Methods for making a neutron converter layer are provided. The various embodiment methods enable the formation of a single layer neutron converter material. The single layer neutron converter material formed according to the various embodiments may have a high neutron absorption cross section, tailored resistivity providing a good electric field penetration with submicron particles, and a high secondary electron emission coefficient. In an embodiment method a neutron converter layer may be formed by sequential supercritical fluid metallization of a porous nanostructure aerogel or polyimide film. In another embodiment method a neutron converter layer may be formed by simultaneous supercritical fluid metallization of a porous nanostructure aerogel or polyimide film. In a further embodiment method a neutron converter layer may be formed by in-situ metalized aerogel nanostructure development.
References Cited

OTHER PUBLICATIONS


FIG. 1
FIG. 2
Machine Aerogel Or Polymer Matrix To Selected Converter Layer Size

Dissolve Neutron Hardening Precursor In Supercritical CO₂ Fluid Above 31.1°C and 7.29 MPa

Infuse Supercritical CO₂ Fluid Into Aerogel Or Polymer Matrix

Lower Pressure

Reduce At Elevated Temperature

Infuse Conductive Precursor

Infuse SEE Element Precursor

FIG. 4
Machine Aerogel Or Polymer Matrix To Selected Converter Layer Size

Dissolve Neutron Hardening, Conductive, SEE Element Precursors In Supercritical CO₂ Fluid Above 31.1°C and 7.29 MPa

Infuse Supercritical CO₂ Fluid Into Aerogel Or Polymer Matrix

Lower Pressure

Reduce At Elevated Temperature

FIG. 5
Form Solution Of Alkoxide, Water, Alcohol, And Catalyst In Presence Of Metal Precursors

Add Carbon Nanotubes or Other Metal Precursors To Adjust Resistivity

Adjust Composition Of Alkoxide Solution, Water, Alcohol, And Catalyst To Control Rate Of Hydrolysis And Condensation To Form Metalized Aerogel

Dry Metalized Aerogel Using Supercritical CO$_2$ Fluid At 31.1°C and 7.29 MPa

FIG. 6
The present invention provides methods for making a neutron converter layer. The various embodiment methods enable the formation of a single layer neutron converter material. The single layer neutron converter material formed according to the various embodiments may have a high neutron absorption cross-section, tailored resistivity providing a good electric field penetration with submicron particles, and a high secondary electron emission coefficient.

In an embodiment method a neutron converter layer may be formed by sequential supercritical fluid metallization of a porous nanostructure aerogel or polyimide film. In another embodiment method a neutron converter layer may be formed by simultaneous supercritical fluid metallization of a porous nanostructure aerogel or polyimide film. In a further embodiment method a neutron converter layer may be formed by in-situ metalized aerogel nanostructure development.
As used herein “a high electron emission coefficient” may be a secondary electron emission coefficient (“SEE”) greater than 1.

As used herein “tailored resistivity” may be resistivity greater than or equal to 10^7 Ohms/cm and less than or equal to 10^9 Ohms/cm.

Materials for neutron radiation detection that can provide a high neutron absorption cross-section, high electron emission coefficient, and tailored resistivity have rarely been studied. Multiple layers have been used to attempt to achieve a high neutron absorption cross-section, high electron emission coefficient, and tailored resistivity, but there are a number of disadvantages to using multiple layers, in particular, the inability to achieve a material with a high neutron absorption cross-section, high electron emission coefficient, and tailored resistivity without disrupting other functions of the material. Multiple layer material has required the use of large amounts of filler material to achieve a high neutron absorption cross-section, high electron emission coefficient, and tailored resistivity. The use of filler material has resulted in increasing the weight of the multiple layer material because fillers are generally denser than the matrix of the multiple layer material, complexity in manufacture of the multiple layer material, and cost increases for the multiple layer material, as larger amounts of neutron attenuating filler material are added. Additionally, processability of the multiple layer material decreases as filler volume increases and negative impacts on other desirable properties of the multiple layer material occur as filler volume increases.

The present invention provides methods for making a neutron converter layer. The various embodiment methods enable the formation of a single layer neutron converter material. The various embodiments may enable the development of a neutron converter layer formed as a one layer porous nanostructure or a one layer solid film. The single layer neutron converter material formed according to the various embodiments may have a high neutron absorption cross-section, tailored resistivity providing a good electric field penetration with submicron particles, and a high electron emission coefficient. In some embodiments, a high neutron absorption cross-section may be achieved by the use of lithium (Li), boron (B), and/or gadolinium (Gd) as precursors. In some embodiments, a high electron emission coefficient may be achieved by the use of Magnesium Oxide (MgO) and/or Cesium Iodide (CsI) as precursors.

Neutron shielding materials for aerospace applications are being developed under the Materials International Space Station Experiments (“MISSE”) program. Emerging materials such as boron nitride nanotubes (“BNN”) and single wall carbon nanotubes (“SWCNT”) as well as B, hexagonal boron nitride (h-BN), and Gd nanoparticles have been studied using a neutron exposure lab with a 1 Curie (Ci) americium/beryllium source. The preliminary study indicates that BNN, h-BN, and Gd exhibited excellent neutron radiation shielding effectiveness compared with polyethyl-

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>Neutron Abs x-sections (barns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth</td>
<td>BN (2.27); BNNT (1.37)</td>
<td>710 (10^{27}; 3835)</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>79</td>
<td>400</td>
</tr>
<tr>
<td>Lead</td>
<td>11.34</td>
<td>0.28</td>
</tr>
<tr>
<td>Titanium</td>
<td>4.54</td>
<td>5.0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>gas</td>
<td>1.9</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>gas</td>
<td>0.33</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.8-3.5</td>
<td>0.0035</td>
</tr>
</tbody>
</table>

FIG. 4 is a process flow diagram illustrating an embodiment method 400 for forming a neutron converter layer by sequential supercritical fluid metallization of a porous nanostructure aerogel or polyimide film. In step 402 a nanostructured aerogel or polymer matrix (e.g., a commercially purchased nanostructured aerogel or polyimide film) may be machined to a selected (e.g., appropriate to the intended application) dimension for the converter layer. In step 404 neutron hardening precursors (e.g., B and/or Gd) may be dissolved in a supercritical carbon dioxide (CO₂) fluid above 31.1 degrees Celsius and 7.29 MPa (72.0 bar). In step 406 the supercritical CO₂ fluid with the precursors dissolved in it may be infused into the aerogel or polymer (i.e., polyimide) matrix. In step 408 the pressure may be lowered, thereby trapping the infused metal precursors into the internal pores and surfaces of the aerogel or polymer matrix uniformly while the highly diffusive CO₂ escapes rapidly. In step 410 the trapped and deposited metal precursors may be reduced.
at an elevated temperature to create nanoparticles. In step 412 conductive precursors may be infused, and in step 414 high SEE element precursors (e.g., MgO and/or CsI) may be infused to provide appropriate conductivity and SEE, respectively to the neutron converter layer.

FIG. 5 is a process flow diagram illustrating an embodiment method 500 for forming a neutron converter layer by simultaneous supercritical fluid metallization of a porous nanostructure aerogel or polyimide film. Method 500 is similar to method 400 described above with reference to FIG. 4, except that in method 500 the neutron hardening, conductive, and SEE element precursors are applied together. In step 502 neutron hardening precursors (e.g., B and/or Gd), conductive, and SEE element precursors (e.g., MgO and/or CsI) may be dissolved in a supercritical carbon dioxide (CO₂) fluid above 31.1 degrees Celsius and 7.29 MPa (72.0 bar). Because the neutron hardening, conductive, and SEE element precursors are applied together, steps 412 and 414 may not be required in method 500.

FIG. 6 is a process flow diagram illustrating an embodiment method 600 for forming a neutron converter layer by in-situ metalized aerogel nanostructure development. In method 600 the aerogel may be created via a sol-gel process in the presence of metal precursors (e.g., Gd₂O₃, B₂O₃, MgO, and/or CsI). In step 602 a solution of alkoxide solution, water, alcohol, and basic catalyst may be formed in the presence of the metal precursors. In optional step 604 the resistivity of the metalized aerogel may be adjusted by adding a small quantity of carbon nanotubes or other metal precursors. In step 606 the composition of the aerogel structure, water, alcohol, and basic catalyst may be adjusted to control the rate of hydrolysis and condensation. The radiation hardening precursors (e.g., B and/or Gd) and the high SEE nanoparticles (e.g., MgO and/or CsI) may uniformly form inside of the aerogel structure. In step 608 supercritical carbon dioxide (CO₂) fluid at 31.1 degrees Celsius and 7.29 MPa (72.0 bar) may employed to dry the condensed gel with the nanoparticles. Method 600 may provide uniformly distributed functional nanoparticles incorporated into an aerogel nanostructure.

All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. Each range disclosed herein constitutes a disclosure of any point or sub-range lying within the disclosed range.

The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. "Or" means "and/or." As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items. As also used herein, the term "combinations thereof" includes combinations having at least one of the associated listed items, wherein the combination can further include additional, like non-listed items. Further, the terms "first," "second," and the like herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the particular quantity).

Reference throughout the specification to "another embodiment", "an embodiment", "some embodiments", and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and can or cannot be present in other embodiments. In addition, it is to be understood that the described elements can be combined in any suitable manner in the various embodiments and are not limited to the specific combination in which they are discussed.

The preceding description of the disclosed embodiments is provided to enable any person skilled in the art to make or use the present invention. Various modifications to these embodiments will be readily apparent to those skilled in the art, and the generic principles described herein may be applied to other embodiments without departing from the spirit or scope of the invention. Thus, the present invention is not intended to be limited to the embodiments shown herein but is to be accorded the widest scope consistent with the following claims and the principles and novel features disclosed herein.

What is claimed is:

1. A method for forming a neutron converter layer, comprising:
   - machining an aerogel or polymer matrix to a selected converter layer size;
   - dissolving a neutron hardening precursor in a supercritical carbon dioxide (CO₂) fluid above a temperature of 31.1 degrees Celsius and a pressure of 7.29 MPa;
   - infusing the supercritical CO₂ fluid with the dissolved neutron hardening precursor into the aerogel or polymer matrix;
   - lowering the pressure to trap the infused neutron hardening precursor in the aerogel or polymer matrix;
   - reducing the aerogel or polymer matrix including the trapped infused neutron hardening precursor at an elevated temperature;
   - infusing a conductive precursor into the reduced aerogel or polymer matrix; and
   - infusing a secondary electron emission coefficient (SEE) element precursor into the reduced aerogel or polymer matrix.

2. The method of claim 1, wherein the neutron hardening precursor is boron or gadolinium.

3. The method of claim 2, wherein the SEE element precursor is magnesium oxide or cesium iodide.

4. The method of claim 3, wherein the neutron converter layer has a high neutron absorption cross-section, a high electron emission coefficient, and a tailored resistivity.

5. A method for forming a neutron converter layer, comprising:
   - machining an aerogel or polymer matrix to a selected converter layer size;
   - dissolving neutron hardening precursor, a conductive precursor, and a secondary electron emission coefficient (SEE) element precursor in a supercritical carbon dioxide (CO₂) fluid above a temperature of 31.1 degrees Celsius and a pressure of 7.29 MPa;
   - infusing the supercritical CO₂ fluid with the dissolved neutron hardening precursor, conductive precursor, and SEE element precursor into the aerogel or polymer matrix;
lowering the pressure to trap the infused neutron hardening precursor, conductive precursor, and SEE element precursor in the aerogel or polymer matrix; and reducing the aerogel or polymer matrix including the trapped infused neutron hardening precursor, conductive precursor, and SEE element precursor at an elevated temperature.

6. The method of claim 5, wherein the neutron hardening precursor is boron or gadolinium.

7. The method of claim 6, wherein the SEE element precursor is magnesium oxide or cesium iodide.

8. The method of claim 7, wherein the neutron converter layer has a high neutron absorption cross-section, a high electron emission coefficient, and a tailored resistivity.

9. A method for forming a neutron converter layer, comprising:
   forming a solution of an alkoxide solution, water, alcohol, and a basic catalyst in the presence of metal precursors;
   adjusting a composition of the alkoxide solution, water, alcohol, and the basic catalyst to control a rate of hydrolysis and condensation and form a metalized aerogel having radiation hardened nanoparticles and secondary electron emission coefficient (SEE) nanoparticles; and
   drying the metalized aerogel having radiation hardened nanoparticles and SEE nanoparticles using a supercritical carbon dioxide (CO₂) fluid at a temperature of 31.1 degrees Celsius and a pressure of 7.29 MPa to form a single layer neutron converter material.

10. The method of claim 9, wherein the metal precursors are selected from the group consisting of Gd₂O₃, B₂O₃, MgO, CsI, and any combinations thereof;
   wherein the radiation hardened nanoparticles include boron or gadolinium, and wherein the secondary electron emission coefficient (SEE) nanoparticles include magnesium oxide or cesium iodide.

11. The method of claim 9, further comprising adding a quantity of carbon nanotubes to adjust a resistivity of the metalized aerogel having radiation hardened nanoparticles and SEE nanoparticles.

12. The method of claim 11, wherein the neutron converter layer has a high neutron absorption cross-section, a high electron emission coefficient, and a tailored resistivity.

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