Thermal stability of titanium hydride modified by the electrochemical deposition of titanium metal

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Abstract

This study aims to address the poor thermal stability of titanium hydride. Surface microstructural observations, differential thermal analysis, and electron-probe analysis of the thermal stability and phase composition measurements of a titanium hydride fraction that was modified by the electrochemical deposition of titanium metal are presented. It is demonstrated that the metallic titanium deposited on the surface of the fraction acts as an effective trap for hydrogen diffusion into the surface layers upon thermal heating. Modification of the surface of the titanium hydride fraction by electrochemical deposition of titanium metal increased its initial temperature of dehydrogenation by 231.8 °C. The concentration of the hydride phase at the surface layer at 500 °C increased to 87.2% due to the structural redistribution of atomic hydrogen and the hydrogenation of metallic titanium at the surface layer.

1. Introduction

The stability of titanium hydride is currently being studied for reducing its dissociation temperature, to obtain efficient hydrogen accumulators, and increasing its thermal stability for use, for example, in the nuclear industry as a neutron-protective material.

The thermal stability of a metal hydride describes its ability to maintain the atomic ratio of hydrogen to metal when exposed to elevated temperatures. The loss of hydrogen from a metal hydride depends on the atomic ratio of hydrogen to the metal and the temperature, composition, and pressure of the environment. The thermal stability of titanium hydride is low (200 °C–250 °C) and depends on the atomic ratio of hydrogen to titanium [1–5].

Metal hydrides at any temperature in a closed volume create an equilibrium partial pressure of hydrogen by hydrogen separation. At room temperature, the equilibrium hydrogen pressure over titanium hydride close to the stoichiometric composition is ~10⁻⁶ Pa [3]. With increasing temperature and atomic ratio, the equilibrium hydrogen pressure over the metal hydride increases. Thus, for titanium hydride saturated to an atomic ratio of 1.9, the equilibrium pressure at 300 °C is ~250 Pa and reaches ~10 kPa at 400 °C [6].

A large number of studies have investigated the interaction of hydrogen with titanium and the production of its hydrides [7–19], the study of the thermal decomposition of titanium hydrides under various conditions [20–23], and increasing the thermal stability of titanium hydride [24–26]. It has been proven that the modification of the particles of powdery materials significantly increases their functional properties [27–29].

The thermal stability of titanium hydride powder has been improved by applying either metallic copper to the hydride, from aqueous solutions of copper sulfate at ~600 °C, or nickel [30]. The thermal stability increased after the deposition of a copper coating because the copper barrier layer decreased the rate of recombination of the hydrogen atoms on the surface of the particles, when the associative desorption of hydrogen molecules was the limiting stage of the thermal decomposition process.
The decomposition temperature of titanium hydride is largely determined by the enthalpy and entropy of defect formation in the hydrogen sublattice of the hydrides [31–34] and depends on the external pressure. The enthalpy and entropy can be changed by introducing various additives [35].

Impurities of oxygen, carbon, and nitrogen located in the octahedral interstices of the titanium hydride lattice, with hydrogen atoms occupying the tetrahedral positions, block the placement of hydrogen atoms in the nearest environment [36–38]. Carbide and oxycarbide coatings exhibit unique, low hydrogen permeability, which significantly increases the surface microhardness [39–43]. The influence of a carbon-oxygen-containing medium on the structural-phase state of diffusion coatings on titanium has been studied, where the parameters of the saturating medium and the conditions for obtaining a diffusion-produced carboxylic coating were determined [44]. However, the formation of such carboxylic coatings requires temperatures above 800 °C, which leads to almost complete dehydrogenation of the system. Therefore, methods based on physicochemical modification have been developed, which create a diffusion barrier for hydrogen atoms and prevent the temperature dissociation of titanium hydride [45–47].

A partial solution to the problem of increasing the thermal stability of titanium hydride was proposed by RFNC-VNIIEF (Sarov, Russia) and FSUE PA Mayak (Ozersk, Russia), based on the hydrogenation of spherical titanium granules of VT 1-0 grade under a pressure of up to 4 atm with a nonstoichiometric hydrogen content of 3.5 wt% [48].

Titanium hydride fractions have smooth, spherical surfaces, are durable, do not form a small explosive fraction, and exhibit increased fluidity and the ability to more densely fill voids. The density of the shot, determined by hydrostatic weighing, is 3.8 g cm$^{-3}$. Simultaneously, the thermal stability of the fraction allows applications at temperatures of up to 300 °C, such as creating composite materials for the radiation shielding of complex geometries. The use of mobile composite solutions, including those based on silicate binders, avoids the formation of voids in the protective structure.

However, scanning electron microscopy (SEM) analysis demonstrated that a titanium hydride fraction exhibited surface microcracks with sizes of 20–30 nm (figure 1). The thermal diffusion of hydrogen is possible through these microcracks, both from the surface layers and bulk fractions. The formation of microcracks was due to difference between the rate of hydrogen adsorption by the fraction surface and the rate of its diffusion into the particles of titanium metal. The resulting internal stresses led to the formation of microcracks on the surface of the hydrogenated metal.

The rate of oxidation and thermal diffusion of hydrogen at 300 °C–400 °C for the cracked titanium hydride is double that for the hydride without cracks [49, 50]. Therefore, developments in this area have aimed to obtain titanium hydride samples with minimal or no cracks. Current research has shown that the regulation of the pressure and temperature regimes for obtaining spherical titanium hydride granules is insufficient to prevent the formation of surface microcracks [48].

Figure 1. Surface of the titanium hydride fraction.
In this regard, the need for the development of methods and technologies for the surface modification of titanium hydride fractions to increase their thermal stability is clear. The artificial creation of a multi-barrier system of energy ‘traps’ in the crystal lattice of titanium hydride slows down the thermal diffusion of hydrogen. These traps can be specially introduced as modifiers of the titanium hydride surface.

This study aimed to investigate the thermal stability and phase composition of a titanium hydride fraction modified by the electrochemical deposition of titanium metal for the creation of energy traps.

2. Experimental

2.1. Materials
A titanium hydride fraction with a nonstoichiometric composition TiH$_{1.75}$, 0.2–2.5 mm in diameter, was obtained by centrifugal spraying from VT 1-0 titanium, followed by hydrogenation under pressure (up to 4 atm). The elemental composition of the titanium hydride fraction with a hydrogen content of 3.5 wt% is presented in table 1.

| Content of elements (wt%) | Ti | H | Al | C | Fe | Si | O | N |
|---------------------------|----|---|----|---|----|----|----|----|
| 95.63                     | 3.50 | 0.40 | 0.5 | 0.20 | 0.08 | 0.10 | 0.04 |

In the regime of the reflected (backscattered) electrons, the contrast largely depends on the crystallographic orientation of the grains relative to the sample surface and the chemical composition of the phases. The image obtained in this mode allows the observation of the microstructure of the material without preliminary etching of the section. Investigations using the diffraction of reflected (backscattered) electrons were carried out using a Quanta 600 FEG scanning electron microscope (FEI Company, USA). This microscope is equipped with an integrated system (Pegasus 2000), which allows the determination of grain characteristics at working magnifications from 50 to 200 000×. The survey was carried out at an accelerating voltage of 20 kV and an electron beam current of 36 nA.

The secondary electron mode provided the best resolution. Since the yield of secondary electrons depends on the angle of incidence of the primary electrons on the surface of the object, a developed surface must be obtained to obtain a high-quality image. In the mode that used secondary electrons, a high-resolution scanning electron microscope (TESCAN MIRA 3LMU, TESCAN ORSAY HOLDING, Czech Republic) was used.

The phase composition of the titanium hydride fraction during heat treatment was determined by electron probe microanalysis on an X-Max 50 energy-dispersive spectrometer (Oxford Instruments Analytical, United Kingdom). An X-Max Silicon Drift Detector was used with an active crystal area of 50 mm$^2$. The resolution stability was less than 1 eV at count rates of up to 100 000 cps. The survey was carried out at an accelerating voltage of 30 kV. This method allowed the study of the phase composition of the surface layer of a material with a thickness of $\sim$1 μm.

Differential thermal, thermogravimetric, and differential thermogravimetric analyses of the samples were performed on an STA-449 F1 Jupiter derivatograph (Germany) at a heating rate of 10 °C min$^{-1}$ in air, with a sample amount of 0.2–0.9 g, a sensitivity of 1/5, and a corundum crucible and reference standard.
3. Results and discussion

SEM analysis using secondary electrons showed that, upon thermal heating at 300 °C for 12 h in an oxygen atmosphere, microcracks grew to 100–150 nm and, with an increase in temperature to 500 °C, microcracks of up to 200–250 nm were found (figures 2(a) and (b)). Microcrack development can be caused by both thermal expansion of crystals and disruption of the surface oxide film of titanium oxides by the hydrogen released during dissociation. The second process is more pronounced than the first in this study, as confirmed by studies of the microstructure of the cleavage of a heat-treated fraction of titanium hydride (figure 3). The micrographs clearly indicate the development of microcracks in the volume of the heat-treated fraction. When heated, hydrogen can accumulate in the available voids inside the fraction, creating significant volumetric stresses which lead to a violation of both the surface and internal microstructure.

Figure 2. Microstructure of the surface of the titanium hydride fraction, heat treated at (a) 300 °C and (b) 500 °C.

Figure 3. Microstructure of the cleaved surface of the titanium hydride fraction, heat treated at 300 °C.
At 700 °C, bubble craters formed on the surface of the fraction, due to the thermal diffusion of hydrogen from the bulk to the surface (figure 4(a)). At 900 °C, the lamellar crystals of the surface were rearranged into granular crystals (figure 4(b)). As a result of oxygen diffusion from the surface into the depth of the fraction, it is possible that the oxygen flow interacts with the counter flow of hydrogen due to the formation of water vapor. This would also have led to stresses in the surface layer of the fraction and the formation of craters.

To reduce the surface defects of the titanium hydride fraction and to increase its thermal stability, its surface was modified by the electrochemical deposition of titanium metal. It was assumed that the titanium metal deposited on the surface of the fraction will act as an effective trap for hydrogen diffusion into the surface layers during thermal heating, due to the formation of a hydride phase.

To remove organic contaminants from the surface that would have interfered with the modification, the initial titanium hydride fraction was preliminarily subjected to treatment with acetone in an ultrasonic bath, followed by rinsing with ionized water.

Surface microstructure analysis of the original and modified fractions at a high resolution showed that, as a result of electrochemical deposition on the fraction surface, a granular structure of titanium molecules with a grain size of 100–200 nm was formed (figure 5).

Figure 6 shows the microstructure of the cleaved surface of the modified titanium hydride fraction. The coating displayed a homogeneous structure with high adhesion to the surface of the fraction and a poorly defined interface. The thickness of the coating was approximately equal over the entire surface at ∼1.0–1.5 μm.

Differential thermal analysis of the initial and electrochemical deposition-modified titanium hydride fractions showed the presence of small endothermic effects at 100 °C–120 °C (figure 7) and some weight reduction due to the removal of sorption water (figure 8). Intense endothermic effects at 557.7 °C and 779.3 °C, respectively, on the unmodified and modified fractions corresponded to the maximum rate of titanium hydride dissociation and were accompanied by weight loss. The dehydrogenation process for the unmodified fraction began and ended, respectively, at 462.9 °C and 722.8 °C. For the modified fraction, these process times corresponded to 694.7 °C and 844.6 °C, respectively (figure 7). For the unmodified and modified fractions of titanium hydride, a broadening of the exo effect was observed at temperature ranges of 700 °C–800 °C and 850 °C–900 °C, respectively. This may have been due to the oxidation of titanium metal in the surface layer. This was indicated by weight gains of 0.12% (figure 8, curve 1) and 0.08% (figure 8, curve 2) in these temperature ranges, respectively, due to the formation of the rutile phase.

Thus, the modification of the titanium hydride fraction by the electrochemical deposition of metallic titanium shifted the onset of hydrogen thermal diffusion up by 231.8 °C, which indicated an increase in the thermal stability of the fraction.
Studies of the phase composition of titanium hydride fractions by electron probe microanalysis have shown that heat treatment of titanium hydride at temperatures of 100 °C–400 °C led to an increase in the hydride phase in the surface layer of up to 85% and a decrease in the phase of metallic titanium. This effect was observed for both the modified and unmodified fractions (table 2). This was due to the redistribution of atomic hydrogen in the structure of the fraction and the hydrogenation of metallic titanium in the surface layer, due to the diffusion of hydrogen from the bulk to the surface during heating. The formation of a submicrocrystalline structure during heat treatment led to a decrease in the effective diffusion coefficient of hydrogen in titanium and an increase in the accumulation of hydrogen in the bulk, which was caused by the longer grain boundaries in submicrocrystalline samples compared to coarse crystalline samples [7].

An increase in temperature to 500 °C led to a decrease in the concentration of titanium hydride in the unmodified fraction to 54.9%. An increase in the titanium metal phase indicated dehydrogenation occurred.

Figure 5. Surface of (a) the initial fraction of titanium hydride and (b) with a sprayed titanium coating.

Figure 6. Microstructure of the chip surface of the fraction modified with titanium metal.
The content of the hydride phase in the modified fraction increased to 87.2% due to the ongoing hydrogenation of titanium metal.

Heat treatment at 700 °C significantly reduced the concentration of titanium hydride in the unmodified fraction to 22.7 wt% and in the modified fraction to 76.8 wt%. In the unmodified fraction, intense oxidation of titanium metal occurred with the formation of the rutile phase. Slight formation of titanium oxide (TiO₂) also occurred in the surface layer of the modified fraction. Heat treatment of the materials at 900 °C led to the intense dissociation of titanium hydride and the formation of titanium oxide in the surface layer (table 2).
4. Conclusions

To increase the thermal stability of titanium hydride, the creation of a multi-barrier system of energy ‘traps’ on its surface which prevent the diffusion of hydrogen into the environment is a promising technique. Titanium hydride obtained by hydrogenation of the titanium fraction exhibited surface microcracks, which increased the surface which prevent the diffusion of hydrogen into the environment is a promising technique. Titanium hydride powder via calciothermic low temperature reduction Scr. Mater. 130 256–9

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