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Increase in Thermal Stability of Hydride of the Titanium

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Abstract

The paper presents the results of studies of the modification of the surface of a fraction of titanium hydride with borosiloxanes in order to increase its thermal stability at high temperatures and protect titanium from oxidation for possible use as a heat-resistant neutron-protective material in nuclear power engineering. A theoretical model has been developed for modifying a fraction of titanium hydride with borosilicate by sol-gel technology from aqueous solutions of sodium organosilicinate and boric acid. The technology for modifying titanium hydride consists in the preliminary chemical activation of the surface of the fraction by a silicone oligomer - sodium organosilicinate (OSN) followed by treatment with boric acid, separation of the solid phase of titanium hydride and subsequent drying at 100 °C. During the synthesis of sodium borosilicate and its thermal treatment in the temperature range 100-500 °C, complex structural-phase rearrangements were observed. At 100 °C, an amorphous-crystalline silicate of CH_3 $(Si_{30.4}B_{1.6}O_{64})$ Na monoclinic syngony with large crystal lattice parameters was formed. The thermal treatment of the borosilicate coating at 300 °C led to a change in the radiographic characteristics of the crystalline phase and the formation of a monoclinic $NaBSi_2O_5(OH)_2$ structure with continuous layers of silicon-oxygen tetrahedra. Further crystallization of borosilicate at a temperature of 500 °C leads to the formation of a silicate of the skeleton type $NaBSi_3O_8$ of triclinic syngony. Above 500 °C, sodium borosilicate passes into a glassy state.

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1. INTRODUCTION

At present, there is an increasing interest in studying the general laws and properties of the titanium-hydrogen system, since the interaction of hydrogen with titanium in a wide range of temperatures is a particularly important problem in physical materials science.

The problem of the stability of titanium hydride is studied both from the point of view of reducing its dissociation temperature to obtain effective hydrogen accumulators and to increase its thermal stability, for example, for possible use in nuclear power engineering as a neutron-protective material [1-2].

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In this direction, the use of titanium hydride in the form of spherical pellets is found. A fraction of titanium hydride, obtained by the through saturation of the melt of metallic titanium with hydrogen in centrifugal spraying plants, has a higher thermal stability in comparison with the powder. This circumstance makes it possible to use a fraction of titanium hydride as a filler for neutron-protective composites on various binders [3-4].

The operating conditions of these materials determine the possibility of thermal diffusion of hydrogen during radiation-thermal heating, which causes the fire hazard of the radiation protection structure. In this regard, the search for ways to increase the thermostability of a fraction of titanium hydride based on modifying its surface is relevant.

It is known that the main glass-forming components of boroaluminosilicate frit-based coatings for metals are oxides of SiO_2, Al_2O_3 and boric anhydride B_2O_3. To improve the technological properties (spreadability, wetting power) alkali oxides are introduced into the coatings.

In this paper, we present the results of studies of the modification of the surface of a fraction of titanium hydride with borosiloxanes in order to increase its thermal stability at high temperatures and protect titanium from oxidation. From the theoretical and practical point of view, it is interesting to use materials of the "core-shell" type, where titanium hydride is used as the core, and the borosiloxane shell and titanium oxide interfere with the hydrogen output during heat treatment of the material.

2. MATERIALS AND METHODS

Modification of the surface of the fraction of titanium hydride was carried out chemically from aqueous solutions of silicone oligomer and boric acid. The use of the boron-containing component is due to the high cross section for neutron absorption in the thermal and epithermal regions of the spectrum by boron atoms, which leads to a decrease in the density of the thermal neutron flux and the level of capture gamma radiation.

The general requirement for coatings is to protect the surface of a fraction of titanium hydride from destructive processes in fractions at macro and micro levels at elevated temperatures (> 3000 °C). The composition of the coating was selected in such a way that during thermal treatment of titanium hydride a solid film, stable at a given temperature, was formed, reliably isolating the surface of titanium hydride from dissociation and subsequent oxidation of titanium.

3. RESULTS

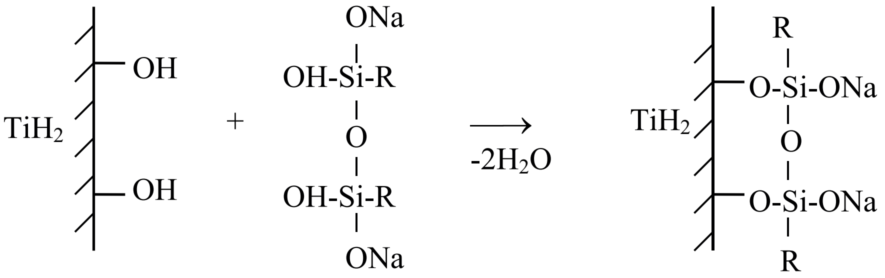
As shown by experiments to achieve a noticeable adsorption of boric acid (H_3BO_3) from the aqueous solution on the surface of the fraction of titanium hydride was not possible. In connection with this, preliminary activation of the surface of the fraction of titanium hydride by the organosilicon oligomer was made using the example of sodium organosilicate.

The theoretical approach to the development of a borosilicate coating for modifying the surface of a fraction of titanium hydride is the following approach.

To create active centers on the surface of the fraction of titanium hydride, on which boron-containing substances, for example boron oxide, can be fixed, a organosiliconate organosiliconate (OSN) organosilicon activator is used, soluble in water and capable of creating a hydrolytically stable bond system on the surface of titanium hydride.

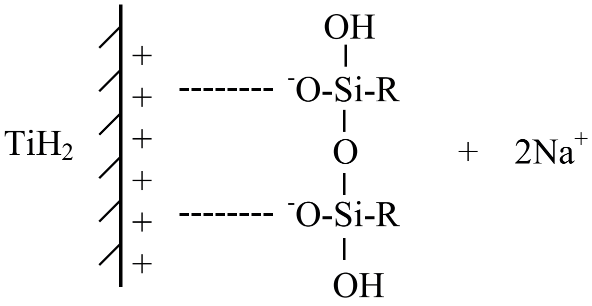
We can assume the following models of interaction of titanium hydride with an organosilicate activator:

a) reaction of sodium organosilicinate with hydroxyl groups of the surface of the fraction



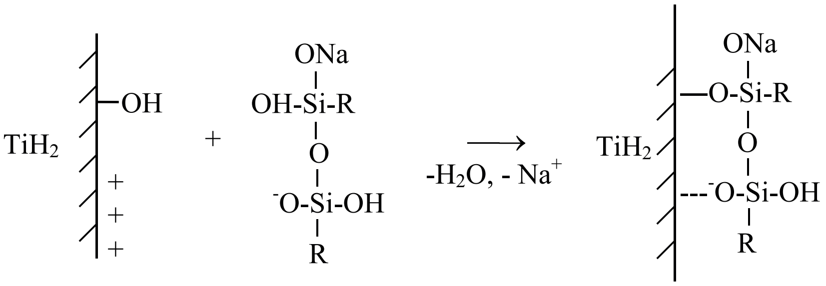
(1)

b) electrostatic attraction



(2)

or summing action:



(3)

Long-chain molecules formed as a result of reactions (1-3) are able to screen large areas of the surface of a fraction of titanium hydride.

The study of the electrokinetic properties of the surface of the fraction is of interest, since the charge of the surface can affect the interaction of the modifier with the substrate and its fixation [5].

The electrokinetic potential of the surface of a fraction of titanium hydride in distilled water is positive (Figure 1). It decreases with increasing pH, passing from a positive value to a negative potential at pH = 12. Thus, the charge of the surface of the fraction is determined by the concentration of the potential-determining ions H + and OH-.

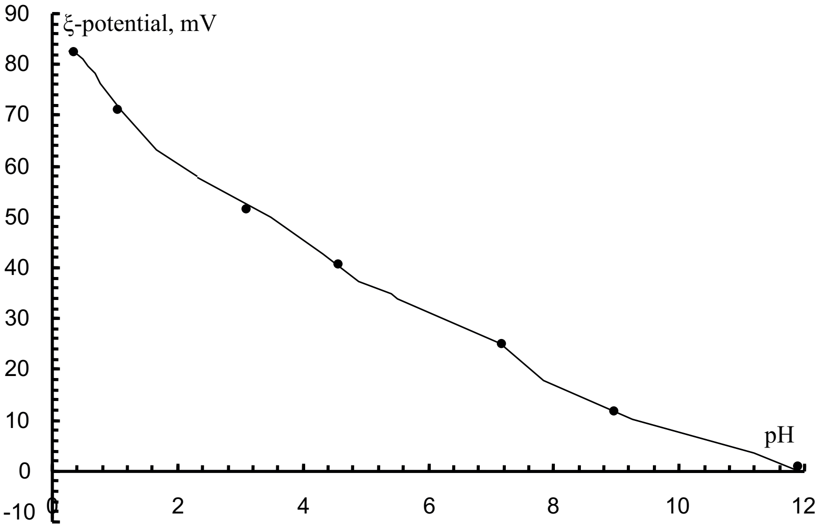


Figure 1: Change in the electrokinetic ξ-potential of the surface of a fraction of titanium hydride as a function of the pH of the aqueous solution.

The isotherms of the adsorption of OSN by the surface of a fraction of titanium hydride from aqueous solutions in the concentration range studied are positive. With an increase in the equilibrium concentration of the activator (OSN) in the solution, the amount of adsorption increases (Figure 2).

An increase in the concentration of OSN (Figure 2) causes a decrease in the electrokinetic potential of the fraction of titanium hydride from +52.5 mV to +22.4 mV at a concentration of OSN in the monolayer of 97.7 mg / g. The kink point on the curves of the dependences T = f (C_{MSN}) and ξ = f (C_{MSN}) corresponds to the completion of the formation of the adsorption monolayer of OSN on the surface of the fraction..

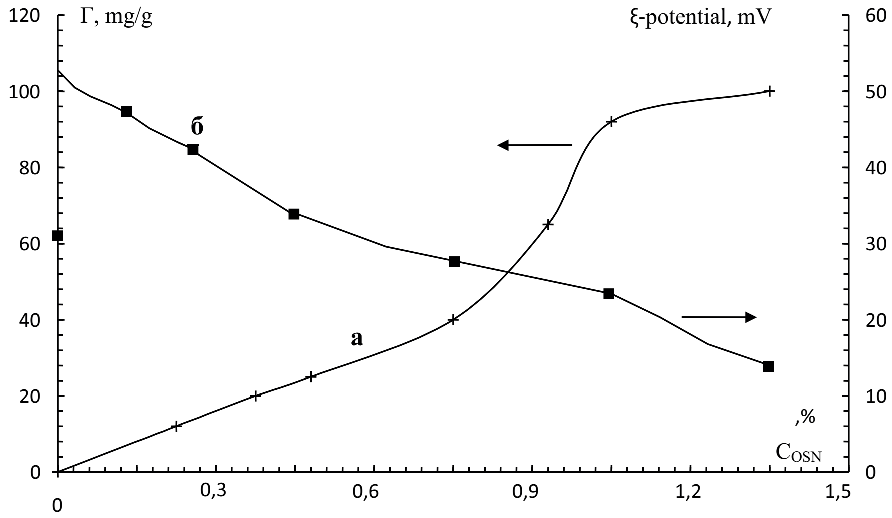
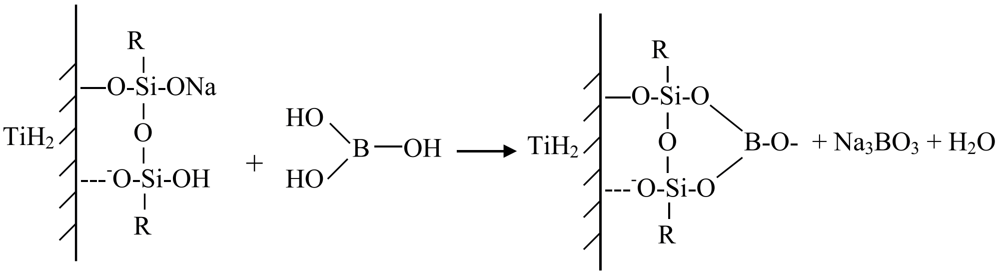


Figure 2: Isotherm of adsorption of OSN from aqueous solutions to fractions of titanium hydride (a) and the change in the ξ potential of the surface of hydride (b) as a function of the concentration of OSN.

The presence on the surface of a fraction of titanium hydride of the polysiloxane shell of the modifier leads to the formation of active centers in the form of silanol (-OH) and silanolate (Si-ONa) groups, on which further modification by the boron-containing component is possible.

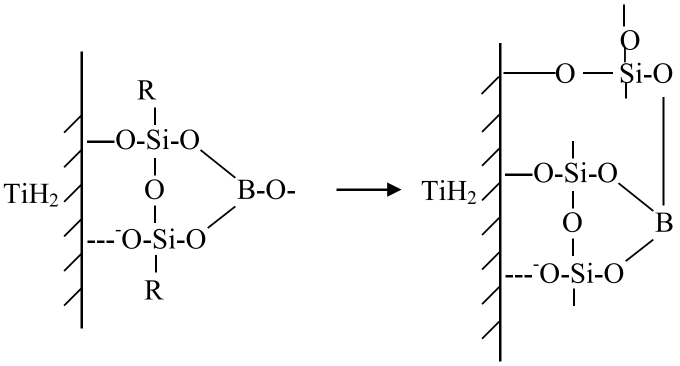
The modification of the fraction of titanium hydride containing the polysiloxane shell from the aqueous solution with boric acid was carried out. Taking into account the formed active centers of the polysiloxane shell on the surface of the fraction of titanium hydride, the interaction in the aqueous solution proceeds according to the scheme:



(4)

Increasing the temperature promotes an increase in the reaction rate 4.

The heat treatment of the adsorbed titanium hydride borosiloxane modifier sorbed on the surface at a temperature of 100 °C resulted in complete condensation of the borosiloxane coating on the surface of the titanium hydride fraction as follows:



(5)

The above schemes (4 and 5) indicate the possibility of chemical interaction of borosiloxane coating with titanium hydride.

In view of the roughness of the surface of the fraction of titanium hydride, the presence of pore space and microcracks on the surface, it can be assumed that the borosiloxane coating on the surface of the fraction will also be formed along the anchoring type with mechanical fixation.

In borosiloxane oligomeric coating, the proportion of the crystalline phase increases significantly compared to the pure borate coating (Table 1, Figure 3).

Table 1: X-ray characterization of boron coating heat-treated at 100 °C for 1 hour (in the base «Crystallographica Search-Match», USA).

Angle	Area	Intensity	Half width	*d*, Å	% Maxm.
7.620	1261.378	7295	0.5050	11.6013	100.00
15.400	576.255	1644	0.6250	5.7534	22.54
23.180	270.365	749	0.7500	3.8370	10.27
24.000	423.981	1653	0.5350	3.7077	22.66
27.240	385.950	946	1.0000	3.2736	12.97
33.080	232.450	838	0.8250	2.7078	11.49
34.201	355.514	931	0.7250	2.6217	12.76
36.841	162.324	1238	0.4300	2.4396	16.97

According to the data base, the reaction product of boric acid and sodium organosilicate is a compound of the composition $CH_3(Si_{30.4}B_{1.6}O_{64})Na$ of monoclinic syngony with large parameters of the crystal lattice (a = 9.659, b = 20.461, c = 9.831 Å).

The heat treatment of the borosiloxane coating at 300 °C resulted in a change in the radiographic characteristics of the crystalline phase (Figure 4, Table 2).

The crystalline phase of the sample is represented by reflexes with d = 11.57; 3.71; 5.77; 2.44 Å. The phase composition of the sample corresponding to the borosilicate $NaBSi_2O_5(OH)_2$, which belongs to sheet silicates, was identified. This silicinate has

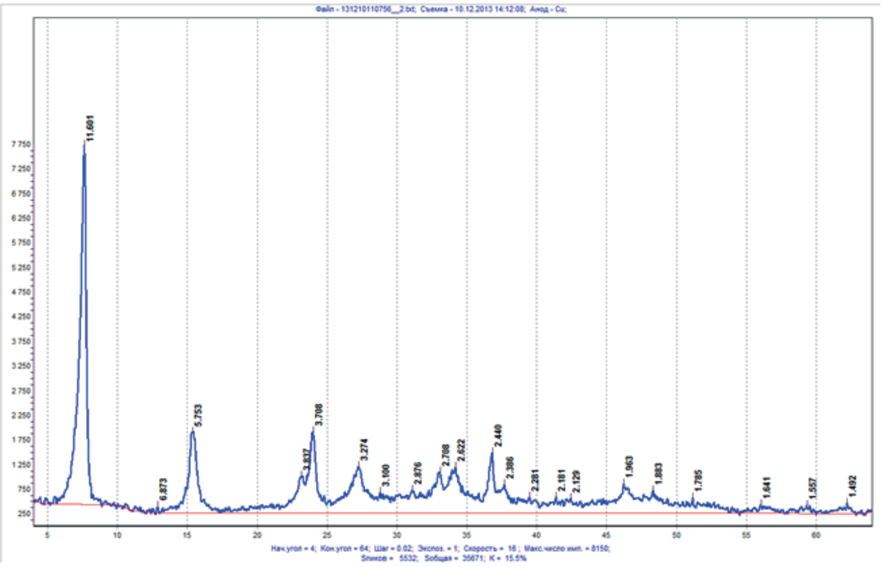


Figure 3: Diffractogram of borosilicate coating, heat-treated at 100 °C for 1 hour.

a monoclinic structure with continuous layers of silicon-oxygen tetrahedra with the parameters: (a -7,992; в-7,085; с-4,918 Å).

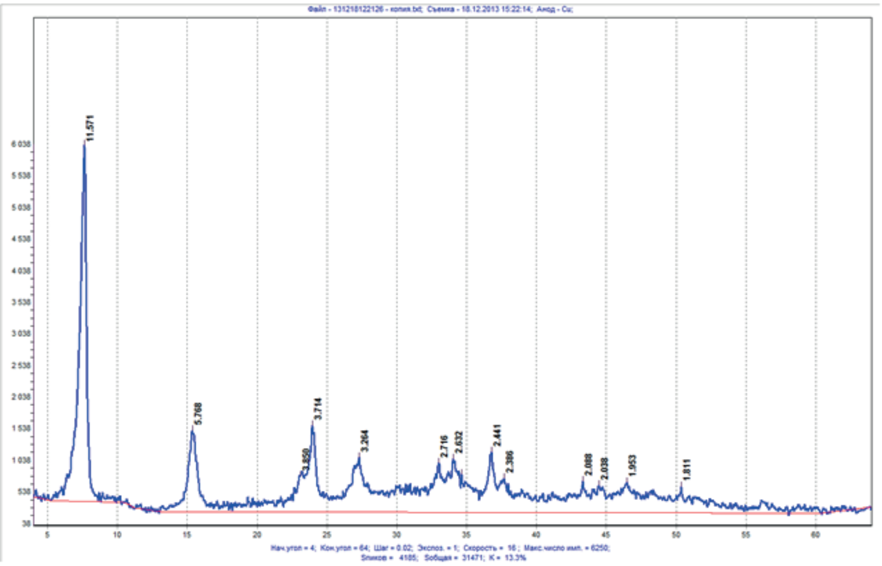


Figure 4: Diffractogram of borosilicate coating, heat treated at 300 °C for 1 hour.

An intensive chemical reaction was observed for the combined coating on the basis of boric acid (modifier) and polyorganosilicic sodium (activator), heat treated at 500 °C for 1 hour, resulting in the crystallization of the reaction product - sodium borosilicate (Figure 5, Table 3).

The crystalline phase of this coating is represented by reflexes with d = 11.5710; 3,7138; 5,7683; 2,4409 Å. According to the database "Crystallographica Search-Match", sodium borosilicate $NaBSi_3O_8$ of triclinic syngony (a = 7.85, b = 12.38, c = 6.81 Å) is

Table 2: X-ray characterization of borosilicate coating, heat-treated at 300 °C for 1 hour (in the base «Crystallographica Search-Match», США).

Angle	Area	Intensity	Half width	d, Å	% Maxm.
7.640	975.558	5642	0.5300	11.5710	100.00
15.360	512.421	1289	0.6750	5.7683	22.85
23.100	410.545	565	1.1000	3.8501	10.01
23.960	399.732	1364	0.5850	3.7138	24.18
27.320	277.046	868	0.8850	3.2642	15.38
32.980	203.615	778	0.6300	2.7158	13.79
34.061	457.878	842	0.6950	2.6321	14.92
34.661	211.013	602	0.4250	2.5879	10.67
36.821	256.796	962	0.5900	2.4409	17.05

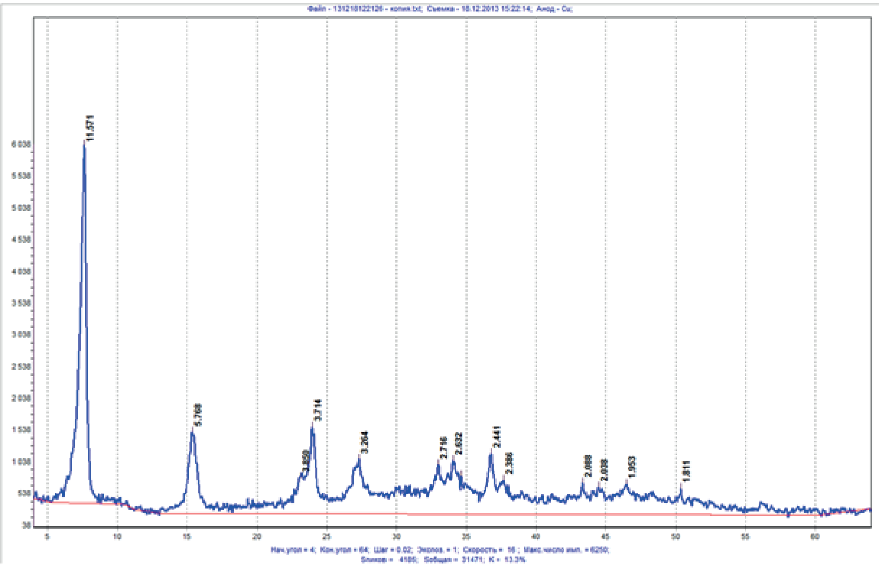


Figure 5: Diffractogram of borosilicate coating heat treated at 500 °C for 1 hour.

synthesized in this system, which has the structure of a silicate of the framework type. A feature of this class of silicates is the presence of internal cavities and entrance windows, in which molecules with a diameter of 0.1-0.3 nm can be absorbed [6, 7].

Thus, during the synthesis of sodium borosilicate and its thermal treatment in the temperature range 100-500 °C, complex structural-phase rearrangements were observed, proceeding according to the following scheme:

water solution: H_3BO_3 + $RSi(OH)_2ONa$ (where, R = CH_3)
↓ (100°C)
oligomer powder: $R(Si_{30-4}\ B_{1-6}\ O_{64})$ Na monoclinic system

Table 3: X-ray characterization of borosilicate coating heat-treated at 5000C for 1 hour (in the base «Crystallographica Search-Match», США).

Angle	Area	Intensity	Half width	d, Å	% Maxm.
7.640	975.558	5642	0.5300	11.5710	100.00
15.360	512.421	1289	0.6750	5.7683	22.85
23.100	410.545	565	1.1000	3.8501	10.01
23.960	399.732	1364	0.5850	3.7138	24.18
27.320	277.046	868	0.8850	3.2642	15.38
32.980	203.615	778	0.6300	2.7158	13.79
34.061	457.878	842	0.6950	2.6321	14.92
34.661	211.013	602	0.4250	2.5879	10.67
36.821	256.796	962	0.5900	2.4409	17.05
37.701	250.865	533	0.6100	2.3859	9.45

↓ (300°C)

borosilicate sheet $NaBSi_2O_5\ (OH)_2$ monoclinic system

↓ (500°C)

borosilicate $NaBSi_3O_8$ of the triclinic system

Monoclinic and triclinic symmetry in crystals belong to the lowest category of syngonies, in which there are no symmetry axes of higher denomination, and there may be second-order axes (L^2) in the monoclinic system and only a center of symmetry in triclinic syngony [8-10].

Crystals of monoclinic syngony are characterized by the shapes of crystals in the form of rhombic prisms (similar to mica), and for crystals of triclinic syngony, combinations of pinacoid and monohedra.

4. CONCLUSIONS

1. A theoretical model has been developed for modifying a fraction of titanium hydride with borosilicate by sol-gel technology from aqueous solutions of sodium organosilicinate and boric acid. The technology for modifying titanium hydride consists in the preliminary chemical activation of the surface of the fraction by a silicone oligomer - sodium organosilicinate (OSN) followed by treatment with boric acid, separation of the solid phase of titanium hydride and subsequent drying at 100 °C.

2. The electrokinetic potential of the surface of the fraction of titanium hydride in the distilled water is positive. It decreases with increasing pH, passing from a positive value to a negative potential at pH = 12. Thus, the charge of the surface of the fraction of titanium hydride is determined by the concentration of potential-determining ions H + and OH-.

3. Adsorption of OSN as a function of the pH of the medium was studied. The adsorption of OSN increases with the increase in the concentration of OSN and the pH of the solution. In the acidic medium, the adsorption of OSN does not occur. Noticeable absorption of OSN by the surface of a fraction of titanium hydride is observed at pH> 6. An increase in the concentration of OSN causes a decrease in the electrokinetic potential of the fraction of titanium hydride from +52.5 mV to +38.4 mV at a concentration of OSN in the monolayer of 7.5 mg / g.

4. The structure-phase composition of borosilicate-coating in the temperature range 100-500 °C continuously changed. At 100 °C, an amorphous-crystalline silicate of $CH_3(Si_{30.4}B_{1.6}O_{64})Na$ monoclinic syngony with large parameters of the crystal lattice (a = 9.659, b = 20.461, c = 9.831 Å) was formed. The thermal treatment of the borosilicate coating at 300 °C led to a change in the radiographic characteristics of the crystalline phase; a crystalline borosilicate of $NaBSi_2O_5(OH)_2$ is formed, a monoclinic structure with continuous layers of silicon-oxygen tetrahedra with parameters: (a-7.992; v-7.085; c-4.918 Å). Further crystallization of borosilicate occurs at a temperature of 500 °C to form a silicate of the framework type NaBSi3O8 of triclinic syngony (a = 7.85, b = 12.38, c = 6.81 Å). Above 500 °C, sodium borosilicate was transformed into a glassy state.

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