Heat-resistant structural composite material based on modified titanium hydride

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Abstract. The paper presents the results of studies of technological parameters of production, physical, mechanical, thermophysical properties and processes of gas formation during thermal heating of a composite material based on a modified fraction of titanium hydride and a Portland cement binder. The introduction of a plasticizing additive into the composite makes it possible to improve the technological and strength characteristics of the protection material. It has been shown that the decrease in the physical and mechanical characteristics of the material does not exceed 10 - 20\%, which indicates its thermal stability in terms of the main performance indicators. The introduction of a boron additive does not significantly affect the physical and mechanical properties of the composite. It was found that the main gas evolution occurs during the drying of composites and practically ends after its completion. Reheating the cooled block to the initial heating temperature (300-350 °C) practically does not cause gas or water evolution, if during the cooling period the material had no contact with water.

1. Introduction

To protect against reactor radiation, materials of various nuclear composition and density are used, according to which they are divided into light (with an increased content of hydrogen, boron, graphite), heavy (metals) and medium density (metal-hydrogen).

The most used light hydrogen-containing material is water, where the concentration of hydrogen nuclei is $6.7 \times 10^{23}$ nuclei/cm$^3$. The relaxation length for fast neutrons of the fission spectrum near water is from 8.0 to 10.6 cm (for the equilibrium spectrum region of 10.0 cm). The main disadvantage of water is its radiolysis and non-structural nature (the need to use metal sheathing) [1-3].

Also effective light materials are polymers, in particular polyethylene, with a hydrogen nucleus concentration of $8 \times 10^{22}$ nuclei/cm$^3$. The relaxation length of fast neutrons ($\lambda_n$) for the equilibrium spectrum is 8.0 cm. The main disadvantage of polyethylene is its low operating temperature (up to 80 °C) and fire hazard [4-7].

To absorb thermal neutrons, boron carbide is widely used as an additive or filling due to the high absorption of the Maxwellian neutron spectrum and the insignificant formation of secondary gamma quanta. When the densities are comparable with graphite, $\lambda_n$ for boron carbide is 10.2 cm [8-10].

Metals are mainly used as heavy protections, among which iron-containing ones (steel or cast iron) are the most relevant due to their high structural design and availability. The steel grade is determined by the operating condition of the protective structure and depends on the amount of carbon and
alloying elements. The use of titanium, tungsten, molybdenum and other heavy metal protections is mainly limited by their cost.

Metal-hydrogen materials are widely used due to their high efficiency with respect to both neutron and gamma radiation. Among the complex protections, iron-water and lead-water materials are used, represented, respectively, by steel or lead sheets in water. This type of shielding is used in VVER reactors located between the core and the steel reactor vessel. By a certain ratio of the water and metal components, one can achieve equality of relaxation lengths, both for neutron and gamma radiation. So for steel protection, the optimal concentration of the metal is 70-80 wt% (the relaxation length for neutrons and gamma quanta is 7.5 cm), and for lead protection 20 wt% (relaxation length 10 cm). The limitation of such protection is the radiolysis of water and the associated formation of hydrogen, the operating temperature and the need to organize heat removal [10].

A special type of metal-hydrogen protection is made up of metal hydrides, in particular, lithium, zirconium and titanium hydrides. Despite their higher cost, they are the most promising materials for heat-resistant structures of metal-hydrogen shields used for ship and space nuclear power. Thus, the relaxation lengths of the neutron dose rate for hydrogenated metal plates based on titanium and zirconium hydride for the equilibrium spectrum region are, respectively, 5.5 and 7.3 cm [11]. The disadvantage of hydrogenated titanium and zirconium metal matrices is the complexity of the production technology, insufficient thermal stability and low structural properties (brittleness).

One of the main characteristics of the radiation-protective properties of concretes is the content of chemically bound water, since physical mixing water (including hydrosilicate water) is removed from the material during its thermal drying. The operating temperature of reactor concrete is 280 ℃. Thus, the content of chemically bound water in concrete should be determined by the hydrogen-containing aggregates used. At the same time, the achievement of the specified properties of the material is ensured not only by the correct choice of the type and amount of filler, but also by the observance of the technological parameters for the production and drying of the concrete composite [12].

One of the most effective fillers of reactor concrete is titanium hydride, which has better protective properties and a lower production temperature (titanium hydrogenation) than zirconium hydride. The problem of low thermal stability and brittleness of titanium hydride is partially solved by its use in the form of a shot. This technology allows titanium hydride to be used as a concrete filler, which provides structural protection properties. However, the possibility of cracking in hydrogenated titanium shot reduces its thermal stability to 250-300 ℃ due to hydrogen diffusion, which significantly limits the possibility of its use for radiation protection.

In this regard, the authors proposed the use of a modified fraction of titanium hydride obtained by chemical and electrochemical deposition of hydrogen traps on the surface of titanium hydride based on boron-containing systems or metallic titanium with a defect structure [13-17].

This paper presents the technological parameters of production, physical, mechanical, thermophysical properties and processes of gas evolution in a composite material based on a modified fraction of titanium hydride and a Portland cement binder.

2. Materials and methods
Modified titanium hydride shot, Portland cement binder, water, and plasticizing additive were used as the main components in the preparation of composites. A titanium hydride shot with a hydrogen content of 3.5% by weight, modified by electrochemical deposition of titanium metal from a titanium oxalate solution, was used.

Portland cement grade CEM I 52.5N in accordance with GOST 31108-2003 with a Portland cement clinker content of at least 95% was used as a binder. For mixing composite mixtures, drinking water is used that meets the requirements of GOST 2874-82.

Anionic plasticizer of the C-3 grade according to TU 5730-004-97474489-2007 was used as a plasticizing additive.

Used boron additive contains 0.78 wt.% Boron atoms.
The analysis of gases released during the thermal treatment of the composite was carried out by the chromatographic method on a 3700 series chromatograph.

3. Results and discussion
Taking into account the performed multi-group modeling to assess the effectiveness of the protective properties of materials based on titanium hydride with respect to neutron and gamma radiation, as well as studies of the thermal stability of titanium hydride fraction, optimal compositions and technology for obtaining a heat-resistant structural composite material for radiation protection have been developed.

Due to the thermal stability of the modified titanium hydride shot, composites based on it can be used in radiation shielding structures operating under prolonged thermal loads above 350 °C. The introduction of a plasticizing additive into the composite makes it possible to improve the technological and strength characteristics of the protection material. The use of a boron-containing additive can significantly reduce the yield of captured gamma radiation, as well as the activation of the material and surrounding structures.

Based on the design features of the radiation protection of a nuclear reactor (stacking the material in metal structures of various geometries), when developing the composition, priority was given to the maximum content of titanium hydride fraction as the main protection material, the density of the protective composite, the degree of compaction and mobility of the prepared composite mixture. The latter circumstance plays a decisive role in the filling of hard-to-reach volumes of metal structures of radiation protection and the possible formation of voids in it.

An important factor affecting the change in strength and deformability is the granulometry of the aggregate, which affects the workability of the composite concrete mixture. The filling of titanium hydride shot has increased fluidity, which makes it possible to better fill difficult-to-reach volumes. When using a cement bond, to obtain the highest density of composites, it is necessary to ensure the maximum packing of the shot particles.

If the particle sizes of polydisperse mixtures are limited to the values of the smallest and largest diameters, in principle two ways of obtaining the maximum packing density are possible. In the first case, two to four discrete fractions with a fixed particle size are mixed. The second way to achieve the maximum packing density is to introduce a polydisperse filler with a continuous size distribution in the range of the smallest and largest particle diameters.

Analysis of literary sources [3-5] reveals a number of features in the methods of stacking and compaction of bulk materials in the form of a shot.

First, to obtain a denser packing of granules, the ratio of the diameter (area) of the container to the diameter of the granules should be more than 15 units. Secondly, when compacting the single-fraction composition of spherical granules, the volume fraction of the packing does not exceed 70 - 74%.

When using two fractions of spherical granules in the package, the volume fraction increases and can be 83 - 86%. When using three fractions of spherical granules, the packing density can be increased up to 90%.

The optimization of the fractional composition of the titanium hydride shot, carried out on the basis of the considered theoretical provisions, made it possible to achieve a bulk density of up to 2.6 g/cm³.

According to the results of the carried out multi-group modeling, technological and operational requirements, the optimal composition and technology for obtaining the radiation protection material have been developed.

The main characteristic of the workability of freshly prepared composite mixtures is the mobility coefficient determined by the truncated cone settlement method. It has been experimentally found that the necessary workability and mobility of the mixture is achieved when the value of the mobility coefficient is not less than 2.0 and 1.4, respectively, for fluid and high-density mixtures. For the developed composite composition, the mobility coefficient was 1.49 ± 0.08 (before the mixture was compacted).
Physicomechanical and thermophysical characteristics of the composite material are shown in table 1.

### Table 1. Physicomechanical and thermophysical characteristics of the composite.

| Indicator                                                                 | Numerical value |
|---------------------------------------------------------------------------|-----------------|
| Bulk density of the composite mixture, g/cm$^3$                           | 3.32±0.03       |
| Density (28 days of hardening), g/cm$^3$                                  | 3.30±0.03       |
| Density (drying 110 °C), g/cm$^3$                                        | 3.28±0.03       |
| Density (drying 300 °C), g/cm$^3$                                        | 3.20±0.03       |
| Ultimate compressive strength after 28 days of hardening (28 days R$_{\text{com}}$), MPa | 39.5±1.8        |
| 28 days R$_{\text{com}}$ (drying 110 °C), MPa                           | 42.7±1.8        |
| 28 days R$_{\text{com}}$ (drying at 300 °C), MPa                        | 36.4±1.8        |
| 28 days R$_{\text{com}}$ (drying 350 °C), MPa                          | 32.8±1.8        |
| Mixture mobility coefficient                                             | 1.49±0.08       |
| Thermal conductivity coefficient at 20 °C, W/(m∙K)                        | 3.27            |
| Linear thermal expansion coefficient, m∙deg$^{-1}$                       | 5.08·10$^{-6}$   |
| Specific heat, kJ/(kg·K) at 20 °C                                       |                 |
| 50 °C                                                                    | 1.018           |
| 100 °C                                                                   | 1.024           |
| 150 °C                                                                   | 1.031           |
| 200 °C                                                                   | 0.894           |
| 250 °C                                                                   | 0.911           |
| 300 °C                                                                   | 0.918           |

Sufficiently complete and reliable data have been obtained on the main physical and technical properties of the developed composite materials based on titanium hydride shot in the range of operating temperatures as applied to long-term operating conditions. Experimental statistical results of the obtained experimental-technological characteristics of the material are presented in table 2.

### Table 2. Experimental and technological characteristics of radiation protection materials.

| Indicator                                                                 | Numerical value |
|---------------------------------------------------------------------------|-----------------|
| The flammability group is not flammable                                   |                 |
| Change in material mass (%) in oxygen atmosphere at a temperature of 300 °C for: |                 |
| 500 h                                                                     | -0.15           |
| 1000 h                                                                    | -0.18           |
| 5000 h                                                                    | -0.20           |
| Change in material volume (%) in oxygen atmosphere at 300 °C for:         |                 |
| 500 h                                                                     | +0.31           |
| 1000 h                                                                    | +0.32           |
| 5000 h                                                                    | +0.36           |
| Change in material density (%) in an oxygen atmosphere at a temperature of 300 °C for: |                 |
| 500 h                                                                     | -0.81           |
| 1000 h                                                                    | -0.92           |
| 5000 h                                                                    | -1.12           |
| Change in material strength (%) in an oxygen atmosphere at a temperature of 300 °C for: |                 |
| 500 h                                                                     | -6.5            |
| 1000 h                                                                    | -8.2            |
| 5000 h                                                                    | -10.4           |

The results of the studies carried out showed a decrease in the mass of the samples within 1% during their heating, due to the loss of moisture collected by them from the air under standard conditions. This is confirmed by the DTA data, where exothermic peaks are noted in the temperature
range 70-100, 150-200, 250-300 °C, corresponding to the stepwise dehydration of bound water from calcium hydroaluminate 2CaO • Al2O3 • 8H2O (α-C2AH8), formed during cement hydration. This is accompanied by the formation of tricalcium aluminate 3CaO • Al2O3, which is capable of absorbing moisture from the ambient air. No other changes in the mass of the samples indicating the occurrence of thermooxidative reactions were found.

The change in the volume of the composite at an elevated temperature in the air atmosphere is of an average character, since for the same composition, both an increase and a decrease in the geometry of the samples within 0.35% are noted. This circumstance indicates the constancy of the geometric characteristics of the composite protection material.

The decrease in the density of the composite during prolonged heat treatment at 300-350 °C is within 1% and corresponds to a decrease in weight due to the removal of moisture sorbed from the air.

The decrease in the strength of the composite with prolonged heating at a temperature of 300-350 °C was 14.8%. In this case, the residual compressive strength of the composite, even after holding for 1000 h, is not less than 30 MPa.

Thus, the decrease in the physical and mechanical characteristics of the material does not exceed 10-20%, which indicates its thermal stability in terms of the main performance indicators. The introduction of a boron additive does not significantly affect the physical and mechanical properties of the composite.

The results of computational and experimental studies of gas evolution from 1 ton of material, starting from the stage of mixing the mixture and until the composite warms up from 110 to 600 °C, are presented in Table 3. The volumes of the evolved gas are reduced to normal conditions.

Table 3. Composition and volume of evolved gases during thermal heating of the composite material.

| Temperature, °C | CO2 | CO | SO2 | Formaldehyde | H2O *** |
|-----------------|-----|----|-----|--------------|--------|
| 25              | -   | -  | -   | -            | 3.9    |
| 110             | -   | -  | -   | -            | 6.7    |
| *300            | 6.27| 0.08| 0.10| 0.014        | 20.7   |
| **300           | 6.29| 0.08| 0.10| 0.014        | 12.3   |
| 400-600         | 49.99| 0.61| 0.77| 0.113        | 3.2    |
| >600            | 563 | 6.95| 8.68| 1.277        | -      |

* temperature rise from 110 to 300 °C and holding at 300 °C for 5 days.
** exposure at 300 °C for 20 days.
*** volume of condensed water.

From the data in Table 3, it follows that when drying 1 ton of material, based on the MPC standards of the working area, the volume of the room for heat treatment of 1 ton of material should be at least 69, 96 and 12 m³ in terms of SO2, formaldehyde and CO, respectively. In practice, the requirements of the MPC standards are met in the presence of supply and exhaust ventilation.

Thus, the main gas evolution occurs during the drying of composites and practically ends after its completion. Reheating the cooled block to the initial heating temperature (300-350 °C) practically does not cause gas or water evolution, if during the cooling period the material did not have contact with water.

4. Summary
1. The thermal stability of the modified titanium hydride shot allows the use of composites based on it in the structures of radiation protection operating under prolonged thermal loads above 350 °C.
2. The introduction of a plasticizing additive into the composite makes it possible to improve the technological and strength characteristics of the protection material.
3. Under prolonged thermal loads, the decrease in the physicomechanical characteristics of the composite based on the modified fraction of titanium hydride does not exceed 10 - 20%, which indicates its thermal stability in terms of basic performance indicators.

4. The main gas evolution occurs during the drying of the composite material. Reheating the composite to the initial heating temperature does not cause gas evolution if the material did not come into contact with water during the cooling period.

5. References

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