Effect of electrochemical modification of titanium hydride fraction on oxygen content in surface and deep layers

R.N. Yastrebinsky, V.I. Pavlenko, A.I. Gorodov, A.A. Karnauhov, N.I. Cherkashina and A.V. Yastrebinskaya

Belgorod State Technological University named after V.G. Shoukhov, Belgorod, 308012, Kostyukova str., 46, Russia

E-mail: cherkashina.ni@bstu.ru

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Abstract

The paper presents a study of the microstructure and oxygen concentration in the surface and deep layers of fractions of unmodified titanium hydride and titanium hydride modified by electrodeposited layers of Ti and Cu at temperatures of 300 °C–900 °C. The composition of the oxide layer and the concentration of titanium and oxygen atoms are estimated. It is shown that an increase in the thickness and compaction of the oxide layer with increasing temperature prevents the penetration of oxygen into the deep layers of the unmodified fraction of titanium hydride. Modification of titanium hydride by electrochemical deposition of metallic titanium at a temperature of 700 °C reduces the oxygen concentration in titanium hydride at a layer depth of 50 μm from 35 wt% to 12.5 wt%. Electrodeposition of coatings based on titanium and copper at 700 °C reduces the oxygen concentration to 9.2 wt%, which may be due to the protective mechanism of the formed copper titanate layer. At 900 °C, in the modification layer based on titanium and copper, due to the eutectoid transformation of the β-phase of titanium, the process of contact melting occurs and a multiphase zone is formed. The oxygen concentration at a layer depth of 50 μm is no more than 12.4 wt%.

1. Introduction

To expand the possibilities of using metal hydride systems in nuclear power, one of the priority research areas is to increase their thermal stability. Metal hydrides almost always dissociate at significantly lower temperatures than their melting point or the temperature at which their strength is significantly reduced. The operating temperature in such systems as in fast reactors is 550 °C–660 °C, which imposes high demands on these materials [1–6]. The real thermal stability of the titanium hydride most used in the design of radiation protection of the reactor is low: it ranges from 250 °C–300 °C [7–11].

The most obvious way to retain hydrogen is to use shells impermeable to it. Analysis of the data on hydrogen leakage leads to a positive assessment of the role of the oxide film on the metal surface in increasing its resistance to hydrogen penetration. Such films as a hydrogen-impermeable barrier are much superior to any metals and alloys [12–15].

A number of studies have shown that the best hydrogen-impermeable barrier is an oxide film on the surface of the shell obtained in the process of metal oxidation in air or in a special gaseous medium [16–20].

Unfortunately, oxide films produced by exposure to the atmosphere on most alloys are partially reduced in contact with hydrogen, contained in the titanium hydride lattice. Thus, if the oxide film is not retained on the metal surface due to the constant maintenance of the oxidizing atmosphere, then the role of the oxide barrier either significantly decreases or disappears completely [21]. Also of great importance is the thickness of the oxide film and the ability of oxygen to penetrate cracks and defects throughout the volume of the titanium hydride fraction. Since under conditions of increasing the thickness of the oxide coating, internal stresses may occur that exceed the strength limit of the substrate material. In this case, on the surface of the metal hydride system, it is
necessary to create additional diffusion barriers on the surface of the metal hydride system in order to limit the growth of the oxide layer to a certain depth and prevent its development into all cracks of titanium hydride.

In order to select barriers impermeable to hydrogen, many materials based on nickel, chromium, aluminum, magnesium, bismuth, lithium, gold, and magnesium silicide have been investigated \[22–31\]. However, their use is limited either by complex technology and application conditions or by low efficiency at operating temperatures above 600 °C.

To establish the nature of hydrogen permeability through oxide films and to select the optimal coating and its thickness for each individual case, further studies are required. This direction is the most promising for the operation of a hydride composition with an optimal hydrogen concentration in a given temperature range.

It is known that even under standard conditions, upon contact with atmospheric oxygen, an oxide film layer with a thickness of 2 to 10 nm forms rather quickly on the surface of titanium hydride, which protects it from further oxidation \[32\]. The main formation of the oxide film occurs in the first few hours. Further oxidation occurs extremely slowly and practically ends in 50–60 days \[33\]. The resulting oxide film consists of bivalent or tetravalent titanium oxide. It should be noted that the oxides are arranged in layers - the upper layer, as a rule, is formed by TiO₂, and the lower one is TiO. In this case, the continuity of the coating is determined by titanium (II) oxide, which determines the thermal stability of the hydride due to the formed metal oxide diffusion barrier \[33\].

An increase in temperature leads to dissolution of the oxide film and thermal diffusion of hydrogen due to dehydrogenation processes as well as further oxidation of titanium itself due to thermal diffusion of oxygen. There is a constant flow of exchange processes between the layers due to the continuous oxidation of metallic titanium \[34\].

In this regard, it is of interest to study the oxygen content in the surface and deep layers of the fraction of unmodified and modified titanium hydride at different temperatures.

2. Materials and methods

2.1. Materials

For the studies, titanium hydride was used in the form of a fraction 1.6–2.6 mm in diameter obtained as a result of hydrogenation of spherical granules of metallic titanium to a nonstoichiometric hydrogen content of 3.5 wt%.

The elemental composition of the fraction of titanium hydride is presented in \[34\].

The studies were carried out on an unmodified and modified titanium hydride fraction.

The modified material was used:

- titanium hydride fraction modified by electrochemical deposition of metallic titanium from a non-aqueous solution of an organic electrolyte. We used an electrolyte consisting of tetrabutoxytitanium - Ti(OC₄H₉)₄,
titanium (IV) chloride, ethanol, and dimethyl sulfoxide with different component ratios. Titanium plates were used as the anode. The current density was 3.5 A dm$^{-2}$, and the electrolysis time was 120 min;

- titanium hydride fraction with a two-layer coating obtained by subsequent electrochemical deposition of metallic titanium and metallic copper. Electrochemical deposition of metallic copper, on the surface of titanium hydride, previously modified with titanium, was carried out from an aqueous solution of copper sulfate ($\text{CuSO}_4\cdot5\text{H}_2\text{O}$) at a current density of 2 A dm$^{-2}$ and an electrolysis time of 10 min. Copper plates were used as the anode.

2.2. Test methods

Electrochemical deposition of titanium metal on the surface of the titanium hydride fraction was carried out on an IPC-Pro 3A Potentiostat installation.
To study the oxidation processes of titanium hydride, heat treatment (for 3 h at each temperature under study) of the fraction in the air atmosphere was performed. The oxygen content in the surface and deep layers of the titanium hydride fraction was determined by electron probe microscopy using the X-MAX 50 Oxford Instruments energy dispersive spectrometer, which is part of the TESCAN MIRA 3LMU (SEM). The
3. Results and discussion

In the photographs of the microstructure of a cleaved unmodified fraction of titanium hydride in the bulk of the fraction at 300 °C, the presence of inhomogeneities in the form of sections of the oxide phase is observed (dark areas in figure 1) due to the oxygen content at the grain boundaries. With an increase in temperature (up to 500 °C), a more uniform distribution of oxygen occurs in the bulk of the titanium hydride fraction due to an increase in its solubility in titanium (figure 2).

The average concentration of oxygen atoms at 300 °C in the surface layer of an unmodified fraction of titanium hydride reaches 34.2 wt% (point B), which is due to the oxidation of metallic titanium and the formation of a phase close to Ti₂O₃. In this case, the intensity of the Kα oxygen line in the x-ray spectrum, measured along segment AB (figure 1(b)), is approximately the same over the entire depth of the oxidized layer (figure 3).
In general, the reaction of metal oxidation with oxygen can be written as:

\[ m \text{Ti}_{(\text{sol})} + \frac{mn}{4} \text{O}_{2(\text{gas})} = \text{Ti}_m\text{O}_{mn/2(\text{sol})} \]  

(1)

where \( m \) is the number of titanium atoms in the titanium oxide molecule and \( n \) is the valence of the titanium atom.

Figure 8. SEM images of a cleaved titanium hydride fraction modified by electrochemical deposition of titanium and heat treated at 700 °C at various magnifications, 1–3 - points to determine the content of elements.

Figure 9. Concentration of titanium and oxygen atoms at 700 °C in the surface layer of titanium hydride fraction modified by electrochemical deposition of titanium (according to figure 8(b)): a - point 2, b - point 3.

Figure 10. SEM images of cleavage (a) and oxygen distribution (b) in titanium hydride fraction modified by electrochemical titanium deposition and heat-treated at 900 °C, 1–3 - points to determine the content of elements.
At 500 °C, the oxide film grows with an increase in the oxygen content in the surface layer to 36.8 wt%, which indicates the onset of oxidative processes (figure 3(b)).

The nonstoichiometric oxygen content indicates the presence of a mixture of Ti$_2$O$_3$ and TiO$_2$ oxides, where the oxygen content varies from 33 (in TiO) to 40 (TiO$_2$) wt%. An increase in the oxygen content to 36.8 wt% characterizes the predominance of the rutile TiO$_2$ phase. The intensity of the Kα oxygen line in the x-ray spectrum, measured along the AB segment (figure 2(b)), slightly increases at a layer depth from 20 to 150 μm (figure 3(d)).

At 700 °C, a loose layer of oxide film 2–3 μm thick is observed on the surface of the titanium hydride fraction (figure 4).

Oxygen penetrates through the surface cracks into the bulk of the unmodified titanium hydride fraction. This is indicated by the presence of characteristic oxygen-enriched areas at points 1 and 4 (figure 4) with an oxygen concentration 40.4 and 39.6 wt%, respectively, (figures 5(a) and (b)), which corresponds to titanium oxide of the composition TiO$_2$.

There is a change in the internal structure of the fraction with the formation of the α and β phases of titanium, characterized by a different density and oxygen solubility in them (figure 4, points 2 and 3). The β-phase of titanium appears as thin lines within the massive regions of the α-phase. The oxygen content at these points is 34.6 and 35.8 wt%, respectively (figures 5(c) and (d)).

At 900 °C, an increase in the thickness and compaction of the oxide layer occurs, which prevents the penetration of oxygen into the bulk of the unmodified fraction of titanium hydride. This is confirmed by the
absence in the bulk of the fraction of oxygen-saturated sections of the layer, which are typical for the samples of the fraction at 700 °C (figure 4, point 4). The oxide layer of the surface is mainly represented by titanium oxide TiO₂ (figure 6, point 1). In this case, the thickness of the oxide layer of the fraction surface reaches 60 μm.

Also at 900 °C, regions of different densities are observed, characteristic of the α and β phases of titanium (figure 6, points 2 and 3), with the concentration of oxygen atoms of 35.3 wt% and 36.1, respectively (figures 7(a) and (b)). The composition of the oxide phase corresponds to titanium oxide Ti₂O₃.

Electron probe microanalysis of a cleaved titanium hydride fraction containing an electrochemically deposited titanium coating shows that at 700 °C, the surface layer of the fraction is oxidized with the formation of a TiO₂ oxide layer up to 4 μm thick (figure 8, point 1). No changes in the internal structure characteristic of the unmodified fraction of titanium hydride are observed. An electrochemically deposited titanium layer heals defects and microcracks on the surface of the fraction, and the surface layer of titanium oxide formed as a result of oxidation prevents oxygen penetration into deep layers of the fraction. As a result, at a depth of up to 20 μm, there are no oxidized areas with an increased oxygen content, and the maximum oxygen concentration does not exceed 13 wt% (figures 9(a) and (b)).

At 900 °C, as in the case of the unmodified titanium hydride fraction, there is a significant increase in the thickness of the oxide layer up to 60 μm and a change in the internal structure occurs (figure 10).

Figure 13. Concentration of copper, titanium and oxygen atoms at 300 °C (a), (b) (points 1a, 2a in figure 12(a)) and at 500 °C (c)–(e) (points 1b, 2b, 3b in figure 12(b)) in the surface layer of titanium hydride fraction containing titanium and copper coating.
In this case, the oxygen concentration in titanium hydride at a depth of 160 μm is no more than 15.5 wt% (figure 11(b), point 3 in figure 10(a)), which is due to the protective mechanism of the oxide shell.

Electrochemical deposition of a copper coating on the titanium-modified titanium hydride surface creates an additional barrier for oxygen atoms and prevents their penetration into deep layers. At 300 °C and 500 °C, the concentration of oxygen atoms behind the modification layer at a depth of ~100 μm is 8.7 and 9.2 wt%, respectively (figure 12, point 2a and point 3b; figures 13(b) and (d)). The internal structure of the titanium hydride fraction is preserved.

At 500 °C in the surface layer at a depth of up to 10 μm, oxidation of the copper coating is observed with the formation of copper (II) oxide (figure 12, point 1b). This reaction is typical for the oxidation of metallic copper at a temperature of 500 °C.

At 700 °C, oxidation processes in the surface layer of the modified titanium hydride fraction are enhanced. The modification shells are saturated with oxygen, and the thickness of the oxidized layer increases to 20 μm.
Figure 15. Concentration of atoms of elements at 700 °C in the surface layer of a titanium hydride fraction containing titanium and copper coatings: a - point 6, b - point 7 (according to figure 14(a)).

Figure 16. SEM image of the cleavage (a) and the concentration of elements in the surface layer of titanium hydride fraction (b)–(e) containing titanium and copper coatings and heat-treated at 900 °C: b - point 1, c - point 2, d - point 4, e - point 5, f - point 7.
Titanium hydride by the method of electrochemical deposition of metallic titanium and copper reduces the penetration of oxygen into the interior of the material with increasing temperature. The modulus different density and oxygen solubility. The increase in thickness and compaction of the oxide layer at 900 °C reduces oxygen concentration in deep layers by a factor of 4.2 (figure 16(a)). The oxygen concentration in the copper coating decreases with depth from 21.6 wt% to 11.5 wt% (figures 14(b) and (c), points 1 and 2). Points 3–5 (figure 14(a)) are characterized by the content of copper and titanium atoms. Probably, the copper and titanium layer is sintered with the formation of copper (II) titanate by the reaction, the course of which is typical for 600 °C:

$$\text{CuO} + \text{TiO}_2 \rightarrow \text{CuTiO}_3$$  \hspace{1cm} (2)

The formation of titanium copper corresponds to point 3 (figure 14(d)) with an oxygen content of up to 23 wt%. Under the copper titanate layer, the oxidation of copper and titanium is insignificant, which corresponds to the oxygen content of 3.1 and 4.6 wt% (figures 14(e) and (f), points 4 and 5).

The concentration of oxygen atoms under the protective coating at a depth of 30–50 μm is 8.5–9.2 wt% (figures 15(a) and (b) (points 6 and 7 figure 14(a)), which is 30% less than in the case of a single-layer coating based on titanium (figure 8). This may be due to the protective mechanism of the formed copper titanate layer.

In this case, it is characteristic that the oxygen concentration slightly increases with depth (points 6 and 7), which may be due to the interaction of oxygen with free hydrogen diffusing into the surface layer to form an H₂O molecule.

At 900 °C, oxygen intensively interacts with the modification surface layer, which increases its thickness to 40 μm (figure 16(a)). A decrease in the copper oxide layer to 5 μm (points 1 and 2 figure 16(a)) and the interaction between titanium and copper are observed at a temperature of the eutectoid transformation of the β-titanium phase of about 800 °C. Electron probe microanalysis showed that the process of contact melting occurs, and a multiphase zone is formed with the concentration of titanium and copper atoms being 13.9 and 64.4 wt%, respectively (points 3 figure 16(d)).

Behind the multiphase zone (at point 4 figure 16(a)), titanium oxide of the rutile composition TiO₂ is formed. At the interface between the oxidized modification layer and the metal hydride phase, as in the case of 700 °C, the formation of copper titanate CuTiO₃ is likely (zone AB figure 16(a)). The oxygen concentration at a layer depth of 50 μm (point 5 figure 16(a)) is no more than 12.4 wt%.

Thus, the presented data indicate the presence of an effective barrier for oxygen atoms in the modified fraction of titanium hydride due to the protective properties of a metal coating based on titanium and copper applied by electrochemical deposition. The use of a titanium–copper coating on the surface of a titanium hydride fraction reduces oxygen concentration in deep layers by a factor of 4.2–4.5 in comparison with an unmodified titanium hydride fraction.

4. Conclusions

The formation of titanium oxides on the unmodified titanium hydride fraction at temperatures of 300 °C–500 °C reduces the oxygen concentration in the deep layers of the titanium hydride fraction. With an increase in temperature, the dissolution of the oxide film leads to further oxidation of the deep layers of the titanium hydride fraction. At 500 °C, the oxygen content at a depth of 200 μm is 36.8 wt%. At 700 °C, the oxygen concentration increases to 40 wt%, due to its penetration through surface cracks of the titanium hydride fraction. There is a change in the internal structure of the fraction and the formation of titanium phases with different density and oxygen solubility. The increase in thickness and compaction of the oxide layer at 900 °C prevents the formation of surface cracks and the penetration of oxygen into the deep layers of the unmodified titanium hydride fraction.

The creation of protective shell on the surface of the titanium hydride fraction significantly reduces the penetration of oxygen into the interior of the material with increasing temperature. The modification of titanium hydride by the method of electrochemical deposition of metallic titanium and copper reduces the penetration of oxygen into the deep layers by a factor of 4.2–4.5 in comparison with the unmodified fraction of titanium hydride.

The creation of a two-layer coating based on titanium and copper at 700 °C reduces the oxygen concentration at a layer depth of 50 μm to 9.2 wt%, which may be due to the protective mechanism of the formed copper titanate layer. At 900 °C, in the titanium–copper modification layer, due to the eutectoid transformation of the β-phase of titanium, the process of contact melting occurs and a multiphase zone is formed. The oxygen concentration at 900 °C at a layer depth of 50 μm is no more than 12.4 wt%.

Fraction of titanium hydride with a two-layer metal coating can find application in nuclear power as a neutron-shielding material.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

N I Cherkashina  https://orcid.org/0000-0003-0161-3266

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