STUDY OF SYNTHESIS AND PROPERTIES OF ALOOH ANISOTROPIC NANOSTRUCTURED AEROGEL

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ABSTRACT

This paper presents a laboratory study on synthesis and properties of ultraporous aluminum oxyhydroxide Al₂O₃·n(H₂O) (ALOOH aerogel) using a method of selective oxidation of Ga-Al and Bi-Al binary liquid metal fusions by water steam. Aerogel properties were studied by using the methods of scanning electron microscopy (SEM), X-ray diffraction (XRD), synchronous differential scanning calorimetry and thermogravimetry (DSC/TG), and energy dispersive X-ray (EDX) spectroscopy. The results of microstructure analysis showed that the aerogel had oriented in the space fibrous nanostructure with a “tensile” type of anisotropy, a fiber diameter varying from 5 to 15 nm. XRD examination showed that ALOOH aerogel kept amorphous up to 1000 °C. Results of the studies on thermal properties of the aerogel and its elemental composition are presented. It has been determined that aerogel has low thermal conductivity (~ 0.02-0.03 W/(m·K)) within a rather wide temperature range. Studies on using of small additives of ALOOH aerogel (0.5-5 max. %) to ceramic materials based on silicon nitride Si₃N₄, silicon carbide SiC, and zirconium dioxide ZrO₂ showed that aerogel additive made it possible to increase physical and mechanical characteristics of ceramics in average on 20-30 %.

Keywords: aerogel, liquid metal fusions, gallium, bismuth, ceramic materials, anisotropic nanostructure, low thermal conductivity.

1. INTRODUCTION

Studies aimed at the synthesis of materials with revolutionary properties are very important for the development of up-to-date science and technology. Without new materials, no development is possible in electronics, power engineering, medicine, or any other area of science and engineering. In this view, great attention is paid today to this issue all over the world. Considerable efforts have been made, as well, by the authors of this paper in the area of designing nanomaterials for the wide range of applications in almost all modern scientific and technological developments.

The unique properties of aerogels attract attention of many researchers from various fields of scientific knowledge. For instance, owing to their low density and thermal conductivity, aerogels have found application in NASA projects [1, 2]. High porosity and internal surface of aerogels make it possible to use them as catalysts in chemical synthesis [3]. Besides, owing to their high volumetric capability, aerosols can be used for storing various liquids and gases, in particular, rocket fuel or hydrogen [4]. Effect of light absorption by SiO₂ based aerogels (Figure-1a) within the quarter-wave range made it possible to prove the possibility of its use in Cherenkov detectors [5]. Aerogels are characterized by the low value of Young’s modulus and low sound velocity, this being of interest from the standpoint of acoustic application. Because of special aspects of structure and phase composition of ALOOH aerogel, it can be used for the development of devices and products having high technical and economical characteristics (ceramics, rubber-technical, composite and polymer materials, sorbents, and other functional materials) [6]. Aerogels play an important role in studies on the effect of impurities on critical phenomena in quantum liquids: ⁴He [7] and ³He [8].

Aerogels of various metal oxides are traditionally produced by sol-gel technology [9], foundations of which were founded by Steven Kistler, who was the first to produce aerogels in 1931 [10]. Kistler used Na₂SiO₃ salt as the initial material, which was put in chlorohydric acid water solution to start the following reaction:

Na₂SiO₃ + 2HCl → SiO₂·nH₂O + 2NaCl

Excess salt was removed from the solution. The final solution was flushed out and filtered, and water was replaced by ethanol or methanol, that is having lower critical values of pressure and temperature as compared to those of water. Then aerogel was dried under supercritical conditions in the autoclave.

Since then, the method proposed by Kistler has been essentially updated making it possible to produce aerogels on the basis of Li₂O, B₂O₃, MgO, Al₂O₃, SiO₂, TiO₂, Fe₂O₃, CuO₂, ZrO₂, and MoO₃ [4, 11-14]. Aerogel with SiO₂ is gained widespread. One of the up-to-date methods of SiO₂ aerogel production is based on hydrolysis of tetramethylorthosilicate [4, 11, 14] according to the following reactions:

Si(CH₃O)₄ + 2H₂O → Si(OH)₄ + 4CH₃OH,
Si(OH)₄→ SiO₂·H₂O

in the presence of acid or base catalysts.

In our studies, essentially different method of aerogel production was implemented. This method was based on selective oxidation by water steam of binary metal fusions: Bi-Al and Ga-Al.
2. MATERIALS AND METHODS

Synthesized specimens of AlOOH aerogel were made as plates with thickness of 2 mm to ~ 10 cm. As a rule, dimensions of the plates were determined by those of liquid metal surface (its width and length are equal up to 15 cm), on which they were produced. All synthesized specimens were “semi-transparent”. Although no special tests of specimens were carried out for optical transmission, however, it should be noted that black text printed on the ruler could be read with little effort under normal lighting conditions through about a thick of 2 cm of AlOOH aerogel specimen lying on the text fragment (Figure-1).

Besides, Rayleigh light scattering was observed on all synthesized specimens. Specimens in the study had blue appearance in reflected light and light-yellow appearance in transmitted light. This effect involves light scattering with constant wave length (so called elastic scattering) on particles, granularities or other bodies, if scattered light frequency is much lower than the fundamental frequency of scattering body or the system.

The equivalent formula is: light scattering on the bodies of size less than its wave length.

Method of AlOOH aerogel production from Bi-Al liquid metal included two phases: 1) aluminum dissolution in bismuth, 2) oxidation of dissolved aluminum by water steam:

\[
\begin{align*}
1) \text{<Al>} + \{\text{Bi}\} & \rightarrow \text{[Al]} + \{\text{Bi}\}, \\
2) \text{[Al]} + (\text{H}_2\text{O}) & \rightarrow <\text{AlOOH}> + \frac{1}{2}(\text{H}_2).
\end{align*}
\]

where types of brackets characterize material state: <> - solid, { } - liquid, [ ] - dissolved, ( ) - gaseous.

This method was used for synthesis of several samples of AlOOH aerogels at various Bi-Al temperatures, with various gas carriers of water steam (hydrogen or argon), modes of delivery of oxygen-rich mixture (below or above liquid Bi-Al level), and water steam contents in oxygen-rich mixture (temperature of wetting agent). Visual examination of samples produced in the surface oxidation mode did not show any significant differences between them, the samples density varying within 7-12 mg/cm\(^3\) range.

Density of aerogel samples produced from liquid Bi-Al with hydrogen-steam mixture supplied below Bi-Al level, turned out to be equal to 26 mg/cm\(^3\) (Figure-2).

![Figure-1. a) AlOOH aerogel (produced from liquid Ga-Al), b) AlOOH aerogel (produced from liquid Bi-Al).](image-url)
The same method was used for aerogel synthesis from liquid Ga-Al: 1) aluminum dissolution in gallium, and 2) aluminum oxidation by water steam:

1) \[ \text{Al} + [\text{Ga}] \rightarrow [\text{Al}] + [\text{Ga}] \],
2) \[ [\text{Al}] + (\text{H}_2\text{O}) \rightarrow \text{AlOOH} + \frac{1}{2}(\text{H}_2) \].

Water steam and argon mixture were used as an oxidizing agent supplied on the surface of liquid Ga-Al.

Experiments were carried out varying aluminum mass added to gallium. Aerogel samples were produced from liquid Ga-Al with aluminum content of 0.19 wt.% and 0.07 wt.%. External view of AlOOH aerogel produced from liquid Ga-Al with aluminum content 0.07 wt.% is presented in Figure-1a). Density of aerogel produced from liquid Ga-Al with aluminum content of 0.19 wt.% was 30 mg/cm$^3$, and the other aerogel sample had density of 8.5 mg/cm$^3$. Comparison of AlOOH and SiO$_2$ aerogels properties (Table-1) demonstrated their good agreement.

### Table-1. Properties of SiO$_2$ and AlOOH aerogels.

<table>
<thead>
<tr>
<th>Properties</th>
<th>AlOOH</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm$^3$</td>
<td>0.005-0.10</td>
<td>0.0011 - 0.65</td>
</tr>
<tr>
<td>Porosity, %</td>
<td>90 - 99</td>
<td>90 - 99</td>
</tr>
<tr>
<td>Specific surface area, m$^2$/g</td>
<td>up to 300 - 800</td>
<td>up to 500 - 950</td>
</tr>
<tr>
<td>Fiber thickness, nm</td>
<td>5 - 10</td>
<td>2 - 3</td>
</tr>
<tr>
<td>Thermal conductivity, W/(m·K)</td>
<td>0.02 - 0.03</td>
<td>0.016 - 0.03</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSIONS

3.1. SEM examination of initial aerogel specimens

SEM examination showed that aerogel had layer-like structure, and the layer interface consisted of many steps (Figure-3). Thickness of the individual layer changing from step to step was within 1-100 μm range of values. Each layer consisted of bundles of filament-wound fibers oriented in the same direction coinciding with that of AlOOH specimen growth in the course of synthesis.

Higher magnification examination of fibers revealed some factors. For instance, in spite of the fact that all fibers are extended in the same direction, they are neither absolutely rectilinear, nor parallel to each other (Figures-3 and Figure-4). Inside the layer, fibers are squirming, interweaving, merging and branching. The thickness of the individual layer varies within the wide range (from 5 to 50 μm). Fiber diameter is within 5 - 15 nm, and the distance between the axes of the adjacent fibers is from 5 to 400 nm, this being in a good agreement with the data from [15]. Fibers density may vary significantly within the aerogel specimen: from almost close-tight bundle structure to that of fibers spaced up to tenths of μm apart. In contrast to the specimens produced from liquid Bi-Al, aerogel made from liquid Ga-Al has more anisotropic structure in the micrometer scale. Such structure was typical for all specimens of AlOOH aerogel.
Figure-3. Microstructure of AlOOH aerogel produced from liquid Ga-Al in the surface oxidation mode.
3.2. Synchronous differential scanning calorimetry and thermogravimetry and X-ray diffraction examination of specimens

Synchronous differential scanning calorimetry and thermogravimetry (DSC/TG) of AlOOH aerogel specimens were carried out. Experiments were conducted using synchronous thermal analysis device STA Jupiter F3. DSC/TG was performed at the temperatures within 20 °C – 1400 °C range. Obtained thermograms (Figure-5) revealed some phase transformations with endothermic and exothermal effects. No phase transformations were detected in the cooling down stage. Neither phase transformations were observed in AlOOH aerogel specimen annealed in the air at 350 °C and tested within 320 °C- 500 °C temperature range. Apparently, these transformations were caused by desorption of damp and other agents, physically and chemically bound with the aerogel fibre surface. Thermal effect at the temperatures of 830 °C – 1000 °C was accompanied by about 3 % mass loss, this probably being caused by the aerogel structural changes, i.e. hydrogen loss. Total reduction of the initial aerogel specimen mass was about 34%. It follows from elemental composition data (energy-dispersive X-ray spectroscopy EDS (EDAX)) on the initial aerogel specimens (Figures-6 and Figure-7) that they contain carbon in the amount from 16 to 22 wt.%. Since no carbon was used in the process of aerogel production, then one can assume that it was adsorbed from the environment. Then the local maximum on dDSC curve at the temperature of about 180 °C refers to carbon, while the local maximum at the temperature of about 110 °C refers to water. It should be noted that the specimen temperature

Figure-4. Microstructure of AlOOH aerogel: a) produced from liquid Bi-Al in surface oxidation mode, b) produced from liquid Bi-Al in volumetric oxidation mode.
can be somewhat lower than the ambient temperature, and therefore, about 10 °C correction can be made. As follows from DSC curve, thermal effects caused by damp and carbon desorption are comparable.

**Figure-5.** DSC/TG examination of aerogel produced from liquid Ga-Al.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Net Int. Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>21.83</td>
<td>30.27</td>
<td>13.15</td>
<td>0.02</td>
</tr>
<tr>
<td>O</td>
<td>50.7</td>
<td>52.78</td>
<td>97.32</td>
<td>0.01</td>
</tr>
<tr>
<td>Al</td>
<td>27.06</td>
<td>16.71</td>
<td>151.56</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**Figure-6.** Elemental composition of aerogel produced from liquid Ga-Al.
Figure-7. Elemental composition of aerogel produced from liquid Bi-Al.

Results of X-ray diffraction examination of aerogel specimens are presented in Table-2. As follows from this data, AlOOH aerogel keeps amorphous up to 1000 °C temperature. Diffraction peaks could be referred to polymorphous forms, which are stabilized by insignificant amounts of the oxide impurities. These impurities can be removed in the course of annealing. In many publications, these forms are considered as metastable compositions emerging in the course of hydrate transformation into the stable phase α-Al2O3. Aerogel is transformed into γ-Al2O3 and α-Al2O3, respectively, at 1000 °C and 1700 °C. The other diffraction peaks might be referred to the unstable polymorphous transformations.

Table-2. Results of X-ray diffraction examination of AlOOH aerogel produced from liquid Ga-Al.

<table>
<thead>
<tr>
<th>Powder states</th>
<th>Phase compositions</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial AlOOH powder</td>
<td>No diffraction peaks referring to oxide or hydrate compounds.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>There is only small peak with d = 4.17 Å</td>
<td></td>
</tr>
<tr>
<td>AlOOH annealed at 100 °C in the air</td>
<td>No diffraction peaks referring to oxide or hydrate compounds.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>There is only small peak with d = 4.17 Å</td>
<td></td>
</tr>
<tr>
<td>AlOOH annealed at 350 °C in the air</td>
<td>No diffraction peaks referring to oxide or hydrate compounds.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Small peaks with d = 4.17 Å and d = 3.15 Å are observed.</td>
<td></td>
</tr>
<tr>
<td>AlOOH annealed at 600 °C in the air</td>
<td>No diffraction peaks referring to oxide or hydrate compounds.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Small peaks with d = 4.17 Å, d = 3.15 Å, and d = 2.75 Å are observed</td>
<td></td>
</tr>
<tr>
<td>AlOOH annealed at 1000 °C in helium</td>
<td>Diffraction peaks refer to γ-Al2O3 phase. Peaks with d = 3.15 Å, d = 1.96 Å, and d = 1.33 Å are observed</td>
<td>Diffraction peaks are small and broadened</td>
</tr>
</tbody>
</table>

3.3. Studies on AlOOH aerogel thermal conductivity

Aerogels belong to the class of materials having, among the other unique properties, min value of thermal conductivity within the wide temperature range. In this view, the domain of aerogels application is growing as regards creation of thermal insulation materials, namely: thermal insulation for liquefied gas flasks and special thermal insulation capable of withstanding high temperature and assuring high temperature gradients. The main specific features of aerogels caused by their low thermal conductivity can be represented as follows:

- effect of thermal conductivity of the solid skeleton on the net value of thermal conductivity is insignificant;
- contact heat transfer between particles (granular and fiber structures) plays the key role under low pressure (vacuum thermal insulation) and at the moderate temperatures, while it can be neglected under normal pressure;
- radiant heat is predominant at high temperatures;
- convective heat transfer in pores and capillaries with d<1+2 mm can be neglected, because no convective flows emerge in such cells;
- thermal conductivity net value strongly depends on thermal conductivity of gas filling pores and capillaries;
- thermal conductivity net value is rather sensitive to the ambient humidity;
- net value of aerogel thermal conductivity is affected by pores diameter and powder density.

In Table-3 are presented the results of measurement of AlOOH aerogel specimen thermal conductivity in steady state thermal modes under various specimen preparation and measurement conditions.

Table-3. Aerogel thermal conductivity coefficient, W/(m·K).

<table>
<thead>
<tr>
<th>Initial specimen</th>
<th>Annealing temperature</th>
<th>At 130 K temperature (initial specimen)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 °C</td>
<td>600 °C</td>
</tr>
</tbody>
</table>

Thermal conductivity of both raw and annealed aerogel specimens was almost the same ($\lambda = 0.020 - 0.027$ W/(m·K)). For the purpose of comparison, value of Al₂O₃ powder varies within the range of 0.08 - 0.1 W/(m·K) at 200 °C. Thermal conductivity of aluminum oxide powder aerogel produced by Kistler method is 0.027 W/(m·K) at 90 °C, and $\lambda$ of silica gel is equal to 0.027 W/(m·K) at 20 °C. Studies of aerogels of some other materials showed, in particular, that their thermal conductivity decreased with temperature decrease. It is also known that thermal conductivity of aerogel powder increases with the increase of thermal conductivity of carrier gas. In helium under atmospheric pressure, $\lambda$ of the aerogel is about three-fold higher and, in hydrogen atmosphere, it is four-fold higher as compared to that in the air. Gas pressure has a strong effect on thermal conductivity of aerogels (under deep vacuum conditions, $\lambda$ decreases by more than the order of magnitude).

Low thermal conductivity of aerogel: ~ 0.02 - 0.03 W/(m·K) within rather wide range of temperatures (130 - 1500 K) speaks for its perspective in the area of development of highly effective special thermal insulation materials capable of withstandng rather high temperature gradients. In order to assure AlOOH aerogel competitiveness in any application area, additional experimental studies are required on its thermal conductivity within the wide range of conditions, i.e. when powder temperatures ranging from cryogenic to max possible temperature $T \geq 1300$ °C, at various air pressure (from $10^{-5}$ at to normal pressure), and in various gases (from inert gases to helium and hydrogen).

3.4. Studies on aerogel effect on the properties of ceramic materials SiC, Si₃N₄ and ZrO₂

In all studies (results of which are presented below), ceramics was produced by technology, which is standard for each specific material, with only one additional procedure, namely: putting additive of nanostructured aerogel AlOOH to the initial matrix powders. As a rule, this procedure was carried out in the stage of adding or preparation of softening agent. Aerogel additive ranged from 0.5 to 5 wt.%. Studies were carried out on the possibility of production of high-density heat-resisting ceramics based on such powders as Si₃N₄ (powder fabricated using self-spaying high temperature synthesis), SiC (plasma chemical synthesis) and some other materials, using small amounts of agglomeration accelerating agent as nanostructured aerogel AlOOH. Studies on the use of small additives of AlOOH aerogel (0.5 - 5 wt.%) as accelerator of Si₃N₄ and SiC powders agglomeration for fabrication of heat-resisting ceramics showed that modifying aerogel additive increases physical and mechanical characteristics of fabricated materials, namely: zero porosity, significant increase of strength, crack resistance and hardness, extension of working temperature range, etc. (there is 20-30% increase of the above parameters values) (Figure-8). It was ascertained that addition of 0.5 - 1 wt.% of aerogel to the certain “Si₃N₄ - 5 wt.% MgO” system provided decrease of open porosity of ceramic material from 1 - 2 % to 0.3 %, increase of its strength up to 750 MPa at the ambient temperature, increase of working temperature range up to 1300 °C, and, hence, at large, provided increase of basic characteristics of fabricated ceramic material by up to 20 %.
It was revealed that small additives of AlOOH aerogel (0.1 - 5wt.%) to the initial powder of partially stabilized zirconium dioxide ZrO$_2$+$Y_2$O$_3$ led (with agglomeration at 1500 °C during 1 hour) to the change of phase composition of produced ceramics toward the increase of high temperature cubic phase with better ion-conductivity, while sufficiently high mechanical strength of the solid electrolyte was kept. Thermal shock tests of specimens of detector elements (ZrO$_2$+$Y_2$O$_3$) of oxygen activity sensor in “liquid Pb-Bi – water” system showed that small additives of aerogel to solid electrolyte increased their thermal shock resistance by about 20%, and the best additive value was 1 wt.% (Figure-9).
Figure-9. Results of thermal shock tests of specimens in "liquid Pb-Bi - water" system (t (H₂O)=200°C, t (PbBi)=200-280°C, t=2.5 s).

One of the problems related to the use of traditional nanostructured oxide powders as composite filling agents, agglomeration accelerating agents or raw ceramics material is powder aging. Because of high surface energy, powder particles are sticking together to produce larger particles with time, resulting in the loss of their assets, aging time ranging from several hours to several weeks. AIOOH aerogel advantage over such powders is that it is not subject to aging and so, its nanostructured form can be kept for indefinitely long time.

4. CONCLUSIONS

As a result of studies, samples of nanostructured aerogel AIOOH were produced using method of selective oxidation of binary liquid metals Ga-Al and Bi-Al by water steam. The results of microstructure analysis showed that AIOOH aerogel had a stable, oriented in space fibrous nanostructure with “tensile” type anisotropy, fiber diameter varying from 5 to 15 nm. It has been demonstrated that properties of AIOOH and those of quartz aerogel SiO₂ produced by sol-gel technology were very similar. However, in contrast to the autoclave-based sol-gel technology, synthesis of AIOOH aerogel takes place under atmospheric pressure, and neither hazardous, nor corrosion agents are used, this allowing to decrease factory labor hours and cost of aerogel. This opens brand new possibilities for practical application of AIOOH nanostructured aerogel synthesized by the liquid metal technology in the development of special thermal and electric insulation, high-temperature, high-strength ceramic materials (to be used as materials of nuclear fuel elements, sensors for detecting impurities in liquid metals, etc.), development of the new sorbents for purifying liquids and gases, new generation catalysts and their carriers for using in chemical industry, and new polymers with improved performance characteristics.

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