The problems of protection and heat insulation of steel tanks which are used in hydrogen power engineering

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The trends in the development of hydrogen power engineering as an alternative environmentally friendly source of energy are given. The problems of hydrogen storage in steel spherical tanks, mainly related to the thermal insulation of the tank, are considered. The structure of steel spherical tanks for storing liquid hydrogen at low temperatures, which, as a rule, is 21 K, the hydrogen condensation temperature, is considered. The characteristics of AISI 316L austenitic stainless steel, developed on the basis of the AISI 304 steel grade, improved by 2.5 % molybdenum addition, which increases its corrosion resistance and allows the use of AISI 316L steel in aggressive environments, and therefore found the widest application in the design of spherical hydrogen tanks, are presented. The chemical composition of AISI 316L austenitic stainless steel is displayed. A number of heat-insulating materials for hydrogen storage in steel spherical tanks are considered. The characteristics of the expanded pearlite currently used for this purpose, which has a number of disadvantages, such as caking of the material, high costs in its production, loss of thermal insulation properties after a certain cycle of thawing - freezing, are shown. The parameters of alternative heat-insulating materials, such as aerogels, polystyrene foam, foam glass, are examined. It has been established that aerogels, despite all their advantages, are not stable in an oxygen environment and are a very expensive as material; expanded polystyrene, being an organic substance, is a subject to flammability, and therefore is not suitable for use in hydrogen energy. Foam glass was identified as the most promising heat-insulating material, which has a number of advantages over other materials. Compositions of charge for obtaining foam glass have been developed, and a series of samples of foam material has been synthesized. The optimal composition of foam glass was chosen, which is most suitable for storing hydrogen in steel spherical tanks.
Key words: hydrogen power engineering, hydrogen storage, steel spherical tanks, heat-insulating materials, porous materials, foam glass.
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Introduction

Hydrogen is an ecologically harmless energy carrier of new generation and has a wide spectrum of application. It is characterized by high energy density 33.3 $kWt \cdot h \cdot kg^{-1}$, what is essentially higher in comparison with hydrocarbon fuel (12.2 $kWt \cdot h \cdot kg^{-1}$). However, its volumetric energy density is rather low, appr. 3 kWt·h·l (for normal conditions) [1, 2]. Thereby, it is necessary to liquefy hydrogen at the condensation temperature 21 K in order to increase volumetric energy density. But high speed of hydrogen diffusion in the air and low sublimation temperature for transportation and storage of liquid hydrogen stipulate demand on advanced technologies and special constructions to provide minimal level of hydrogen losses [2, 3].

As soon as the temperature of liquid hydrogen is very low, the facilities for hydrogen storage and transportation should be designed in such way that they can keep this temperature. Ice forming around the facilities for hydrogen storage and transportation is unacceptable, because it can lead to material destruction [3].

At the same time hydrogen embrittlement of tank material can occur during hydrogen storage and transportation. Crack forming and consequent destruction are caused by diffusion of hydrogen molecules in material. Hydrogen molecules are accumulating in material and increase internal stresses, what leads to material destruction [4]. Long-term operation in a liquid hydrogen medium promotes hydrogen embrittlement [5]. Thereby, it is necessary to use special materials which don't cause metal destruction.

Stainless steel is characterized by resistance to hydrogen embrittlement, stability at cryogenic temperatures and corrosion resistance, si it is rather interesting for liquid hydrogen storage and transportation.

It is known that austenite stainless steel AISI 316L has the most wide application for designing of tanks for hydrogen storage [6-8]. This steel has high strength, corrosion resistance, heat resistance and ductility. Due to presence of molybdenum,

Table 1. **Chemical composition of the steel AISI 316L**								
Component	C	Si	Mn	P	S	Cr	Ni	Mo
Content, % (mass.)	≤0.03	≤0.75	≤2.0	≤0.045	≤0.03	16.0-18.0	10.0-14.0	2.0-3.0

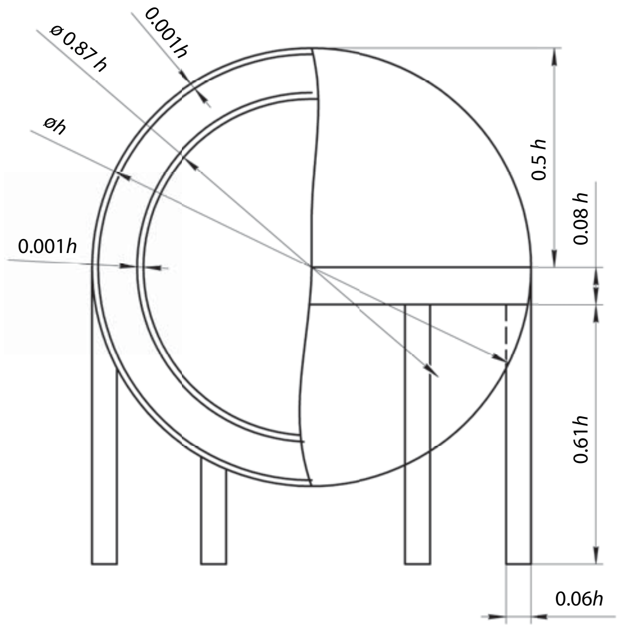

Fig. 1. Technical drawing of a tank for liquid hydrogen storage

chromium and nickel in its composition, the steel AISI 316L can be operated in very aggressive media. At the same time this steel grade is easily subjected to mechanical processing and thereby can be used in different application areas, such as designing of tanks and containers for storage of chemical substances, building and architecture, machine-building, mining industry etc.

Chemical composition of this steel is presented in the **Table 1**.

The tanks for liquid hydrogen storage have usually spherical or cylindrical form. Cylindrical tanks have larger surface square than spherical ones, with the same volume, and larger pressure appearing as a result of evaporation, which is distributed in non-uniform mode [9]. Thereby it is perspective to use spherical tanks. Cryogenic spherical tank for liquid hydrogen storage is a tank with double walls, with space between these walls filled by heat-insulating material in deep vacuum conditions (**Fig. 1**) [10].

As it was mentioned above, the tanks for liquid hydrogen storage should keep extra-low temperatures, thereby tank shells should include heat-insulating layer, which is able to keep the temperature 21 K.

In order to obtain optimal heat-insulating properties, it is necessary to develop heat-insulating materials with density lower than 200 kg/m^3 [11]. There are several materials, which are able to provide such density level. The most widely used is perlite – rock of volcanic origination, containing 70 % of silicon dioxide, 10-15 % of aluminium oxide and 4-8 % of sodium and potassium oxides, as well as small amount of crystallized water (usually several percents). Perlite is heated to the temperature 900-1200 °C and it is resulted in its bloating, owing to water heating [12]. Bloated perlite is characterized by lowered density (usually about 100 kg/m^3), low heat conductivity (0.031 Wt/m·K), non-combustibility, high chemical resistance and non-toxicity [13]. Despite several advantages, production of bloated perlite is accompanied by high energy consumption, forming of large amount of wasted during its crushing, what leads to contamination of the environment. Additionally, bloated perlite has liability to packing, which results in its shrinkage achieving 10 % and more. Bloated perlite keeps up to 15 cycles of defrosting and frosting, and afterwards destruction of several fractions occurs; as a result, the material loses its heat-insulating properties [14].

Aerogels, foamed polystyrene, foam glass etc. can be alternative materials for bloated perlite. Aerogels seem to be among the most efficient heat-insulating materials, existing at present time. Aerogel is a gel where liquid phase is completely replaced by gaseous one. This material is characterized by density 3-350 kg/m^3, porosity 85-99.9 % and specific surface 500-1,200 m^2/g. Based on these properties, heat conductivity of Aerogels achieves low values 0.003-0.02 Wt/m·K. However, use of Aerogels is restricted mainly due to their high cost and material non-stability in oxygen medium [15].

Foamed polystyrene is gas-filled foamed material, which is produced from copolymers of styrene, polystyrene or its products. This material is obtained via foaming of raw material by vapours of low-boiling liquids. Foamed polystyrene has uniform porous structure with size of pores 115-1,200 μm [16]. Having heat conductivity 0.028 Wt/m·K, resistance to water steam effect, ability to keep up to 60 cycles of defrosting and frosting, foamed polystyrene however is subjected to aging and combustion and has low physical and mechanical properties, being an organic substance. It restricts essentially its use as heat-insulating material for liquid hydrogen storage [17].

Foam glass is a high-porous formed material, obtained by sintering of the mix of fine ground glass powder and pore-forming agent. This foam material is characterized by high strength, good heat-insulating properties, water resistance, non-combustibility, low thermal conductivity. Foam glass is easily subjected to mechanical processing (sawing, drilling, grinding). Such list of advantages makes foam glass a perspective material for heat insulating of spherical tanks for hydrogen storage.

It is known that there are several enterprises in Russian Federation which manufacture foam glass with density lower than 200 kg/m^3. E.g., “Kammet” JSC (Krasnoyarsk) manufactures heat-insulating foam glass plates and blocks since 2014 (annual production makes 1,200 m^3). The company “STES-Vladimir” JSC (Vladimir) was established in 2000-2005 as a pilot-experimental enterprise, and since 2014 in became a national level works. It manufactures blocks, plates and complicated shapes from foam glass at the two production lines, annual capacity of each of them makes 13,000 kg/m^3 of heat-insulating material.

When designing of tanks for hydrogen storage using foam glass, application of shaped plates or segments is possible. However, such designing of tanks is connected with definite difficulties, due to their substantial volume. In this connection, it is expedient to use granulated foam glass. Its granules are filled compactly in the space between tank walls and air pumping from this space with creation of deep vacuum is carried out afterwards.

Table 2. **Chemical composition of sheet glass of L grade**

The content of oxides [wt. %]						
SiO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	MgO	SO_3
73.0	1.3	0.1	13.4	9.0	3.2	0.3

Table 3. **Relationship between density of obtained samples and amount of pore forming agent**

No. of sample	Sample composition [wt. %]			Sample density [kg/m^3]
	Broken glass	Liquid glass	Glycerin	
1	90	9	1	217
2	90	8	2	216
3	90	7	3	211
4	90	6	4	213
5	90	5	5	191
6	90	4	6	265
7	90	3	7	277
8	90	2	8	290
9	90	1	9	303

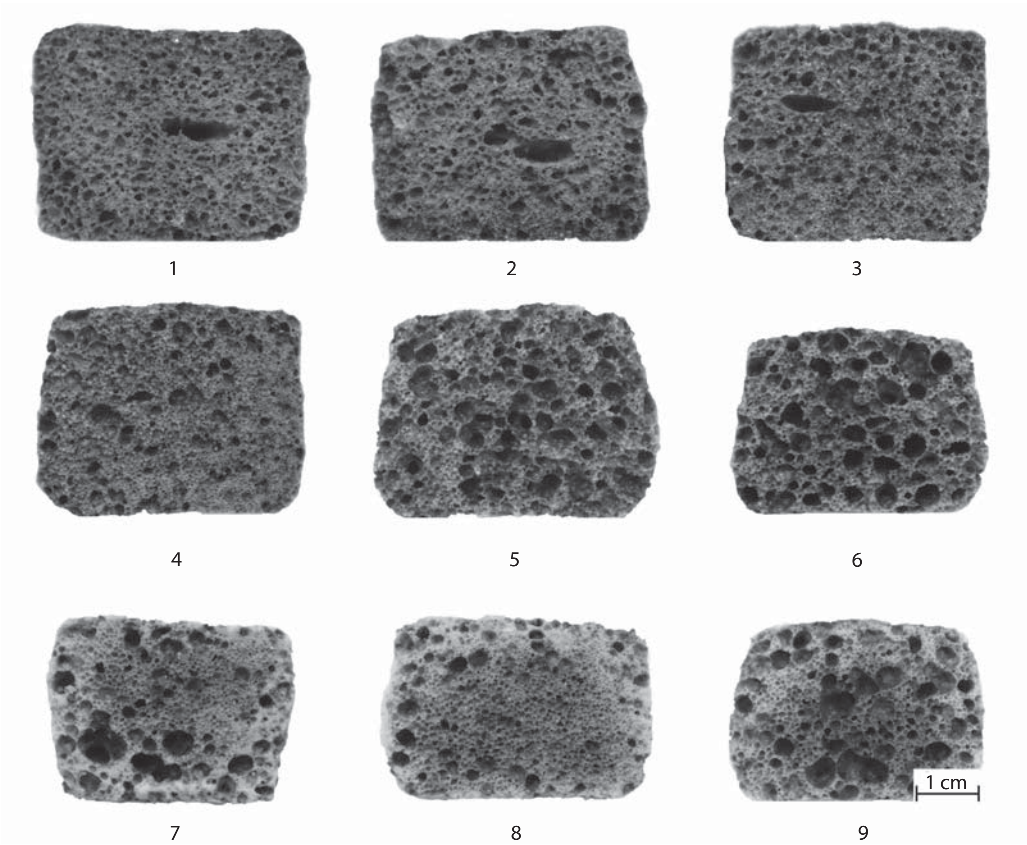

Fig. 2. Macrostructure of obtained samples

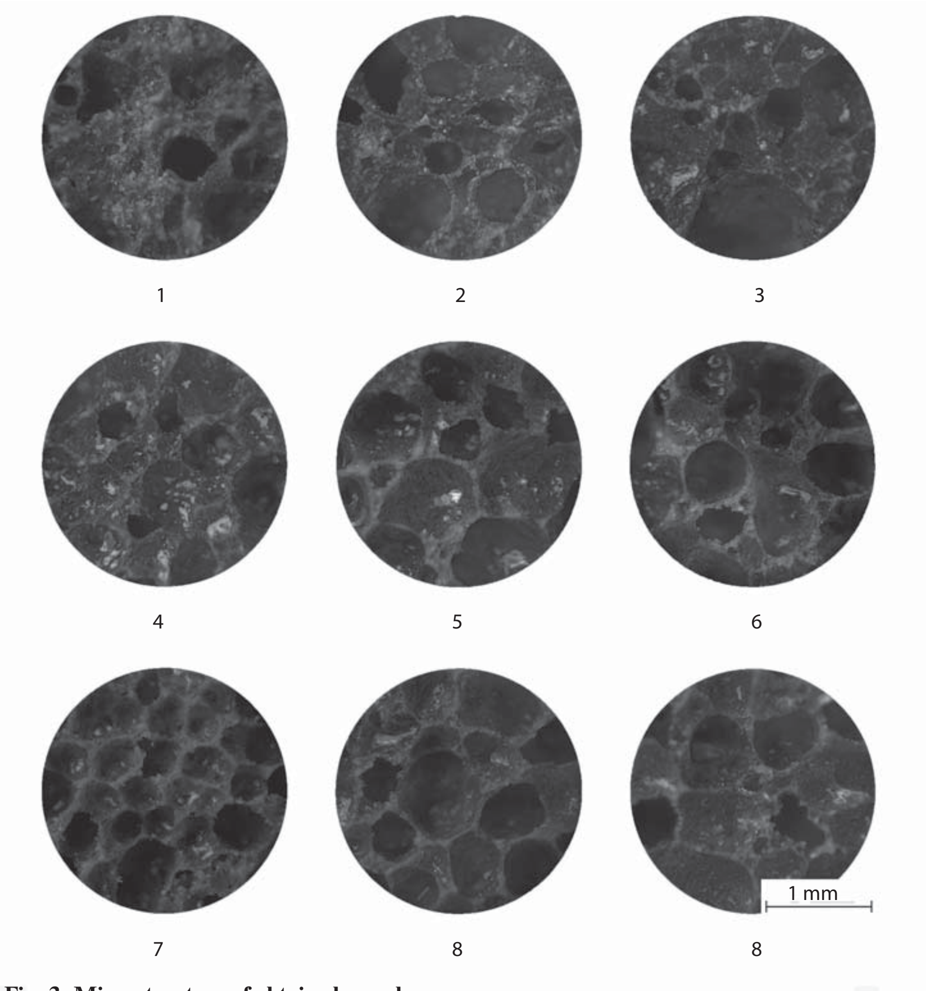

Fig. 3. Microstructure of obtained samples

Materials and methods

Foam glass synthesis was conducted via addition of different amount of stabilizer (liquid glass and glycerin as pore-forming agent) to broken sheet glass of L grade (**Table 2**).

Crushing and grinding of sheet glass was preliminarily conducted in a ball mill with consequent screening through a sieve No. 025 before preparation of charge material. Obtained glass powder was mixed with glycerin and liquid glass in preset proportions until reaching homogenous structure of reacting mix. Prepared charge was presses with load 5 MPa to form cubic samples with plane length 20 mm. Then prepared samples were put into electric muffle furnace for heat treatment in the air atmosphere. After heating, samples were held during 10 minutes at the temperature 850 °C and were critically cooled down to 600 °C for fixing the material structure. As soon as surface layers of material can be overcooled, a stage of slow cooling during 4-5 hours was carried out.

Mass of the samples was measured on laboratorial scales with accuracy up to 0.01 g. Average density ρ, kg/m³, was calculated via the equation (1):

$$\rho = m / (a \cdot b \cdot c), \quad (1)$$

где m – sample mass, g; a – sample length, m; b – sample width, m; c – sample height, m.

Results and discussion

Use of organic pore forming agent (glycerin) allows to reach uniform distribution of pore forming agent through the whole charge volume and, respectively, to obtain more homogenous porous structure. The foaming mechanism of foam glass passes according to the reactions (2) and (3) [18-20]:

$$2C_3H_5(OH)_3 + 7O_2 = 6CO_2 + 8H_2O \quad (2)$$

$$\text{glass} - SO_3 + 2C = \text{glass}{-}S^{2-} + CO + CO_2 \quad (3)$$

Glycerin effect is based on its burning with forming of carbon dioxide and water vapours, which are foaming molten glass mass. During glycerin burning, carbon is partly forming; it reacts with glass mass and forms carbon monoxide and carbon dioxide, which also provide foam-forming effect.

Minimal density was revealed for the sample No. 5, it was equal to 191 kg/m³, what makes this composition an optimal one. Lowering of glass mass density occurs due to decrease of toughness and increase of gas pressure in pores (**Table 3**).

Macrostructure of obtained samples is presented on the **Fig. 2**.

The foam glass samples No. 1-6 are characterized by homogenous porous structure, what provides high physical and mechanical material properties and, what is most important, its loh thermal conductivity. It is caused by less intensive heat transfer via convection and decrease of diameter of foam material pores. The samples No. 7-9 are characterized by heterogeneous porous structure with defects; it can be caused by high content of foam forming agent (glycerin) and low content of stabilizer (liquid glass).

Fig. 3 displays that the samples have closed spherical pores with diameter 300-500 μm, which are separated by thin walls from vitreous substance. The following properties were determined for the sample No. 5 with minimal density [21, 22]: thermal conductivity coefficient 0.05 Wt/(m·K); tensile strength for compression 0.8 MPa; water absorption 4.6 % (vol.); vapor penetration 0.005 mg/(m·h·Pa).

Thereby, obtained foam glass with density less than 200 kg/m^3 can be used as heat-insulating material in spherical tanks for hydrogen storage. However, it is necessary to develop new compositions of raw materials allowing to decrease material density down to 150 kg/m^3; it will be the base for manufacturing of so-called extra-light foam glass with preferential properties for application in hydrogen power engineering.

Conclusion

It was established that hydrogen power engineering is a perspective way for decarbonization of power engineering systems. However, the problems of hydrogen storage, connected with heat insulation of steel spherical tanks, are considered as obstacles for wide putting into practice of hydrogen power engineering in different application areas. Several heat-insulating materials for hydrogen storage were examined, and the optimal one (foam glass) was chosen, it meets all necessary requirements. 9 compositions of charge materials for synthesis of foam glass with different correlation between glycerin and liquid glass were developed, the synthesis itself was carried out. It was found out that the composition No. 5 (containing 90 % of broken glass, 5 % of glycerin and 5 % of liquid glass) has minimal density 191 kg/m^3. This value of material density allows to use it for heat insulation of steel spherical tanks for hydrogen storage; however, it is required to search the ways for decrease of foam material density down to 150 kg/m^3 in order to obtain extra-light foam glass that will be more competitive in comparison with currently used heat-insulating materials for hydrogen storage.

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