The foam-glass material for a radio frequency echoless chambers

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Abstract. The conducted experiment of foam glass modification by carbon nanotubes shows increased radio absorbing properties in comparison with a foam glass without additives. Addition of carbon nanodimensional tubes in number of 1,5 wt.% increases a tangent of dielectric losses angle by 2,5 times. The coefficient of electromagnetic radiation absorption in the range of frequencies of 120 - 260 GHz increases for a foam glass with carbon nanotubes (1,5 wt. %) twice in comparison with a foam glass without additives. The foam glass modified by carbon nanotubes is recommended as the effective radio absorbing material for the device of anechoic cameras. This material is fire safety, nonflammable, environmentally friendly, rather light-weight.

1. Introduction
Materials which interact efficiently with electromagnetic radiation (EMR) find wide application to solve problems of electromagnetic compatibility, to protect biological objects against harmful impact, to decrease radio visibility, to manufacture various elements of high frequency radio electronics [1, 2]. Facing of the inner surfaces of echoless chambers, which began to use widely in last decades, is one of direction of application of such materials. From one side it is connected with tendency of complication and increasing of accuracy of antenna measurements and panel tests of radio complexes, from other one it is connected with widespread use of the chamber in the technique for testing new wide band radio wave absorbing materials. A radio frequency echoless chamber is a closed electromagnetic screen which inner surfaces are coated completely with radio wave absorber. To install chambers one uses a porous pyramid shaped material. Such surface form widens frequency range, increases additionally absorbing capacity and decreases reflection of electromagnetic waves from the walls. One uses the material, which contains current conducting carbonaceous particles (soot and graphite) and magnetic components (ferrites), as material of a radio wave absorber. Such composition in combination with porous structure provides efficient absorbance of electromagnetic waves in wide frequency range.

The material must have the high absorption coefficient and be fire proof, durable, strong, have relatively low density, and be mounted and be processed easily. Foam glass [3] meets these
requirements, but it is inferior to traditional radio wave absorbers. Therefore, the study of foam glass modifications with various additives which increase its absorption capacity [4 – 6] has practical significance. An added modifier changes the physical and mechanical properties, size and shape of the foam glass pores. It is shown in [7] that the radio wave absorbing ability of foam glass can be increased with the addition of ilmenite. It is known that carbon nanotubes (CNT) having the complex of unique mechanical and heat-physical properties interact effectively with the electromagnetic radiation that allows to use them in radio wave absorbing composites [8]. The purpose of this work is to investigate the CNT impact on foam glass properties and its radio wave absorbing ability.

2. Raw materials and methods of investigations
Feedstock for production of foam glass is of lamp glass powder with specific surface area of 6000 cm$^2$/g, which composition is given in Table 1. This glass belongs to the group of silicate and contains together with the main components barium oxide, which is introduced into furnace – charge as barium sulfate that increases foaming ability of fluid glass. We used soot as gasifier and its amount in all samples was 0.5 wt. %. Multilayer carbon nanotubes of relatively high purity (Table 1) have been used as modifying additive.

CNTs were synthesized by catalytic CVD technique using ethylene decomposition at 680°C [9] Bimetallic Fe-Co/Al2O3 catalyst with Fe2Co alloy as active component [10] was used to produce CNT. The study was carried out using CNTs average diameter of 20-25 nm, длину около 1 мкм. Carbon nanotube oxidation was performed by refluxing of CNTs (1–2 g) in the excess of nitric acid for ~90 min [11]. Dimensions of tubes have been chosen to reduce the percolation threshold, after which conductivity and reflectance coefficients increase. For this reason, the amount of CNT introduced into the foam glass has been changed within small range from 0.5 to 1.5 wt. %.

Table 1. Chemistry of glass and CNT

| material | Oxides and dirt content (wt.%) |
|----------|-------------------------------|
|          | SiO$_2$ Al$_2$O$_3$ Fe$_2$O$_3$ CaO MgO Na$_2$O K$_2$O BaO |
| glass    | 71,9 0,60 0,10 5,50 3,20 16,10 0,80 1,80 |
| CNT      | 0,0169 (Si) 0,0011 (Fe) 0,005 (Ca) следы (Ti, Co, Cu, Al, Sn) |

The process of production of foam glass includes such technological operations as preparation of glass powder, mixing it with gasifier and modifying additive, foaming of the foaming mixture with following gradual cooling and processing of the finished material up to given sizes and shapes (Figure 1).

Figure 1. Technological scheme of foam glass producing

The electromagnetic characteristics were investigated using the equipment of the «Center of Radio Measurements at Tomsk State University». The reflection and transmission coefficients were
measured by the method of free space using a radio spectroscope built around an E8363B Vector Network Analyzer (Agilent Technologies) in the range 26–36 GHz and an STD-21 terahertz spectrometer in the range 60–260 GHz [12, 13].

3. Experimental results

The necessary condition to obtain high quality foam glass with uniform fine pore structure is homogeneous foaming mixture. Given the difficulty of uniform distribution of CNT in the mixture the method of inserting of nanotubes in a dry form has been developed in the course of the experiment.

For this purpose, previously the premix was prepared by mixing of the components in a defined sequence with addition of surfactant which improves wettability of particles. At that modifying additives which have been mixed in the rotary-vane-mixer, are sufficiently evenly distributed by powder volume. Further, the binder mixture was added in the form of a 15% solution of sodium silicate in amount of 5%. The mixture was stirred in the mixer that leads to appearance of small granule germs. This operation allows to obtain premix in the form of a granular powder, which is not dusty, is not foliated, is not prone to aggregation and is easy dosed. Prepared premix, containing the carbonaceous gasifier in full volume and CNT, is mixed with glass powder in a planetary mill for 1 minute. Foaming has been performed at maximum temperature of 800 °C with an exposure of 15 minutes.

Radio-wave absorbing properties of the foam glass depend on the value of complex dielectric permittivity (DP) of the glass at the given frequency, system porosity and pore diameter. The absorbing material will correspond to the destination in the event if it has no reflection of electromagnetic waves from the outer surface, and the energy penetrating into the material, will be absorbed completely. Accomplishment of these conditions are achieved by appropriate choice of construction (for example: single-layer, multi-layer) and selection of electrical and magnetic properties of the material, owing to coordination with the free space and transformation of EMR into thermal energy is achieved. For better absorption of radiation it is preferable to use materials with higher values of the dissipation factor of a dielectric.

The measurements of the electromagnetic response of the samples to be studied showed that if concentration of modifying additives in foam glass is increased, losses are increased faster than real component of DP. The samples with 1.5 wt. % of CNT have the highest loss tangent values. It is established that introduction of carbon nanoscale tubes in amount of 1.5 wt. % increases dissipation factor of a dielectric by 2.5 times (Figs. 1 and 2).

Qualitative indicators of material are absorption, transmission and reflection coefficients of wave. The reflection coefficients for all samples practically do not differ and are near to zero. Table 2 shows the results of measurements of the absorption and transmission coefficients of electromagnetic radiation in the high frequency range from 120 to 260 GHz for samples of foam glass with the addition of the CNT and without it. The absorption coefficient of modified foam glass, on average, is twice as high as in comparison with foam glass without additives.

Density, mechanical strength, heat conductivity and water absorption are important exploitation characteristics of foam glass together with its electrical and physical properties. Values of these indicators are listed in Table 3 from which one can see that density and strength of material are slightly decreased at increase of inserted CNT. Physical and mechanical properties are directly connected with porous structure of the material. It is found that the pore size of modified foam glass is increased on average up to 2.5 mm in comparison with pore size of foam glass without additives (0.5-1 mm). Thus, differences in electrophysical properties of porous samples are caused by not only with changes in the material composition, but also its macrostructure.
Figure 1. Output of the dielectric constant versus frequency for foam glass containing carbon nanotubes (weight %): 1 – 1.5; 2 – 1; 3 – 0.5.

Figure 2. Output of the dielectric constant versus frequency for foam glass containing carbon nanotubes (weight %): 1 – 1.5; 2 – 1; 3 – 0.5.
| number of CNT, (wt. %) | transmission coefficients at frequency, dB | adsorption |
|------------------------|------------------------------------------|-------------|
|                        | 120 GHz | 260 GHz | 120 GHz | 260 GHz |
| 0                      | -4,0    | -11,2    | -2,2    | -0,15    |
| 0,5                    | -7,0    | -24,0    | -2,2    | -0,1     |
| 1,0                    | -6,9    | -20,5    | -2,3    | -0,3     |
| 1,5                    | -10,5   | -24,3    | -0,9    | -0,3     |

| number of CNT, (wt. %) | property values |
|------------------------|-----------------|
|                        | density, kg/m³ | water adsorption, wt.% | durability, MPa | thermal conductivity, W/m·K |
| 0                      | 175             | 1,2                  | 1,2             | 0,073                        |
| 0,5                    | 163             | 1,4                  | 1,1             | 0,070                        |
| 1,0                    | 156             | 1,6                  | 1,1             | 0,068                        |
| 1,5                    | 151             | 1,5                  | 1,0             | 0,065                        |

4. Conclusions
The effect of CNT on the physical and mechanical and radio wave absorbing properties of foam glass has been revealed. Introduction of CNT nanotubes in amount of 1.5 wt. % increases imaginary component of dielectric permittivity of foam glass by five times and real component by two times. The absorption coefficient of electromagnetic radiation in the frequency range of 120 - 260 GHz is increased in average for foam glass with carbon nanotube (1.5 wt. %) by two times in comparison with foam glass without additives. Foam glass, modified with carbon nano-tubes, is recommended as the effective radio absorbing material to arrange echoless chambers. At that the material meets the requirements of fire safety, is non-flammable, environmentally friendly and relatively easy (density in the range of 180 kg/m³).

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