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**C03C 11/00** (2006.01) **F25B 9/00** (2006.01)

(56) Documents Cited:  
**US 4359872 A** **US 4303732 A**  
**US 20120258022 A**

(58) Field of Search:  
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(54) Title of the Invention: **High heat-capacity material for low temperature applications**  
Abstract Title: **High heat-capacity material for low temperature applications**

(57) A material is disclosed which comprises hollow elements, such as glass microspheres, which contain cryogen, and the hollow elements are each provided with a coating of graphene. The cryogen may be by helium, hydrogen, nitrogen or neon. The hollow elements may be embedded in a matrix and form part of a heat storage element forming part of a cryostat in a superconducting magnet device. A method of preparing the material is disclosed which comprises exposing hollow elements to an atmosphere of cryogen gas, allowing the cryogen gas to diffuse into the hollow elements and then depositing graphene on the surface of the hollow element.

FIG 1

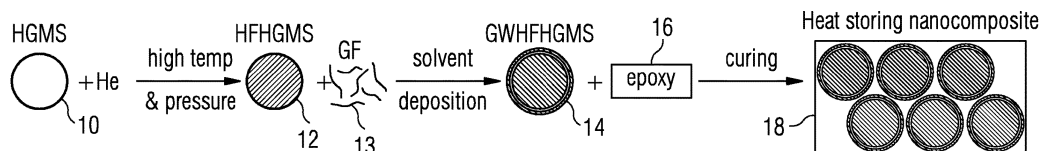


FIG 1

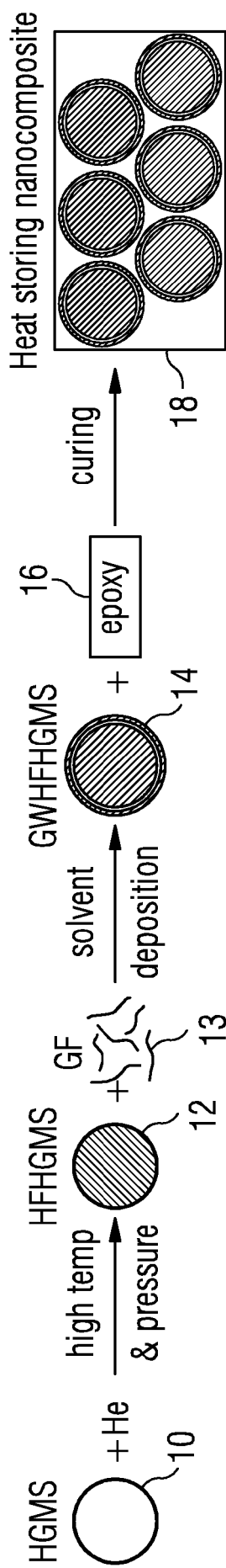


FIG 2

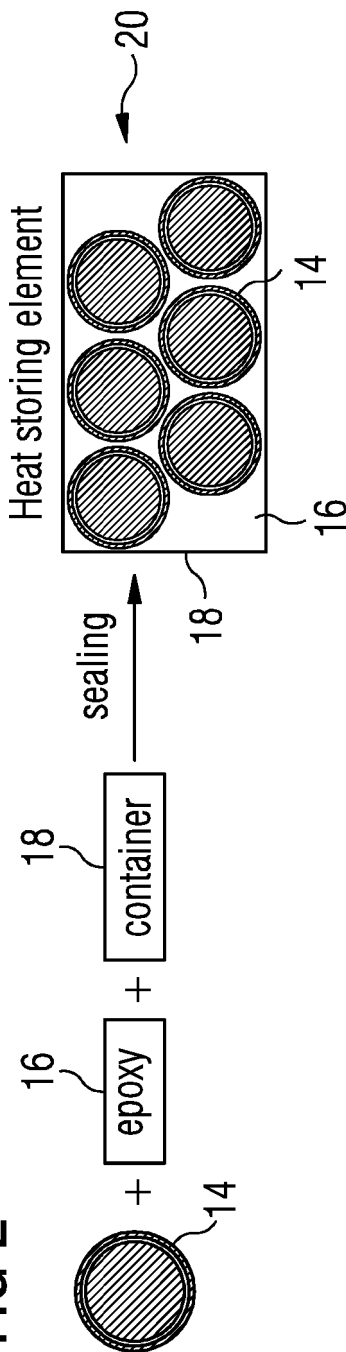


FIG 3

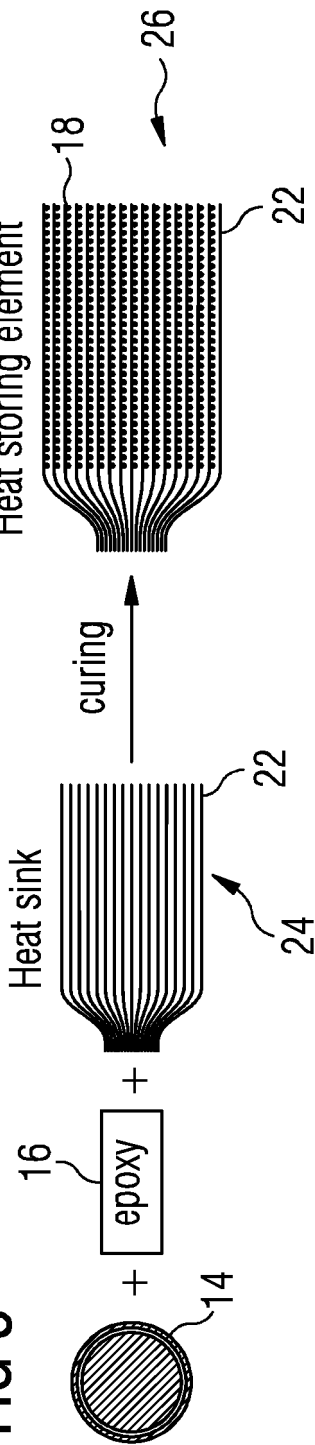


FIG 4

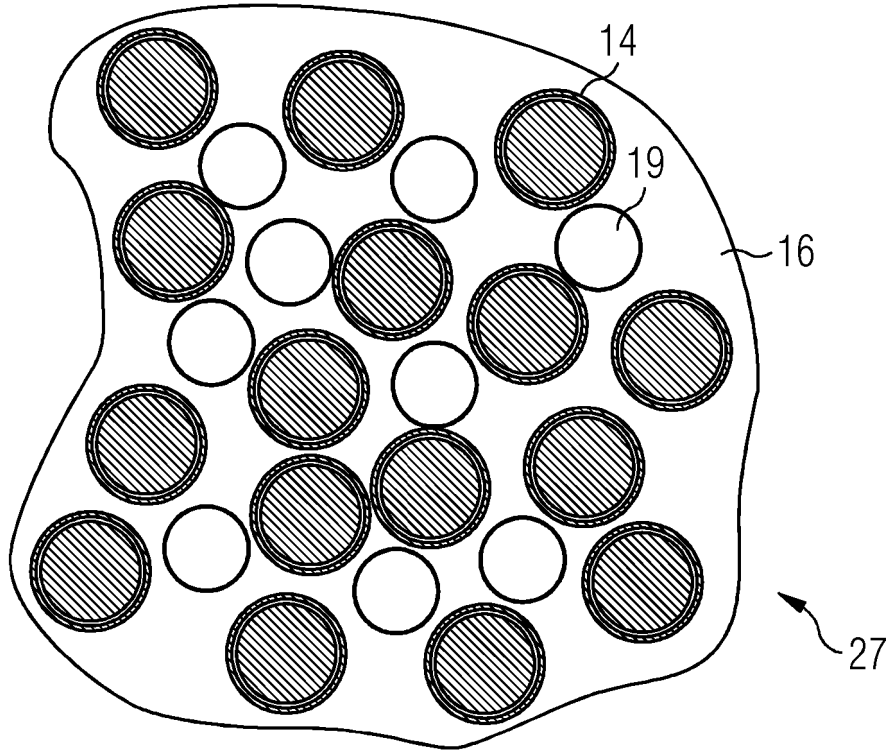


FIG 5

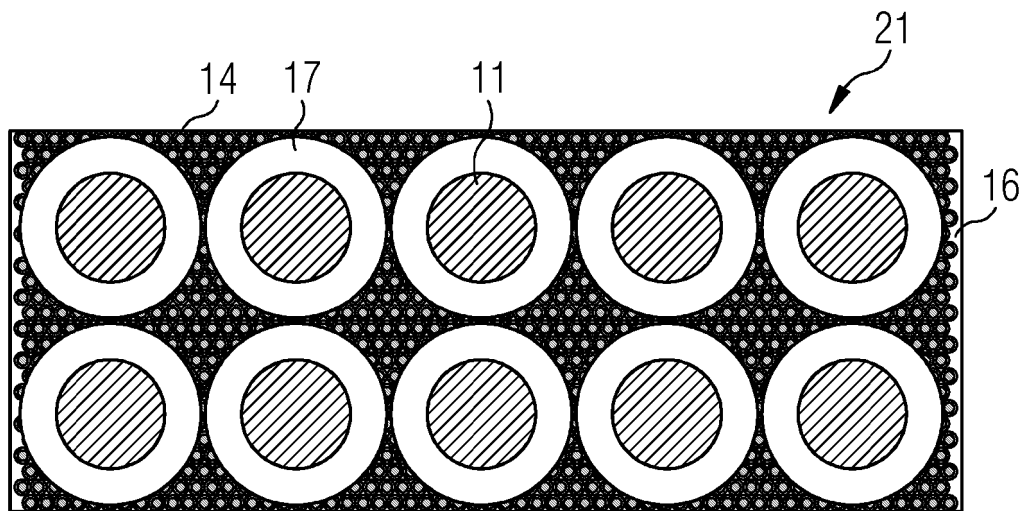


FIG 6

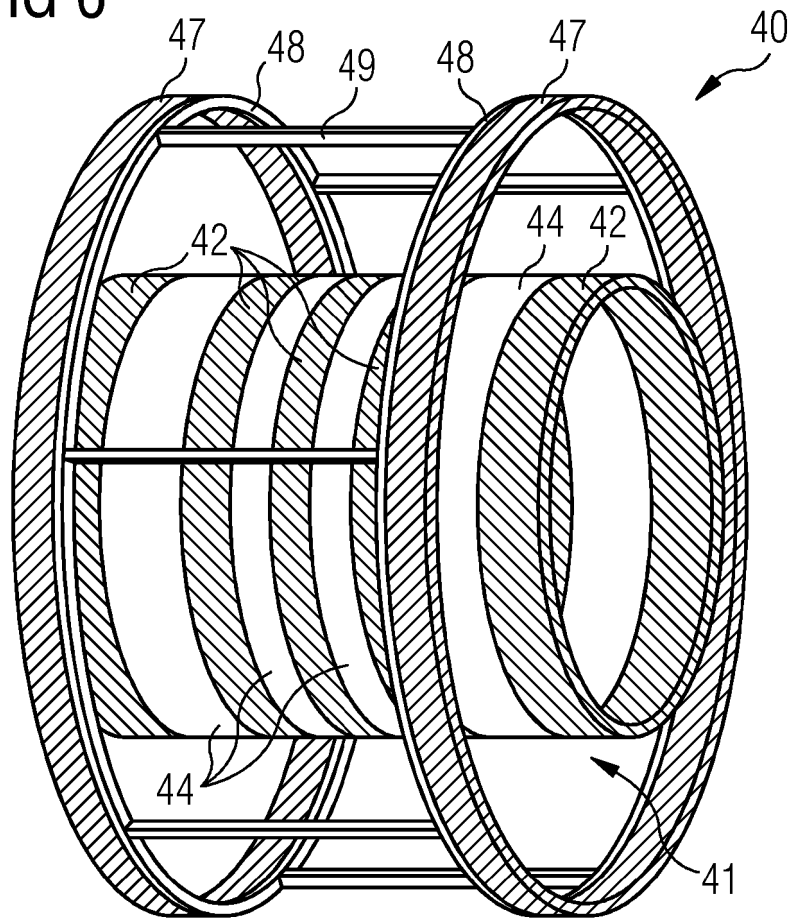


FIG 7A

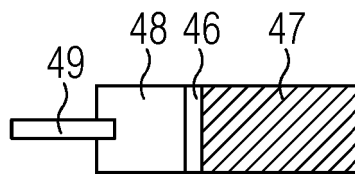


FIG 7B

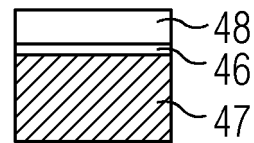
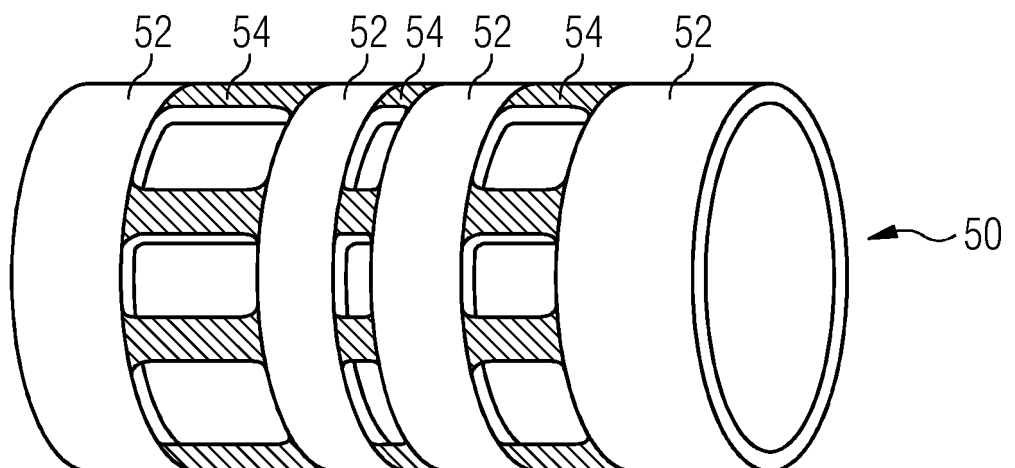


FIG 8



## HIGH HEAT-CAPACITY MATERIAL FOR LOW TEMPERATURE APPLICATIONS.

In the field of superconducting apparatus, such as superconducting magnets for MRI systems, it is required to maintain a relatively large mass of superconducting material at a cryogenic temperature, even in case of a failure or unavailability of active cooling such as refrigeration.

Conventionally, a superconducting magnet has been kept cool by at least partial immersion in liquid cryogen within a cryogen vessel forming part of a cryostat. During transit, or other times that active cooling is not available, some of the liquid cryogen boils to maintain the temperature of the superconducting magnet and the boiled-off cryogen is lost to atmosphere. Alternatively, the cryogen vessel is a high-pressure vessel to contain significant increase in internal pressure due to the boil-off of the cryogen. Both alternatives are costly - the first in terms of cryogen consumption, the second in terms of material and handling cost of a heavy cryogen vessel and subsequent transport costs.

The present invention seeks to provide a high heat-capacity material which may be provided within the cryogen vessel, preferably as a part of the superconducting magnet, or other cryogenically-cooled apparatus as appropriate. Such a material may be cooled with the superconducting magnet or other cryogenically-cooled apparatus when active cooling is available. During times that active refrigeration is not available, such as during transport, heat influx into the cryogen vessel will cause a rise in temperature of equipment within the cryogen vessel, but by providing a high heat-capacity material, the resultant rise in temperature will be minimised.

The material of the invention exhibits particularly high heat capacity at cryogenic temperatures. This renders it suitable for a wide range of uses including: superconducting magnets and regenerators for a closed thermodynamic cycle cryogenic coolers.

The following pieces of prior art provide some background to the present invention, and copies of the non-patent prior art are filed with the present application.

- [1] US 4,359,872 - Low Temperature Regenerators For Cryogenic Coolers
- 5 [2] US 2006/0201163 A1
- [3] P. C. Souers et al., "Permeation Eccentricities of He, Ne, and D-T from Soda-Lime Glass Microbubbles" - Journal of The American Ceramic Society Vol. 61, No. 1-2 pp. 42-46.
- [4] J. S. Bunch et al., "Impermeable Atomic Membranes from Graphene
- 10 Sheets" - Nano Letters, 2008 Vol. 8, No. 8, pp. 2458-2462
- [5] O. Leenaerts et al., "Graphene: A perfect nanoballoon" - Applied Physics Letters 93, 193107 (2008);
- [6] US 4133854 A - Method for producing small hollow spheres
- [7] US 4257799 A - Method for producing small hollow spheres
- 15 [8] R. T. Tsugawa et al., "Permeation of helium and hydrogen from glass-microsphere laser targets" Journal of Applied Physics, Vol. 47, No. 5, May 1976, pp. 1987-1993.
- [9] Y. Tong et al., "Graphene based materials and their composites as coatings" - Austin J Nanomed Nanotechnol - Volume 1 Issue 1 - 2013,
- 20 pp. 1-16.
- [10] W. Fan et al. - " Graphene-Wrapped Polyaniline Hollow Spheres As Novel Hybrid Electrode Materials for Supercapacitor Applications" - ACS Appl. Mater. Interfaces 2013, 5, 3382-3391.
- [11] US 4,303,732 - Glass Microspheres plastics
- 25 [12] US 20120301707 A1 - Graphene polymer composite
- [13] US 2014/0299475 A1 - Composite Graphene Structures
- [14] US 2015/0232343 A1 - Metal-free CVD coating of Graphene on Glass and other Dielectric Substrates
- [15] Yu-Ze Chen et al., "Low Temperature Growth of Graphene on Glass
- 30 by Carbon-Enclosed Chemical Vapor Deposition Process and its Application as Transparent Electrode" Chem. Mater. 2015, 27, 1646-1655.
- [16] Jingyu Sun et al., "Direct Chemical Vapor Deposition-Derived Graphene Glasses Targeting Wide Ranged Applications" Nano Lett. 2015,
- 35 15, 5846-5854.

Hollow glass microspheres are small glass containers capable of high pressure gas storage. Such storage offers inherent safety due to the small capacity of each individual hollow glass microsphere. Damage to

any one microsphere will release only a very small quantity of gas, and is unlikely to cause any damage to adjacent microspheres. Hollow glass microspheres may have a very high tensile strength. For example, the tensile strength for steel is in a range of 300-700 MPa compared the strength of many glasses reported to be in the range of 2-7 GPa.

Gases can diffuse into the hollow cores of glass microspheres through the thin glass wall at a rate dependent on wall temperature, and pressure differential across the wall of the glass microsphere. The hollow glass microspheres may therefore be filled with gases by placing them in high temperature and high pressure chambers.

In order to store helium gas in hollow glass microspheres for a useful time, the gas diffusion rate through walls of the hollow glass microspheres needs to be decreased by decreasing the temperature of the hollow glass microspheres. Room temperature helium storage in the hollow glass microspheres as described in [1,2] can be done for a relatively short time (days) due to relatively high helium diffusion through glass. This means that helium filled hollow glass microspheres need to be kept at cryogenic temperatures to slow down helium diffusion rate and extend helium storage time to months and years.

With data for helium permeability through silica lime glass published in [3] it can be calculated that in order to store helium at pressure of 500BAR and lose only 0.5% of initial pressure over 25 years period the temperature of hollow glass microspheres needs to be lowered to around 150K. For storage at room temperature (300K) helium pressure inside hollow glass microspheres will decrease from 500BAR to 36BAR and 2BAR after 24h and 48h period, respectively (for 8 $\mu$ m OD and 7.5 $\mu$ m ID spheres). The present invention seeks to address this issue and provide helium storage inside hollow glass microspheres at room temperature for a significant duration.

The present invention accordingly provides high heat capacity material and methods for manufacturing high heat capacity material as defined in the appended claims.

The above, and further, objects, characteristics and advantages of the present invention will become more apparent from the following description of certain embodiments thereof, in conjunction with the accompanying drawings, wherein:

- 5 Fig. 1 schematically shows production steps of a method for manufacture of a heat storing nanocomposite material according to an embodiment of the invention;
- Fig. 2 schematically illustrates the manufacture of a heat storing element from the material manufactured by the method of Fig. 1;
- 10 Fig. 3 schematically illustrates the manufacture of a heat sink from the material manufactured by the method of Fig. 1;
- Fig. 4 schematically illustrates a three-part composite material according to an embodiment of the present invention;
- Fig. 5 schematically illustrates a structure of an electrically
- 15 conductive composite material according to an embodiment of the invention;
- Fig. 6 shows a serially bonded magnet including annular spacers and support elements constructed from a material of the present invention;
- Figs. 7A and 7B show detail of example constructions of magnets similar
- 20 to that shown in Fig. 6 and
- Fig. 8 shows a serially bonded magnet including intermittent spacers constructed from a material of the present invention.

In the following description, hollow glass microspheres will be

25 referred to, but other hollow elements may be used. Similarly, helium is preferentially referred to as the cryogen, but other cryogens may be used.

Helium-filled hollow glass microspheres have been described as high heat capacity storage for example in: US4359872 (1982) and in

30 US2006/0201163A1. However, at room temperature helium diffuses out through thin glass walls at relatively high rate. This diffusion makes usage of helium filled hollow glass microspheres a challenge due to helium and heat capacity loss over time at ambient temperature. In the manufacture of superconducting magnets, the equipment is present at

35 ambient temperature during magnet production, during transport or on-site when active cooling is lost.



According to the present invention, the known cryogen storage use of glass microspheres and other hollow elements is improved by the addition of a gas-impermeable coating layer of graphene on the outer surface of the hollow elements after the cryogen is added. Graphene coating of the hollow elements stops cryogen diffusion from hollow elements.

The graphene-coated, cryogen-filled hollow elements may be used in this form, for example as a regenerator for a closed thermodynamic cycle cryogenic cooler, in the manner described in US4359872.

Preferably, the cryogen-filled hollow elements are then embedded in a matrix material, which may be a polymer or resin material - a thermoplastic or thermosetting material - or a metal or other suitable material. The matrix may itself be a composite of different materials, such as metal powder or filaments such as glass fibres in a resin. The result is a material which may be cast, moulded or machined into useful components. The heat capacity will largely be determined by the cryogen content. The matrix material may contribute to the thermal conductance of the material and its mechanical properties. The mechanical properties of the hollow glass microspheres mean that such a material still has a significant mechanical strength. Mechanical damage causing cracks and leaks from few glass microspheres does not greatly affect heat storage capacity or mechanical strength of such composite.

In certain embodiments of the invention, the material is used to make parts of cryogenically-cooled equipment, such as components of superconducting magnets and regenerators for a closed thermodynamic cycle cryogenic coolers.

The material of the invention, which may be referred to as a "nanocomposite", may be both electrically insulating and non-magnetic, depending on the matrix material used and the material of the hollow elements, which are both useful properties for producing parts of a superconducting magnet.

Fig. 1 schematically shows production steps of a method for manufacture of a heat storing nanocomposite material according to an embodiment of the invention.

Hollow glass microspheres (HGMS) 10 are provided, such as the commercially available 3M™ Glass Bubbles iM30K.

5 The hollow glass microspheres are exposed to high pressure (e.g. about 500BAR) and temperature (e.g. about 450°C) cryogen (e.g. helium) atmosphere. The temperatures and pressures are at least in excess of ambient temperature and pressure: preferably much in excess of ambient temperatures and pressures. It may be preferred to gradually increase  
10 pressure from ambient to some elevated level during diffusion, to maintain a constant pressure difference across the wall of the hollow element as the hollow element fills, then bring the pressure gradually back to ambient. The hollow glass microspheres will fill more quickly if the helium is provided at high temperature and pressure. Helium  
15 diffuses through glass walls to the inside of the hollow glass microspheres. The elevated temperature aids the diffusion of the helium through the glass walls of the microspheres, but is not high enough to cause softening of the microspheres. The high pressure also assists with helium diffusion through the glass walls of the  
20 microspheres.

After filling with helium to become helium-filled hollow glass microspheres (HFHGMS) 12, the temperature of the microspheres is lowered to slow down the helium diffusion process through walls of the  
25 microspheres. When cooling down is completed the helium pressure is reduced to atmospheric pressure.

An optional chemical treatment of the surface of the microspheres may be applied to provide surface functionalization or better graphene  
30 coating adhesion.

Graphene layer(s) is/are deposited, for example by known techniques as a coating of graphene flakes (GF) 13 on the surface of the microspheres. This process results in graphene-wrapped, helium-filled  
35 hollow glass microspheres (GWHFGMS) 14. Alternatively, graphene oxide flakes may be used.

In another alternative process, a continuous coating of graphene may be provided on the hollow glass microspheres, by a process of

deposition on the surface of glass spheres by chemical vapour deposition method (CVD) [14], [15], [16]. Graphene can be also deposited by CVD methods assisted by catalysts like Cu or Ni (Catalytic CVD) and also to plasma enhanced CVD (PECVD).

5

During a CVD deposition process, the CVD deposition atmosphere preferably comprises the cryogen gases which is inside the hollow elements, and the CVD process should be carried out under high pressure to minimise loss of cryogen from the hollow elements.

10

The temperature of the CVD deposition will depend on the material of the hollow elements, but in general it should be chosen in a way to achieve an acceptable rate of deposition but to avoid softening of the material of the hollow elements. For glass, typically this is in the range from 500 to 1100 deg C. Other materials such as  $\text{Al}_2\text{O}_3$  would allow higher deposition temperatures than glass.

15

An optional protective layer may be provided to cover the graphene layers. This may be any suitable material, for example a metal layer. Preferably, a different material is used for the protective layer as compared to the matrix material. More than one protective layer may be applied, of differing materials.

20

The graphene-wrapped, helium-filled hollow glass microspheres 14 are mixed with a matrix material. In the example of Fig. 1, this is an epoxy 16 and a forming process such as casting or moulding is applied to manufacture an end product, such as an ingot of material 18 of heat storing nanocomposite.

25

Fig. 2 shows that graphene-wrapped, helium-filled hollow glass microspheres 14 can be mixed with matrix material 16 such as epoxy and poured into containers 18 to form heat storing elements 20. The container 18 may simply serve as a mould, and may be removed after this process. Optionally, the container can be left in place around the resultant block of heat storing nanocomposite material 18, and used for a functional purpose e.g. to make it easy to attach heat conducting members to cool down or warm up a heat storing element comprising the nanocomposite material.

30

35

Fig. 3 shows another method in which graphene-wrapped, helium-filled hollow glass microspheres 14 are mixed with epoxy 16 and injected in between cooling fins 22 of heat sink or heat exchanger 24. This option allows for fast heat transfer to and from a heat storing element made with the heat storing nanocomposite material. The resultant heat storing element 26 comprises heat exchanger 24 with cooling fins 22 in thermal contact with high heat-capacity material 18 of the present invention.

Although the addition of the matrix material 16 may be optional, since the graphene-wrapped helium filled glass microspheres will have their essential properties of heat capacity and low cryogen outdiffusion, retaining a high pressure helium gas at room temperature, the matrix material provides protection for the graphene coating, reducing its tendency to absorb moisture and react with oxygen.

Fig. 4 illustrates a three-part composite material 27, comprising graphene-wrapped, helium filled hollow glass microspheres 14 are mixed with matrix material 16 which itself is a fibre 19 reinforced composite. Fibres 19 can be continuous or chopped fibres and be made of glass, carbon, aramid, polyethylene, boron, ceramic, metal, metal alloy or natural fibres. In this case, high heat capacity, fibre reinforced three-part composite 27 may be produced by bag-molding, compression molding, poltrusion, filament winding, sheet molding and various lay-up techniques as will be obvious to a person skilled in the art. Resin used to produce fibre reinforced composite 27 will be loaded with helium filled hollow glass microspheres 14.

Fig. 5 shows a structure in which graphene-wrapped, helium filled hollow glass microspheres 14 mixed with matrix material 16 to form a composite material for use in immobilising wires 11. Wires 11 may be provided with insulation 17 and embedded within the mixture of graphene-wrapped, helium filled hollow glass microspheres 14 with matrix material 16. The resulting structure of insulated wires in a composite material may be regarded as an electrically conducting composite 21 which can be used in the structure of a superconducting magnet. Wire 11 may be of copper, aluminium, steel, stainless steel or other metals or alloys.

Insulation 17 can be made by hard insulating wire with enamel or braiding wires with polyester or glass fibre braid.

It has been demonstrated [4] that perfect graphene sheets are impermeable to standard gases, including helium. The electron density of aromatic rings in graphene is high enough to repel the penetration of atoms or molecules. The energy barrier was calculated with local density approximation (LDA) to be 18.8 eV in a non-defective graphene monolayer. When a monatomic molecule, such as helium (He), approaches the centre of a carbon ring, this energy barrier is too high for the He atom to penetrate and therefore helium atoms are retained [5].

According to one aspect of the present invention, there is provided a heat storing nanocomposite material comprising: hollow elements such as glass microspheres filled with cryogen gas such as helium; a graphene or functionalized graphene coating on the hollow elements; and a polymer, resin or metal matrix in which all the coated hollow elements are embedded. Optionally, an adhesive component may be provided for adhering the graphene or functionalized graphene coating to the surface of hollow glass microspheres. Alternatively, the surface of the hollow glass microspheres may be electrically charged to electrostatically attract the graphene flakes onto the surface of the hollow glass microspheres. Similarly, a protective layer may optionally be provided to cover the graphene or functionalized graphene coating.

Chemical functionalisation of the graphene may assist in the manufacturing of the nanocomposite (e.g. by aiding dispersion of the graphene flakes in solution used for coating of hollow glass microspheres). Chemical functionalisation of the graphene may also improve the interface between the graphene and hollow glass microspheres, which can lead to a decrease in the helium leak rate from the hollow glass microspheres. In this regard, it is possible to tune the interface between the graphene component and the hollow glass microspheres component by selecting an appropriately functionalized, or partially functionalized, graphene component for a particular glass to manufacture glass microspheres, or other material used to make the hollow elements. However, pristine graphene itself has the highest impermeability as compared with functionalised graphene, which should

mean a lower helium leak rate provided that it is correctly adhered to the surface of the hollow glass microspheres. Thus, when the nanocomposite is to be stored for a long time at room temperature, it is desirable to balance the highest impermeability of the graphene component itself, typically provided by pristine graphene, with the possibility of improved interface between the graphene and glass spheres, typically provided by functionalised graphene.

The finished nanocomposite material may be enclosed by a protective layer or a coating. This layer or coating may be used as an element to which heat conducting elements are attached.

The nanocomposite material may be enclosed by or in good contact with a heat exchange element or elements such as a metal container. Such heat exchanger has large surface contact area with the heat storing nanocomposite and increases heat exchange rate between cooling elements attached to the heat exchanger and heat storing nanocomposite.

Such heat storing nanocomposite material as provided by the present invention can be used to make spacers in a serially bonded superconducting magnet (SBM). Such an arrangement may ensure that a the high heat capacity nanocomposite material of the present invention is in direct thermal contact with superconducting coils so no heat conducting elements are needed to transfer heat to the heat storage elements from the superconducting magnet coils. The nanocomposite is both electrically insulating and magnetically transparent which makes it acceptable as a spacer material. Thermal expansion coefficient of the nanocomposite can be adjusted by changing ratio of hollow elements to matrix material or by changing shape of the hollow elements such as glass microspheres from spheres to cylinders.

Fig. 6 schematically illustrates a type of serially bonded superconducting magnet which may benefit from the present invention. It will be enclosed within a cryostat, although the cryostat itself is not illustrated. Inner magnet comprises coils of superconducting wire. These may be mechanically self-supporting coils which include a resin impregnation. The coils are bonded by their axial end-surfaces to annular spacers which contain, or are

made of, a material of the present invention. Also provided are shield coils 47, of greater diameter than the inner magnet 41. The shield coils 47 may be bonded to support elements 48. The support elements 48 may contain, or be made of, a material of the present invention.

5 As illustrated in Figs. 7A and 7B, the support element 48 may be bonded to either an axial end surface of the shield coils 47 of the magnet or a radially outer surface of the shield coils 47 of the magnet. Additional material 46 with low Young's modulus can be placed between inner coils 42 and annular spacers 44 and/or between shield  
10 coils 47 and support elements 48 to lower mechanical stress resulting from different thermal expansion coefficients of coils 42, 47 and annular spacers 44 or support elements 48. Thermal expansion mismatch can also result from different rate of warming up of coil 42, 47 and annular spacers 44 or support elements 48 for example during quench of  
15 the magnet.

The spacers have a high heat capacity, according to a feature of the present invention. In operation, the magnet 40 is cooled to a cryogenic temperature, typically in a dedicated cryostat. When cooling is absent, for example in case of a failure of active  
20 refrigeration or during transport, the high heat capacity of the material of the present invention, within the annular spacers 44 and support elements 48, will keep the magnet near its operating temperature, as the spacers 44 and support elements 48 are in thermal contact with the inner coils 42 and the shield coils 47. The spacers  
25 may be cast, moulded or machined from a material of the present invention. A thermally-conductive container may be provided, defining an outer surface of each spacer, the container being filled with the material of the present invention, in the manner of Fig. 2.

The annular spacers 44 and the support elements 48 may be formed of an  
30 electrically conductive material as described with reference to Fig. 5. The wire 11 preferably forms a closed loop coil which absorbs energy during quench of superconducting coils. During quench, the magnetic field of the superconducting magnet decreases and this induces an opposing current in wire 11 thus causing Ohmic heating and  
35 temperature increase of composite 21. Annular spacers 44 and support elements 48 comprising electrically conducting composite 21 will warm up during quench at similar rate as superconducting coils and this

lowers mechanical strain on the interfaces between annular spacers 44 and support elements 48 and respective superconducting coils 42 and 47.

5 In other embodiment of present invention, a structure similar to that of Fig. 5 is used to construct a superconducting coil 42. Wire 11 is superconducting and electrically conducting composite 21 represents cross-section of the superconducting coil. In this case graphene-wrapped, helium filled hollow glass microspheres 14 are in close proximity of superconducting wire 11 and provide additional cryogenic  
10 stability for wire 11 and lower the likelihood of quench of superconducting coil 21.

Fig. 8 schematically illustrates another type of serially bonded superconducting magnet 50 which may benefit from the present invention. Coils 52 of superconducting wire are provided. These may  
15 be mechanically self-supporting coils which include a resin impregnation. The coils are bonded by their axial end-surfaces to separate, intermittent spacers 54 which contain, or are made of, a material of the present invention. The spacers have a high heat capacity, according to a feature of the present invention. In  
20 operation, the magnet 50 is cooled to a cryogenic temperature. When cooling is absent, for example in case of a failure of active refrigeration or during transport, the high heat capacity of the material of the present invention, within the separate spacers 54, will keep the magnet near its operating temperature, as the separate  
25 spacers 54 are in thermal contact with the coils 52. The spacers may be cast, moulded or machined from a material of the present invention. A thermally-conductive container may be provided, defining an outer surface of each spacer, the container being filled with the material of the present invention, in the manner of Fig. 2

30 In a similar manner to the intermittent spacers 54 of Fig. 8, the support structure 48 of Figs. 7A, 7B may be intermittent, provided as required only to act as an interface between tensile elements 49 and shield coils 47 in the example of Fig. 7A, or only as required to provide mechanical support for the shield coils, in the example of  
35 Fig. 7B.



In certain embodiments of the present invention, it may be found sufficient to provide the helium filled hollow glass microspheres, or other cryogen-containing hollow elements, in spacer 44, 54 or support element 48 only in the region of its interface with the associated coil(s), to control cost while still providing a high heat capacity material at the interface with the coil(s).

The material of the invention may also be used to manufacture regenerators for closed thermodynamic cycle cryogenic cooler. For example, US4359872 describes helium-filled hollow glass microspheres used for this purpose. The material of the present invention will provide regenerators for closed thermodynamic cycle cryogenic coolers but which are simpler to transport and store. Use of a thermally conductive matrix material, such as a metal, may be found appropriate in such structures.

#### Alternative Embodiments

The glass microspheres may be replaced by other hollow elements, for example spheres made of alternative material including carbon, silicon, ceramics, plastics, metals and metal alloys.

The hollow elements may be spheres or may be replaced by other closed containers like cylinders and cubes. The hollow elements preferably have a diameter of 1mm or less if spherical, and corresponding volume of other shapes, although larger hollow elements may be used. In practice, commercially available hollow elements tend to have a volume of 1mm<sup>3</sup> or less.

Although the invention has been particularly described with respect to helium filling of the hollow elements, the hollow elements can be filled with alternative cryogens - low boiling point gases - including but not limited to hydrogen, neon and nitrogen. The hollow elements may be filled with a mixture of helium and one or more of these other gases.

The graphene coating on the hollow elements may be 'pristine' graphene - graphene that has not been previously chemically modified; alternatively, the graphene coating on the hollow elements may be

'functionalised' graphene - graphene that has been previously chemically modified, such as graphene oxide. The skilled person will be familiar with the various synthetic procedures for manufacturing functionalised graphene.

5

The graphene coating on the hollow elements may be present as a one-atom thick layer or in certain cases several graphene layers may be built up. Such multiple graphene layers can increase the tortuosity of a gas diffusion path. Multilayered, highly interlocked stacked  
10 graphene layers would be much preferred.

The matrix material of the nanocomposite material component may be any polymeric material. However, ideally to ensure good adhesion and retention of the graphene it is important for the polarity of the  
15 polymer to be compatible with the graphene. Suitable polymer substrates include polyolefins, such as polyethylenes and polypropylenes, polyacrylates, polymethacrylates, polyacrylonitriles, polyamides, polyvinylacetates, polyethyleneoxides, polyethylene, terphthalates, polyesters, polyurethanes and polyvinylchlorides.  
20 Preferred polymer substrates are epoxies, polyacrylates and polymethacrylates.

The matrix material of the nanocomposite material may be a metal, metal alloy or composite or mixture of metal and metal alloys. Matrix  
25 material of the nanocomposite can comprise be fibre reinforced composite, including glass reinforced epoxy, glass reinforced plastics and carbon fibre reinforced plastics.

The matrix material may comprise one or more plastics materials,  
30 selected from the group consisting of: poly(ethylene), poly(styrene), poly(propylene), poly(amide), PTFE, para-aramid, poly(vinyl chloride), poly(ethyl acetate), poly(vinyl alcohol), poly(vinyl acetate), epoxy, viton, polyphenylenebenzobisoxazole (PBO), vectran. In another embodiment, the plastics material is a material selected from the  
35 group consisting of: polyaryletherketones, polyphenylenesulphides, liquid crystalline polyesters, polyamide imides, polyarylates, polyarylsulphones, polybutylene, polybutyleneterephthalates, polyethyleneterephthalate, polycarbonate, polychlorotrifluoroethylene, polyvinylid difluoride, polyperfluoroalkoxy, polydimethylsiloxanes,

thermoplastic polyesters, thermosetting polyesters, unsaturated polyesters, polyetherimides, polyethersulphones, thermosetting and thermoplastic polyimides, polyoxymethylene, polyphenylene oxide, polyurethanes, polyvinylidene chloride, acrylic resins, vinylacetate  
5 resins, perfluorinatedpolyethylenepropylene, polyphenylenes, polybenzimidazole, fluoropolymers, thermoplastic continuous and discontinuous fibre composites, thermosetting continuous and discontinuous fibre composites, fluorinated elastomers, rubbers, styrene butadiene rubbers, bismaleimides, and  
10 polyacrylonitrilebutadienestyrene. In an embodiment, the plastics material is a blend, alloy or copolymer of a subset of the above materials.

US Patent 8306589 describes heaters mounted in, or on, spacers in a  
15 magnet structure similar to that shown in Fig. 8 or Fig. 6. Such heaters may be applied to spacers constructed of the material of the present invention. The heaters may be used to warm the spacers during quench, to reduce a temperature differential between spacers and coils during a quench. With spacers constructed of the material of the  
20 present invention, the high heat capacity of the material means that the spacers would warm up only very slowly in case of a quench, maintaining an undesired temperature differential, which may be cured, or at least alleviated, by provision of heaters as taught in US Patent 8306589.

25 The material of the present invention may be formed into a product by one or more manufacturing steps selected from the group consisting of: injection moulding, hot pressing, drawing, extrusion, autoclaving, annealing, heat treating, sintering, compression moulding, machining, welding, adhesively bonding, thermoforming, vacuum forming, blow  
30 moulding, stretch blow moulding, transfer moulding, calendaring, compounding, orienting, tape laying with in situ consolidation, diaphragm forming, rotational moulding, centrifugal moulding, foam blowing and pultruding.

## CLAIMS

- 5 1. A material comprising hollow elements each containing cryogen,  
wherein the hollow elements are each provided with a coating of  
graphene.
2. A material according to any preceding claim, wherein the hollow  
10 elements are made of ceramic, glass, metal or plastic.
3. A material according to any preceding claim wherein the hollow  
elements are spheres.
4. A material according to claim 1 or claim 2 wherein the hollow  
15 elements are cylinders.
5. A material according to any preceding claim, further comprising a  
matrix material with the hollow elements embedded within the matrix  
material.
- 20 6. A material according to claim 5, wherein the matrix material  
comprises a fibre-reinforced composite.
7. A material according to any preceding claim, wherein the cryogen  
includes at least one of helium, hydrogen, nitrogen and neon.
- 25 8. A material according to any preceding claim, wherein the volume  
of each of the hollow elements is less than  $1\text{mm}^3$ .
9. A material according to any preceding claim wherein the graphene  
coating comprises a coating of graphene flakes.
10. A material according to any preceding claim wherein the graphene  
30 coating comprises a coating of flakes of graphene oxide.
11. A material according to any of claims 1-8 wherein the graphene  
coating comprises a continuous coating of graphene.

12. A material according to any preceding claim wherein the graphene coating comprises functionalised graphene or functionalised graphene oxide.

5 13. A material according to any preceding claim wherein an adhesive layer is provided between the surface of each of the hollow elements and the coating of graphene.

14. A material according to any preceding claim wherein one or more protective layer(s) is/are provided over the graphene coating of each  
10 of the hollow elements.

15. A heat storage element (20) comprising a container (18), itself containing material according to any preceding claim.

16. A heat storing element (26) comprising a heat exchanger (24) in thermal contact with material according to any preceding claim.

15 17. A cryostat containing a superconducting magnet, comprising a heat storing element according to claim 15 or claim 16.

18. A component of a superconducting magnet comprising a material according to any of claims 1-14.

19. A superconducting coil comprising a coil of superconducting wire  
20 embedded in a material according to any of claims 1-14.

20. A component according to claim 18, being a spacer for a serially-bonded superconducting magnet.

21. A component according to claim 18, being an annular spacer for a serially-bonded superconducting magnet.

25 22. A component according to claim 21, comprising a closed loop coil of wire embedded in a material according to any of claims 1-14.

23. A component according to claim 20, comprising a plurality of separate, discontinuous spacers for a serially-bonded superconducting magnet.

24. A component according to claim 18, being a support structure for a shield coil.

25. A component according to claim 24, being an annular support structure for a shield coil.

26. A component according to claim 24, comprising a closed loop coil of wire embedded in a material according to any of claims 1-14.

27. A component according to claim 24, comprising a plurality of separate, discontinuous parts.

28. A regenerator for closed thermodynamic cycle cryogenic cooler comprising a material according to any of claims 1-14.

29. A method for preparing a material comprising hollow elements containing cryogen, the hollow elements each being provided with a coating of graphene, the method comprising:

- providing hollow elements (10);
- exposing the hollow elements to an atmosphere of cryogen gas at a temperature and pressure at least equal to ambient temperature and pressure;
- allowing cryogen gas to diffuse into the hollow elements;
- depositing one or more graphene layers on the surface of the microspheres.

30. A method according to claim 29 wherein the graphene layer(s) is/are formed of flakes of graphene.

31. A method according to claim 29 or claim 30 wherein the graphene layer(s) is/are formed of flakes of graphene oxide.

32. A method according to claim 29 or claim 30 wherein the graphene layer(s) is/are formed of a continuous coating of graphene oxide.

33. A method according to any of claims 29-32 further comprising chemical treatment of the surface of the hollow elements to provide surface functionalisation.

5 34. A method according to any of claims 29-33, further comprising the step of applying at least one protective layer over the graphene layer(s).

10 35. A method according to any of claims 29-34, wherein the step of depositing one or more graphene layer comprises electrically charging the surface of the hollow elements prior to the application of the graphene.

15 36. A method according to any of claims 29-35 wherein the pressure of the cryogen atmosphere is ramped from ambient pressure to an elevated pressure, thereby increasing the rate of diffusion of the cryogen gas into the hollow elements, then reduced from the elevated pressure to ambient pressure.

20 37. A method according to any of claims 29-36 wherein the temperature of the cryogen atmosphere is increased above ambient, thereby increasing the rate of diffusion of the cryogen gas into the hollow elements.

25 38. A method according to any of claims 29-37 wherein the pressure of the cryogen atmosphere reaches about 500BAR.

39. A method according to any of claims 20-28 wherein the temperature of the cryogen atmosphere reaches about 450°C.

30 40. A method according to any of claims 20-29, further comprising mixing the hollow elements with a matrix material.

Amendments to the claims have been made as follows

CLAIMS

- 5 1. A material comprising hollow elements each containing cryogen,  
wherein the hollow elements are each provided with a coating of  
graphene or of graphene oxide, further comprising a matrix material  
with the hollow elements embedded within the matrix material.2. A  
material according to any preceding claim, wherein the hollow elements  
10 are made of ceramic, glass, metal or plastic.
3. A material according to any preceding claim wherein the hollow  
elements are spheres.
4. A material according to claim 1 or claim 2 wherein the hollow  
15 elements are cylinders.
6. A material according to claim 5, wherein the matrix material  
comprises a fibre-reinforced composite.
7. A material according to any preceding claim, wherein the cryogen  
20 includes at least one of helium, hydrogen, nitrogen and neon.
8. A material according to any preceding claim, wherein the volume  
of each of the hollow elements is less than  $1\text{mm}^3$ .
9. A material according to any preceding claim wherein the coating  
comprises a coating of graphene flakes.
- 25 10. A material according to any preceding claim wherein the coating  
comprises a coating of flakes of graphene oxide.
11. A material according to any of claims 1-8 wherein the coating  
comprises a continuous coating of graphene.
12. A material according to any preceding claim wherein the coating  
30 comprises functionalised graphene or functionalised graphene oxide.

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13. A material according to any preceding claim wherein an adhesive layer is provided between the surface of each of the hollow elements and the coating.

14. A material according to any preceding claim wherein one or more protective layer(s) is/are provided over the coating of each of the hollow elements.

15. A heat storage element comprising a container, itself containing material according to any preceding claim.

16. A heat storing element comprising a heat exchanger in thermal contact with material according to any preceding claim.

17. A cryostat containing a superconducting magnet, comprising a heat storing element according to claim 15 or claim 16.

18. A component of a superconducting magnet comprising a material according to any of claims 1-14.

19. A superconducting coil comprising a coil of superconducting wire embedded in a material according to any of claims 1-14.

20. A component according to claim 18, being a spacer for a serially-bonded superconducting magnet.

21. A component according to claim 18, being an annular spacer for a serially-bonded superconducting magnet.

22. A component according to claim 21, comprising a closed loop coil of wire embedded in a material according to any of claims 1-14.

23. A component according to claim 20, comprising a plurality of separate, discontinuous spacers for a serially-bonded superconducting magnet.

24. A component according to claim 18, being a support structure for a shield coil.

25. A component according to claim 24, being an annular support structure for a shield coil.

26. A component according to claim 24, comprising a closed loop coil of wire embedded in a material according to any of claims 1-14.

5 27. A component according to claim 24, comprising a plurality of separate, discontinuous parts.

28. A regenerator for closed thermodynamic cycle cryogenic cooler comprising a material according to any of claims 1-14.

10 29. A method for preparing a material comprising hollow elements containing cryogen, the hollow elements each being provided with a coating of graphene or of graphene oxide, the method comprising:

- providing hollow elements;
- exposing the hollow elements to an atmosphere of cryogen gas at a temperature and pressure at least equal to ambient temperature and pressure;
- allowing cryogen gas to diffuse into the hollow elements;
- depositing one or more layers of graphene or graphene oxide on the surface of the hollow elements, further comprising mixing the hollow elements with a matrix material.

15 30. A method according to claim 29 wherein the coating comprises graphene layer(s) formed of flakes of graphene.

20 31. A method according to claim 29 or claim 30 wherein the coating comprises graphene layer(s) formed of flakes of graphene oxide.

25 32. A method according to claim 29 wherein the coating comprises graphene layer(s) formed of a continuous coating of graphene oxide.

30 33. A method according to any of claims 29-32 further comprising chemical treatment of the surface of the hollow elements to provide surface functionalisation.

34. A method according to any of claims 29-33, further comprising the step of applying at least one protective layer over the coating.

35. A method according to any of claims 29-34, wherein the step of depositing one or more graphene layer comprises electrically charging the surface of the hollow elements prior to the application of the graphene.

36. A method according to any of claims 29-35 wherein the pressure of the cryogen atmosphere is ramped from ambient pressure to an elevated pressure, thereby increasing the rate of diffusion of the cryogen gas into the hollow elements, then reduced from the elevated pressure to ambient pressure.

37. A method according to any of claims 29-36 wherein the temperature of the cryogen atmosphere is increased above ambient, thereby increasing the rate of diffusion of the cryogen gas into the hollow elements.

38. A method according to any of claims 29-37 wherein the pressure of the cryogen atmosphere reaches about 500BAR.

39. A method according to any of claims 29-38 wherein the temperature of the cryogen atmosphere reaches about 450°C.



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**Claims searched:** 1-40

**Date of search:** 18 May 2016

## Patents Act 1977: Search Report under Section 17

### Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
Y	1-3, 7-9, 11, 15, 29-30, 32, 36-37	US 2012/0258022 A (HUGHES) see paragraph 66
Y	1-3, 7-9, 11, 15, 29-30, 32, 36-37	US 4359872 A (GOLDOWSKY) see abstract
A	-	US 4303732 A (TOROBIN) see col. 15 lines 61-66, col. 17 46-51

### Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

### Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC<sup>X</sup> :

Worldwide search of patent documents classified in the following areas of the IPC

C03C

The following online and other databases have been used in the preparation of this search report

WPI EPODOC INSPEC ELSEVIER SPRINGER

### International Classification:

Subclass	Subgroup	Valid From
C03C	0011/00	01/01/2006
F25B	0009/00	01/01/2006