hydrogen under high pressure. The secon-

dary factors include various impurities, surface hydrides and oxide films, and the stressed state of metal.

In Ref. [21], several problems were highlighted, the solution of which makes it possible to advance in the issue of the mechanism of hydrogen effect on the physicochemical and mechanical properties of metallic materials. Among these problems, the most important is the identification of the influence of different forms of hydrogen on the elastic and plastic deformations that can cause various types of brittle fractures. The authors of Ref. [21] note that hydrogen can be found in nature in molecular, atomic, and ionic states; so, there is a variety of phenomena of the interaction of it with a metal that deforms. Usually, changes in the processes of deformation and fracture are attributed to the interaction of the metal with hydrogen (in the atomic or ionic state), whereas hydrogen in the molecular state does not significantly affect these processes. It was noted that the study of the phenomena that take place during the interaction of hydrogen and its active forms with deforming metals is of interest not only concerning the mechanical processing of metals but also for theoretically based use of this interaction. This will provide the protection of structural metals and alloys against the undesirable consequences of these processes.

As to titanium and its alloys, the author of Ref. [22] substantiated the expediency of dividing the direct and indirect effects of hydrogen. The direct effect of hydrogen is associated with its direct effect on the mechanisms of nucleation and propagation of cracks. The indirect one is associated with structural changes caused by hydrogen, namely, a change in the type of structure, sizes and morphology of phases.

Three following main types of hydrogen embrittlement were considered in Ref. [23]: internal, external, and chemical. The internal one occurs when the metal absorbs hydrogen during processing. This phenomenon can lead to structural changes in the metal that have never been exposed to hydrogen before; it is associated with the absorption of hydrogen by internal cracks (on average no more than 0.1–10 ppm). The effect is observed from –100 to 100 °C.

The external hydrogen embrittlement occurs when the material is exposed to an environment containing hydrogen, *e.g.*, in storage tanks. Hydrogen absorbed or adsorbed at room temperature changes the mechanical properties of the material without forming a second phase. Hydrogen-saturated solid solutions formed in this case disintegrate under prolonged action of applied loading that leads to the brittleness of the material. The rate of this process strongly depends on the stresses applied to the metal, which is described in the literature [24] as 'hydrogen cracking'.

The chemical embrittlement is a phenomenon when hydrogen chemically reacts with a metallic material to form new microstructural compounds or phases, such as hydrides [25–27], or to produce methane bub-
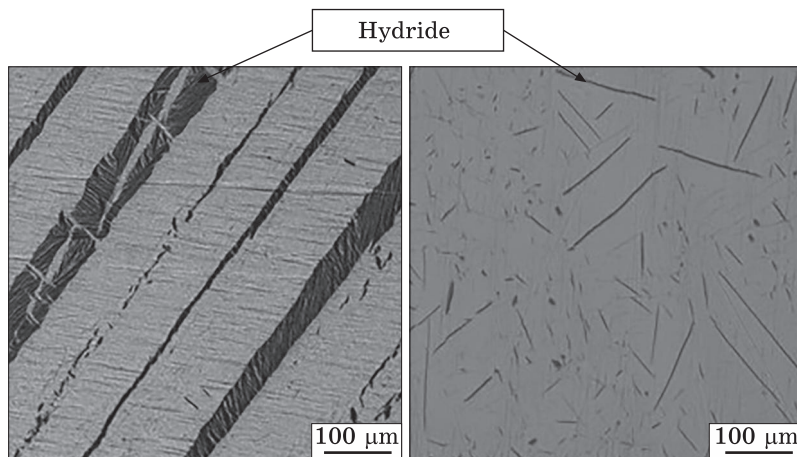
Fig. 1. Hydride precipitations in titanium matrix [9]

bles due to the reaction with carbon that segregates along the grain boundaries in metals. In particular, during the hydrogenation of titanium, hydride forms as plates along certain crystallographic directions inside the grains or along grain boundaries. The type and morphology of the hydrides depend on many factors: hydrogen content, grain size, hydrogenation temperature, preliminary thermal treatment of titanium, the stressed state of the metal during the interaction with hydrogen, and impurity content. With an increase in the hydrogen content in the titanium, the tendency to the formation of compact clusters along the grain boundaries increases (Fig. 1) [28].

3. The Ways to Counteract the Hydrogen Embrittlement of Ti

Ti-based alloys provide an excellent combination of high strength-to-weight ratio and high corrosion resistance that makes these alloys one of the most important modern materials. Due to this excellent combination, Ti-based alloys are promising for use not only for a wide variety of biomedical materials, aerospace and chemical equipment and in shipbuilding but also in other industries. Although titanium and its alloys are considered chemically resistant, in many technological and commercial applications they are exposed to hydrogen-containing environments. Therefore, serious problems related to hydrogen embrittlement can arise, since they can absorb a large amount of hydrogen, especially at elevated temperatures. The intensity of the interaction of hydrogen with Ti-based alloys strongly depends on their microstructure and chemical composition [29−31].

To estimate the hydrogen embrittlement in titanium and its alloys in specific cases, it is necessary to know the minimum concentrations of hydrogen that lead to their failure. Currently, maximum permissible hydro-

gen concentrations have been determined for many standard alloys [32–34]. Based on experimentally determined thermodynamic and kinetic data on the interaction of hydrogen with β-titanium alloys, the authors of [35] determined the maximum allowable concentrations of hydrogen (up to 8 at.%) in three standard alloys. However, these maximum concentrations are not absolute. The maximum allowable concentrations of hydrogen, determined based on laboratory tests of samples with small cross-sections, as a rule, turn out to be overestimated and do not guarantee the absence of hydrogen embrittlement in large-sized structures under a hard stress state. When titanium alloys work at low temperatures, their hydrogen content should be lower than the specified one. For a coarse-grained material, tolerances for the maximum hydrogen content are significantly lower than for a fine-grained one. When using titanium and its alloys in welded joints, the level of the maximum allowable hydrogen content should be set based on the results of tests on slow brittle fracture of welded samples. This is because the stress field in the weld seam and nearby zone contributes to the directed movement of hydrogen atoms and the development of premature failure.

When the material (for example, titanium or Ti-based alloys) during the operation or production of semi-finished products is exposed to an atmosphere of gases containing hydrogen, it is necessary to take measures that prevent the penetration of hydrogen into the volume of the material. In this case, there are the following ways to prevent hydrogen embrittlement:

• alloying that reduces the rate of interaction of the metal with a hydrogen-rich environment and increases the maximum allowable concentrations of hydrogen [36];

• modification of the surface of the material by methods of high-energy impact [37];

• deposition of protective coatings on the surface, that prevent the penetration of hydrogen into the bulk material [38];

• heat treatment [39].

For titanium and Ti-based alloys, the protective alloying element is aluminium [40], which increases the solubility of H in α-phase and inhibits the precipitation of the hydride phase [41]. Therefore, increasing the aluminium content in the α-titanium is considered an effective way to reduce the susceptibility to hydrogen embrittlement. For example, hydrogen embrittlement appears in pure titanium at hydrogen content above 0.01 wt.%, and in the VT5 alloy (Ti+5% Al), above 0.035 wt.% [42]. This method of preventing hydrogen embrittlement has proven itself quite effective in specific cases of use. However, only the surface layer is usually in contact with a hydrogen atmosphere, and alloying of the entire volume of a material (in the case of large-size parts) may be economically impractical. In addition, alloying can lead to a change in the phase composition of the base material [43, 44] (the formation of an intermetallic phase) and, as a

Fig. 2. Hydrogen atoms trapped at grain boundaries in thin films [48]

result, deterioration of its physical and mechanical properties.

Protective coatings are widely used in industry, and their use provides a great economic effect [45]. The methods of their deposition are very diverse: electrolytic deposition of metals and alloys, vacuum evaporation with subsequent condensation on a cathode substrate, gas transport reactions, ion implantation, chemical and thermal treatment, *etc*. The compositions of protective coatings are also very diverse: oxides, borides, nitrides, carbides, and silicides [46, 47]. In addition, it was schematically shown in Ref. [48] that grain boundaries in a protective coating can act as additional traps for hydrogen atoms (Fig. 2).
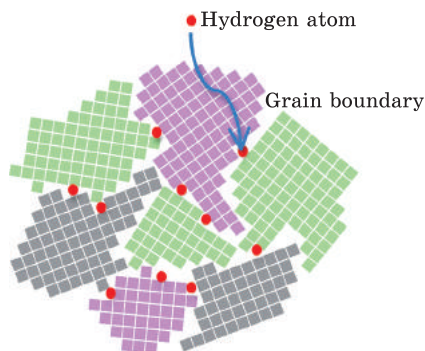
Aluminium oxide thin films are widely used because of their excellent properties, especially chemical, thermal, abrasive, and corrosion resistance. They are also widely used as protective barrier layers to reduce hydrogen permeability [49]. For example, the authors of [50] found out that aluminium oxide (500 nm thick) deposited by the vacuum arc technique on amorphous tungsten oxide WO_3 could reduce hydrogen permeability by 300 times. According to the results of [51], it was found that the hydrogen permeability through the Al_2O_3 film under hydrogen partial pressure in the range of 2–50 kPa at 1200–1450 °C and a film thickness of $\cong$500 nm was two orders of magnitude lower for such metallic materials as vanadium, niobium, molybdenum, and uranium.

The authors of Refs. [52–55] also concluded that the Al_2O3 film is a good barrier to the penetration of hydrogen into the bulk metallic material, especially under low-pressure conditions. It was found that, regardless of the coating deposition technique, a coating thickness of more than 40 μm did not significantly affect the permeability of hydrogen and the protective properties of the Al_2O_3 film.

However, the authors of [56, 57] determined that the coating prevents the penetration of hydrogen into titanium when the exposure time in a hydrogen atmosphere did not exceed 3 h at a pressure of 0.2 MPa and at 400 °C. Increasing the exposure time led to a crucial increase in the amount of absorbed hydrogen. This is explained by the fact that the coefficients of thermal expansion of metals and coatings of this type are extremely different, which leads to large thermal stresses in the coating. These stresses cause deformation defects, cracking and delamination, and, as a result, a decrease in penetration resistance. This process was studied in Ref. [55] using a three-dimensional model (Fig. 3).
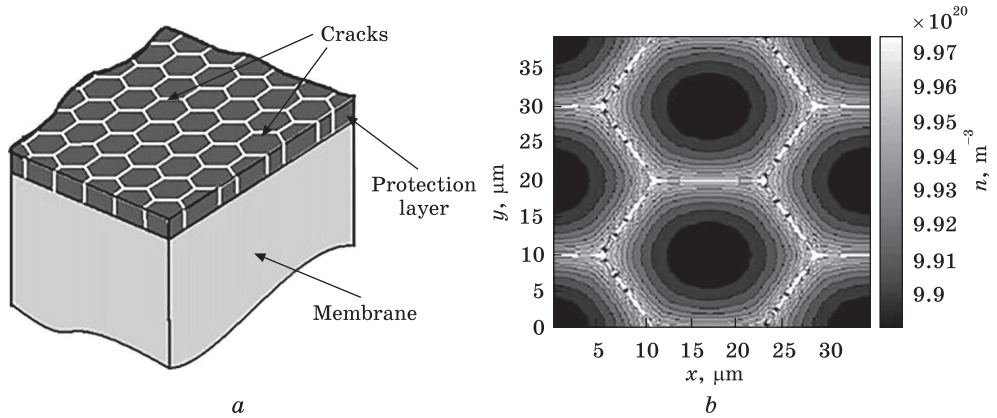
Fig. 3. Scheme of 3D model of membrane with cracks in protective layer (*a*), and hydrogen concentration map on outer surface of membrane with cracks in protective layer (*b*) [55]
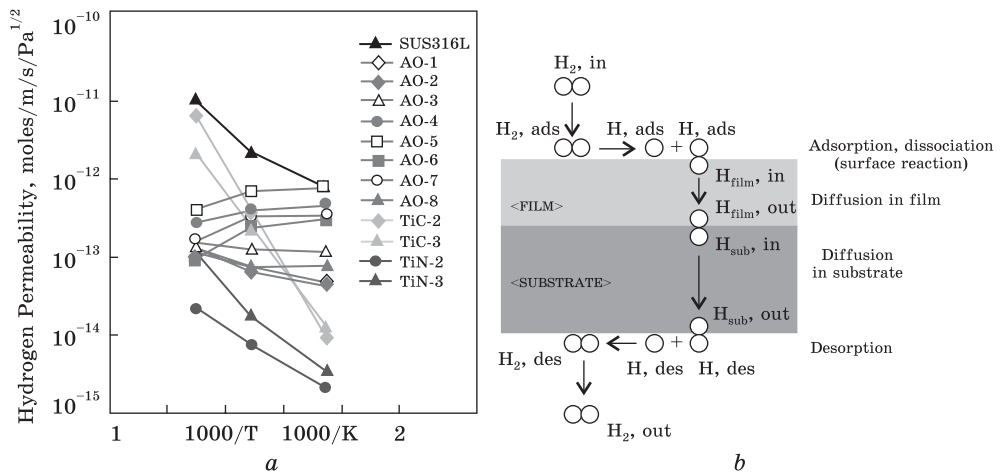

Fig. 4. Arrhenius plot of hydrogen permeability as a function of temperature (*a*) and schematic illustration of the permeation mechanisms (*b*) [48]

Morphology and hydrogen permeability of typical thin films [48]

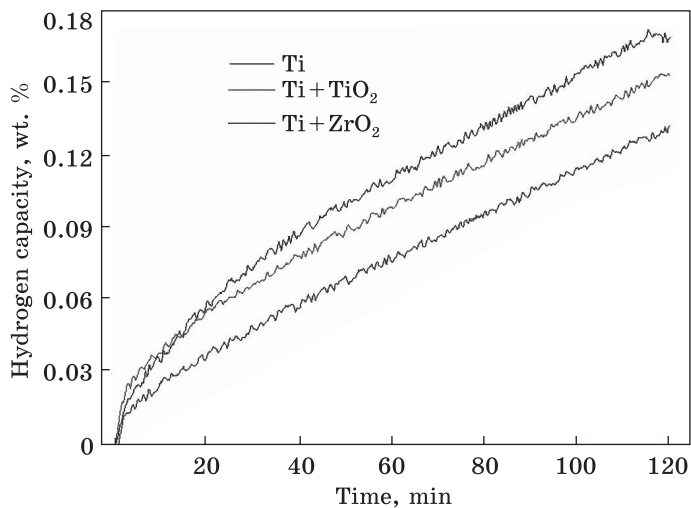| Type	Film thickness, μm	Grain size, μm	Hydrogen permeability, moles/m/S/$P^{1/2} \cdot 10^{-14}$		
			300 °C	400 °C	500 °C
Al_2O_3	2.03	20	7.59	7.49	11.8
TiC	2.5	70	1.14	23.7	216.0
TiN	2.2	56	0.21	0.76	2.21

Fig. 5. Hydrogen absorption by CP titanium VT1-0 in initial state and with coatings [64]

Another type of coatings actively used to combat the negative effects of hydrogen is titanium nitrides and carbides, separately or in combination as composite coatings [58–63]. In Ref. [48], the hydrogen permeabilities of Al_2O_3, TiC, and TiN coatings were compared (Fig. 4, *a*). In addition, the authors showed how hydrogen penetrates through the coating (Fig. 4, *b*), which is consistent with the data of [6, 55]. The authors explain the differences in the hydrogen permeability of Al_2O_3, TiC, and TiN (*Table*) by the fact that thin films usually have very different microstructures. The microstructure is typically characterized not only by grain size, but also by crystallographic orientation, lattice defects, phase composition, and surface morphology.

Although TiC and TiN have low internal hydrogen permeability as compared to steels, titanium and zirconium, this potential is not reached in deposited films. They often have activation energies of penetration comparable to those of the materials they are supposed to protect. This indicates that hydrogen permeability is controlled by defects in the coating rather than by penetration through the coating material [30]. Thus, the penetration reduction coefficients did not reach the predicted values.

According to the literature [64], titanium oxide can also be used as a coating as an inexpensive and chemically resistant material. In addition, this coating significantly increases the hardness, strength and wear resistance, as well as the corrosion resistance of substrate material [65–68].

In Ref. [64], ZrO_x and TiO_x coatings were deposited on CP titanium VT1-0 by magnetron and plasma-arc sputtering. Hydrogenation was carried out from a gas atmosphere at 450 °C and a hydrogen pressure of 0.2 MPa for 160 min (Fig. 5). It was found out that during the saturation from a gaseous atmosphere at 450 °C, the rate of hydrogen adsorption by
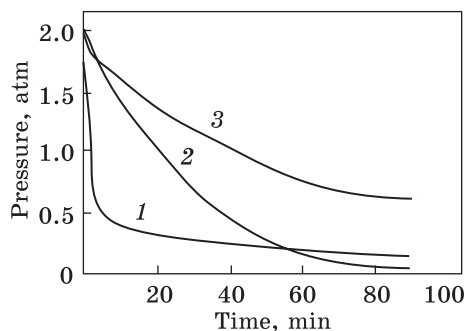
Fig. 6. Kinetic curves of pressure in chamber during hydrogen adsorption for samples modified with carbon ions: *1* — unprocessed material, *2* — after 3 pulse, and *3* — after 6 pulses [75]

titanium with surface oxide film with a thickness of 3 µm or more decreased by only ≈1.2 times. This was explained by a rough surface. As known, the quality of the surface has a great effect on the kinetics of hydrogen absorption by a metallic material. Hydrogen accumulates in any defects on the surface. The higher the amount of these defects, the more H is absorbed by the metal, and the TiO_x coating deposited by the plasma-arc spraying technique is porous and contains a large number of microparticles.

Besides applying protective coatings, it has also been found to be effective to grow the oxide scale [69]. Titanium films sublimated in high vacuum absorb hydrogen at room temperature; iodide titanium annealed in a vacuum begins to interact with hydrogen above 250 °C, and CP titanium with a natural oxide scale on the surface does not noticeably absorb hydrogen up to 350 °C. No noticeable interaction of hydrogen with titanium exposed at 450 °C for 10 h was detected after the material was annealed in air at 700 °C for 2–6 h. In Ref. [32], the surface of titanium samples was oxidized for 5 min at different temperatures (400–800 °C), which led, according to the authors, to the formation of oxide scales of various densities on the surface of the samples; the effect of these scales on hydrogen absorption was different. The scale formed at a low temperature almost did not hinder the absorption of hydrogen by titanium, whereas the scale formed at high temperatures hindered the penetration of hydrogen into the metal, *i.e.*, it acted as a barrier layer. When the integrity of the oxide scale is broken by annealing in a vacuum at high temperatures, and, according to [70–72], 'oxygen diffuses from the surface into the volume of metal', hydrogen can be absorbed even at room temperature. Therefore, the oxide scale formed during activation annealing or heating in a hydrogen atmosphere does not affect the hydrogenation process as a whole, but only determines the duration of the incubation period.

The scale defects, cracks and delamination are the problems that should be solved when applying protective coatings. Therefore, many researchers [73–75] are inclined to the opinion that it is more promising not to form a certain coating, but to modify the surface, *e.g.*, using a pulse accelerator of carbon ions. When the surface is treated with a pulse ion beam, the grain size is significantly reduced as compared to the initial material. This is primarily due to the recrystallization of titanium after

rapid heating up to the melting point and then rapid cooling [76]. This modification of the surface leads to increased hardness of the samples. The thickness of the hardened layer is just 2 μm. According to [73–75], the hardening of titanium during pulse ion processing is primarily caused by the structural and phase changes in its surface layers. In order to evaluate the hydrogen stability of the initial samples and those modified by pulse ion beam, the rate of hydrogen absorption during saturation in a gas atmosphere was studied (Fig. 6).

As seen in Fig. 6, the decrease in pressure in the chamber indicates the process of hydrogen absorption by the materials, and the slope of the kinetic curves characterizes the intensity of the hydrogenation. The studies showed that the rate of hydrogen absorption by titanium in the initial state was ≈ 0.1 cm³H$_2$/(s·cm²); after surface modification with three pulses, it was 0.03 cm³H$_2$/(s·cm²), with six pulses — 0.02 cm³H$_2$/(s·cm²) [75]. Using CP titanium VT1-0, the authors of [75] experimentally proved that surface modification allows for reducing the rate of H absorption in Ti.

Current methods of protecting titanium from hydrogen embrittlement lead to a decreased catalytic ability of the surface; its value depends on the chosen method of protection. In each specific case, one can choose the chemical composition of the protective surface layer or alloying with certain elements or even their combination, depending on the operating conditions of titanium parts.

4. Conclusions

I. Three main types of hydrogen embrittlement of metallic materials are distinguished: internal, external, and chemical:

the internal one occurs when hydrogen penetrates the metal during its processing;

the external one occurs when the metal is exposed to a hydrogen-containing atmosphere;

the chemical one occurs when hydrogen chemically reacts with material, forming new compounds or phases.

II. Various options for surface passivation and forming barrier layers to protect metal parts against the penetration of hydrogen into the volume of the material are considered in an example of titanium. These options prevent the hydrogen embrittlement.

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ВОДНЕВА КРИХКІСТЬ ТИТАНУ:
ПРОЯВИ ТА ОСНОВНІ ШЛЯХИ ЗАПОБІГАННЯ

Робота стосується питання про погіршення механічних властивостей металевих матеріалів (на прикладі Ti) у присутності водню (воднева крихкість). Визначено три основні форми руйнування через наявність водню в металевих матеріалах. Перша — пошкодження у внутрішніх порах, тріщинах, що виникають через захоплення бульбашок газоподібного водню в процесі затвердіння розплаву або дифузії Гідроґену через металеву ґратку. Другу форму спричинено Гідроґеном, що утворює гідриди і змінює тип кристалічної ґратки металу. Третя форма включає решту руйнувань, пов'язаних із присутністю Гідроґену в об'ємі матеріалу в умовах довготривалих статичних навантажень. Встановлено основні методи унеможливлення реакції взаємодії металевих матеріалів із Гідроґеном: (1) леґування, що зменшує швидкість взаємодії металевого матеріалу з Гідроґеном, (2) модифікування поверхні методами високоенергетичного впливу, (3) нанесення захисних покриттів, (4) відпал вже готових виробів.

Ключові слова: титан, воднева крихкість, захисні покриття, модифікування поверхні, структура, гідрид.