Improving the radiation-thermal stability of titanium hydride

R N Yastrebinsky, A A Karnauhov and A V Yastrebinskaya
Belgorod State Technological University named after V.G. Shukhov, 46, Kostyukova str., Belgorod, 308012, Russia

E-mail: yrndo@mail.ru

Abstract. The paper presents the results of studies of the thermal stability of titanium hydride and titanium hydride containing a borosilicate framework. It is shown that the presence of chemically attached boron atoms on the surface of titanium hydride particles increases the initial dissociation temperature of titanium hydride. The phase composition and imperfection of titanium hydride crystals in the temperature range of 100-700 °C were studied. An increase in the defectiveness of the structure of a titanium hydride crystal during its heat treatment is shown. Mechanisms for modifying the surface of titanium hydride by surface assembly and the creation of a borosilicate framework have been established. It was shown that the ongoing structural-phase transformations in the borosilicate coating activate solid-phase interactions and contribute to the fixation of borosilicate. Based on the data of thermogravimetric analysis, it was shown that the modification of titanium hydride increases its thermal stability by 185 °C, shifting the onset of dehydrogenation processes to the high-temperature region from 463 °C to 649 °C.

1. Introduction
One of the priority areas of research for metal hydride systems is to increase their radiation-thermal resistance in order to expand the scope of application in modern energy as neutron protection materials. The most promising is the use of titanium hydride as a neutron moderator, having 9.12×10^{22} hydrogen atoms per 1 cm^{3} of material. In titanium hydride, neutron attenuation in the fast energy region occurs not only due to their interaction with hydrogen nuclei, but also with titanium nuclei, and the neutron interaction cross sections in the energy region of more than 2-3 MeV are approximately equal. Thus, the total cross section for the interaction of neutrons with an energy of 5 MeV with titanium nuclei is 3 barn, and the cross section for inelastic scattering, due to which a significant energy release occurs, is 1.3 barn, which is comparable to the cross section for hydrogen at the same energy. All this determines the optimality of using titanium hydride as a material for radiation protection, especially in cases where minimization of the dimensions and mass of a nuclear power plant (NPP) is required. Due to its high efficiency, titanium hydride is used in a number of projects as part of radiation protection at nuclear facilities [1-3].

Increasing the initial temperature of thermal diffusion of hydrogen in titanium hydride is one of the main problems of its use in radiation protection constructions and ensuring the safe operation of stationary and transport nuclear power plants. The evolution of hydrogen from titanium hydride during thermal diffusion not only causes a loss in the performance properties of titanium hydride, but also leads to embrittlement of metals and, in some cases, the formation of explosive explosive gas mixture [4-5].

One way to increase the radiation-thermal stability of titanium hydride is to artificially create hydrogen impurity "traps" on its surface. The main parameter of these "traps" is the energy of their
interaction with hydrogen. In this direction, the use of framework borosilicates having borate groups with 2p unfilled atomic orbitals at the external level is effective. The boron atoms acting as substitutional impurities are able to efficiently form boron-hydrogen complexes. The creation of a borosilicate framework on the surface of titanium hydride is possible by modifying it from solutions using the sol-gel technology [6-8].

In this regard, this work presents the results of studies of the thermal stability of unmodified titanium hydride and titanium hydride modified from a solution with sodium borosilicate.

2. Materials and methods
A dispersed titanium hydride powder with a particle size of 10–20 μm and a content of the main phase TiH$_{1.924}$ was used as a radiation protective filler.

Modification of titanium hydride was carried out from the solution according to the "sol-gel" technology by surface assembly. The essence of this method is the preliminary immobilization on the surface of titanium hydride particles of chemically active compounds in the form of sodium alkyl silicates, capable of further interaction with anchor groups (BO$_3^-$, B(OH)$_4^-$) of the main modifier solution in the form of boric acid through chemical bonds [9].

As modifiers, boron acid H$_3$BO$_3$ of the grade "c.p." (GOST 9656-75) and sodium ethyl siliconate (RSi(OH)$_2$ONa, where R = C$_2$H$_5$, TU-6-02-696-76) were used.

Differential thermal (DTA), thermogravimetric (TG) and differential thermogravimetric (DTG) analyzes of the samples were carried out on a STA-449 F1 Jupiter derivatograph (Germany) at a heating rate of 10 deg/min.

X-ray phase analysis (XRD) and X-ray diffraction analysis were performed on an ARL XTRA X-ray diffractometer (Switzerland) with CuK$_\alpha$ radiation ($\lambda_{K\alpha} = 1.542$ Å) and a nickel filter according to the procedure using an ASTM card file (USA).

3. Results and discussion
Analysis of the diffraction patterns of titanium hydride heat-treated in the temperature range 100-700 °C showed the constancy of the phase composition up to 500 °C (figure 1). At 100 °C, interplanar spacings d = 2.5636; 2.2220; 1.5691 correspond to titanium hydride with a non-stoichiometric hydrogen content TiH$_{1.924}$ cubic crystal system and crystallographic indices hkl {104}. Heat treatment of titanium hydride at temperatures from 300 to 500 °C does not lead to a change in the phase composition. In this case, there was a change in the intensity and values of interplanar distances d of the main reflex.

![Figure 1. Diffraction patterns of a fraction of titanium hydride, heat-treated at different temperatures: 1 - TiH$_{1.924}$; 2 - TiO$_2$; 3 – TiO.](image-url)
At a temperature of 700 ºС, the diffraction pattern of the titanium hydride samples changes with the formation of the main reflexes with an interplanar distance d = 3.2608; 1.8715 Å, corresponding to titanium oxide TiO hexagonal crystal system, and reflexes with d = 2.2675; 1.7554 Å, corresponding to the rutile phase of TiO$_2$ tetragonal syngony. In this case, the titanium hydride phase is maintained with an interplanar distance d = 2.5601; 1.5643 Å.

The assessment of the defectiveness of titanium hydride crystals in the temperature range 100-700 ºС on the basis of the maximum reflection data is presented in the table 1. These changes indicate a defective structure and a change in the unit cell parameters of the crystal.

**Table 1. Diffraction characteristic of the maximum titanium hydride reflex at different temperatures.**

| T, ºС | 2θ, º  | Area | Intens., imp/s | Half Width, Å | d, Å | % max. |
|-------|--------|------|---------------|---------------|------|--------|
| 100   | 35,100 | 637,259 | 6069 | 0.4150 | 2.5565 | 100,00 |
| 300   | 35,100 | 658,807 | 5707 | 0.4250 | 2.5565 | 100,00 |
| 400   | 35,100 | 693,768 | 5749 | 0.4350 | 2.5565 | 100,00 |
| 500   | 35,100 | 745,622 | 6459 | 0.4100 | 2.5565 | 100,00 |
| 700   | 35,150 | 393,607 | 1040 | 0.8350 | 2.5530 | 78,02  |

It is known that titanium hydride of stoichiometric composition TiH$_2$ is characterized by a face-centered cubic lattice [10]. Moreover, compositions with a lower hydrogen content also have cubic syngony, but with the presence of tetrahedral voids at titanium atoms [11].

The analysis shows that in the temperature range 100-400 ºС, the diffraction line is broadened d = 2.5565 Å from 0.4150 to 0.4350 Å. In this case, the interplanar spacing remains constant, which indicates the invariability of the unit cell period of the crystal (a). According to the data of [12–13], the broadening (smearing) of diffraction lines is due to the presence of microstrains of the crystal lattice and indicates an increase in the dislocation density (ρ), and their growth is proportional to the square of the broadening value (β) by the formula:

$$\rho = \frac{\pi \beta^2 c \theta}{16 b^2}, \text{m}^{-2}$$  \hspace{1cm} (1)

where θ is the angle corresponding to the maximum of the x-ray line; b is the Burgers vector.

Thus, in the temperature range from 100 to 400 ºС, the dislocation density in the structure of the titanium hydride crystal increases. An increase in temperature to 500 ºС reduces the density of dislocations, which, according to [14], is caused by the annealing regime without changing structural elements. A further increase in temperature to 700 ºС leads to a sharp increase in the density of dislocations and the degree of imperfection of the crystal. In this case, the interplanar distance decreases to d = 2.5530 Å, which indicates the presence of microstresses in the crystal lattice of titanium hydride and a less dense filling of the plane of atoms by the structural elements. At titanium atoms, tetrahedral voids arise due to the diffusion of hydrogen. This is consistent with data [14], where it was shown that a decrease in the hydrogen content in titanium hydride leads to structural imperfection and the presence of voids in the fcc sublattice between titanium atoms.

A change in the interplanar distance leads to a change in the period of the unit cell of the crystal, which for the cubic system of titanium hydride is determined by the formula [15]:

$$a = d \sqrt[3]{h^2+k^2+l^2}$$  \hspace{1cm} (2)

For the temperature range of 100-500 ºС, the cell period is a = 4.4280 Å, and for 700 ºС, a = 4.4219 Å. In this case, the unit cell period of the reference crystal is a = 4.4200 Å (according to the ASTM card index for the TiH$_2$ crystal). Thus, an increase in temperature to 700 ºС leads to an approximation of the unit cell parameters to the parameters of the reference crystal. It can be assumed that an increase in temperature and hydrogen thermal diffusion processes lead to additional hydrogenation of titanium metal in the surface layer and the formation of crystals with a structure close to TiH$_2$. In this case, a
general significant decrease in the intensity of hydride phases and the formation of a rutile phase occur, which indicates intense processes of oxidation and dissociation of titanium hydride (figure 1).

Modification of titanium hydride was carried out according to the method of surface assembly with preliminary immobilization of an activating organosilicon layer based on sodium ethylsilicate (ESN) according to the figure 2 and 3:

Figure 2. Surface activation of titanium hydride with sodium organoborosilicate.

Figure 3. Synthesis on the surface of titanium hydride borosilicate.

The heat treatment of the modified titanium hydride at a temperature of 150 °C leads to the intense occurrence of polycondensation processes and the formation of a spatially cross-linked organoborosilicate polymer structure on its surface. Further heat treatment at 300 °C leads to the removal of ethyl radicals and screening of the surface of titanium hydride particles with borosilicate (figure 3).

Differential thermal analysis of the initial and titanium hydride modified with borosiliconate showed the presence of small endo-effects at 50-100 °C and some decrease in mass due to the removal of sorption water (figure 4 and 5). Intensive endothermic effects at 557.7 and 732.7 °C, respectively, on unmodified and modified titanium hydride are caused by dehydrogenation processes and are accompanied by weight loss. In this case, the beginning of dissociation of unmodified titanium hydride begins and ends, respectively, at 462.9 °C and 722.8 °C (figure 4), and for modified titanium hydride, these processes correspond to 648.6 °C and 797.2 °C (figure 5).

For the modified titanium hydride, the presence of an endo-effect at 505.5 °C was noted, which may be due to surface fusion of borosilicate. The endo-effect at 884.4 °C can be caused by the polymorphic conversion of α-Ti with a hexagonal crystal lattice into β-titanium with a cubic body-centered lattice having a lower atom packing density. This polymorphic transition contributes to the intensification of
further processes of titanium oxidation, which is expressed by the presence of exoeffects in the range of 900–950 °C.

Figure 4. Derivatogram of unmodified titanium hydride.

Figure 5. Derivatogram of modified titanium hydride.

Thus, the studies have shown the feasibility of a preliminary process of modifying a tungsten oxide-based powder filler in order to increase its compatibility with the polymeric polyimide matrix, which increases the density gain of the polymer composite by 16.0%.
4. Conclusion

- The creation of substitutional impurities in the form of boron atoms on the surface of titanium hydride makes it possible to increase its thermal stability due to the capture of diffusing hydrogen in the surface layer and the formation of boron-hydrogen complexes.
- As a surface modifier of titanium hydride, it is effective to use borosilicates having borate groups with 2p atomic orbitals unfilled at the external level.
- During heat treatment of unmodified titanium hydride, an increase in the density of dislocations and a decrease in the period of the unit cell of the crystal occur.
- Modification of titanium hydride leads to the constancy of the structural elements of the crystal and an increase in the initial temperature of thermal diffusion of hydrogen by 185 °C.

Acknowledgments

The reported study was funded by RFBR, project number 19-38-90024.

References

[1] Yastrebinsky R N 2016 Distribution neutron and gamma of radiation in the protective composite with various content of atoms of boron Probl. of Atom. Sci. and Techn. 5 66–72
[2] Yastrebinsky R N 2017 Decrease gripping gamma–radiation scale composite neutron and protective material on the basis of the modified hydride of the titan with various content of atoms of bor Probl. of Atom. Sci. and Techn. 4(110) 103–6
[3] Sickafus K E 2007 Radiation-induced amorphization resistance and radiation tolerance in structurally related oxides Nature materials 6(3) 217-23
[4] Fukai Y 1993 The Metal-Hydrogen System. Basic Bulk Properties Springer Series in Materials Science 21 1237
[5] Yastrebinsky R N 2018 Attenuation of Neutron and Gamma Radiation by a Composite Material Based on Modified Titanium Hydride with a Varied Boron Content Rus. Phys. J. 12(60) 2164–8
[6] Chernov V M 2007 Structural materials for fusion power reactors - the RF R&D activities Nuclear Fusion 8(47) 839-48
[7] Schneider M and Froggatt A 2016 The World Nuclear Industry Status Report Mycle Schneider Consulting (MSC) 12
[8] Yastrebinsky R N, Yastrebinskaya A V, Pavlenko Z V and Karnauhov A A 2019 Modified tungsten oxide-based filler for radiation protective polyimide composites J. of Phys.: Conf. Series 1353 012073
[9] Lisichkin G 2003 Chemistry of grafted surface compounds (Moscow: FIZMATLIT) p 592
[10] Wang P, Li H, Ren X and Yuan R 2017 HfB2-SiC-MoSi2 oxidation resistance coating fabricated through in-situ synthesis for SiC coated C/C composites J. of Alloys and Compounds 722
[11] Zhou L, Fu Q, Huo C and Tong M 2019 Mullite whisker-mullite/yttrium aluminoisilicate oxidation protective coatings for SiC coated C/C composites Ceramics International 45(18)
[12] Fantidis J G 2009 Multiple fast neutron and gamma-ray beam systems for the detection of illicit materials J. of Radioanalytical and Nuclear Chemistry 295(2)
[13] Pogozhev Yu S, Lemesheva M V, Potanin A Yu and Rupasov S I 2019 Heretophase Ceramics in the Hf–Si–Mo–B System Fabricated by the Combination of SHS and Hot Pressing Methods Russian Journal of Non-Ferrous Metals 60(4) 380-9
[14] Choi E and Ejiri H 1996 Search for Time-Correlated Fast Neutrons from DD Fusion at Room Temperature Japanese Journal of Applied Physics A 5(35) 2793-6
[15] Nasseri M M 2018 Comparison of HfB2 and ZrB2 behaviors for using in nuclear industry Annals of Nuclear Energy 114 603-6