

US 20110048690A1

### (19) United States

# (12) Patent Application Publication Reppel et al.

(10) Pub. No.: US 2011/0048690 A1 (43) Pub. Date: Mar. 3, 2011

(54) ARTICLE FOR MAGNETIC HEAT EXCHANGE AND METHOD FOR MANUFACTURING AN ARTICLE FOR MAGNETIC HEAT EXCHANGE

EXCHANGE (2

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(21) Appl. No.: 12/526,199

(22) PCT Filed: May 16, 2008

(86) PCT No.: PCT/IB08/51937

§ 371 (c)(1),

(2), (4) Date: **Aug. 6, 2009** 

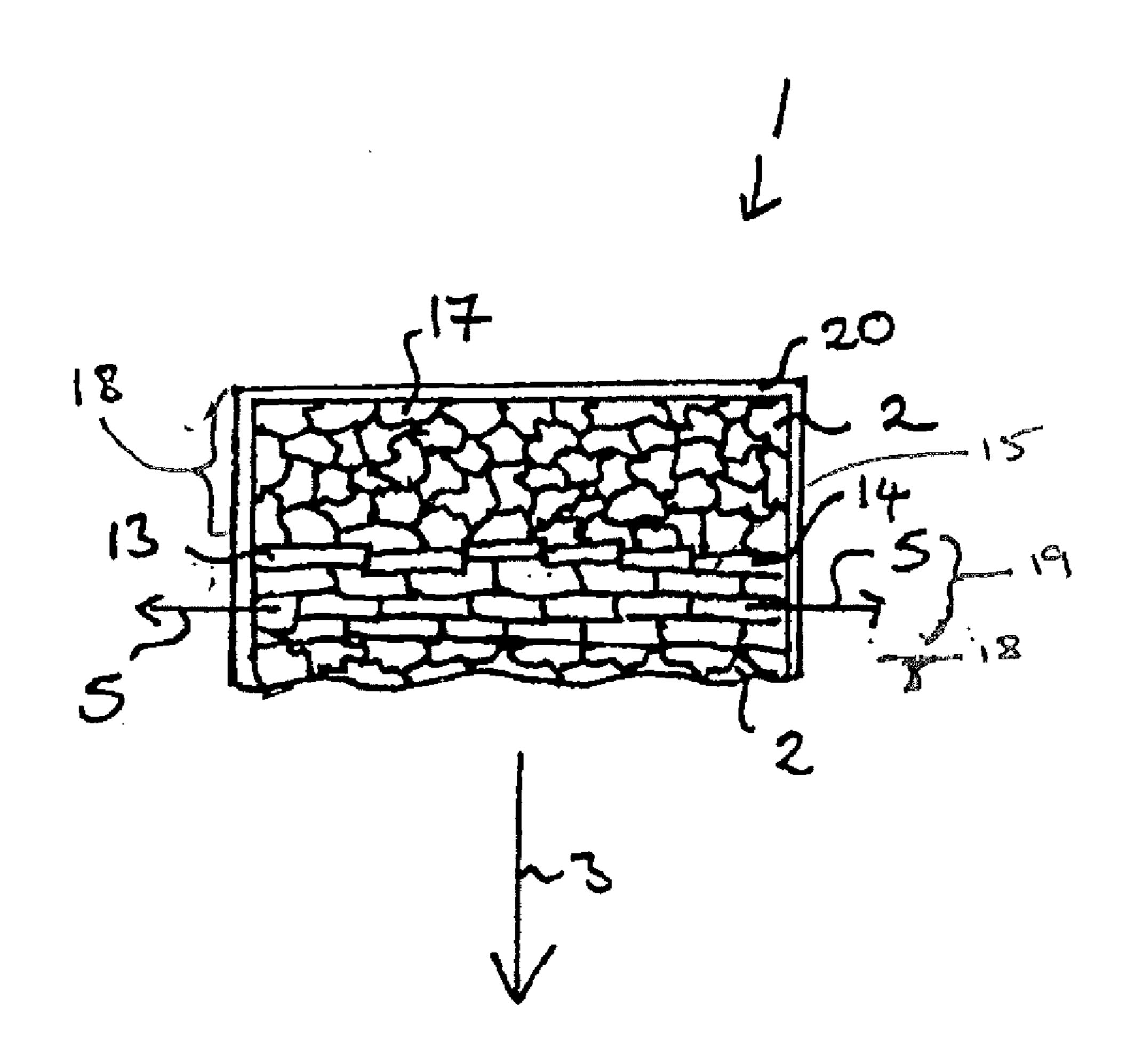
#### **Publication Classification**

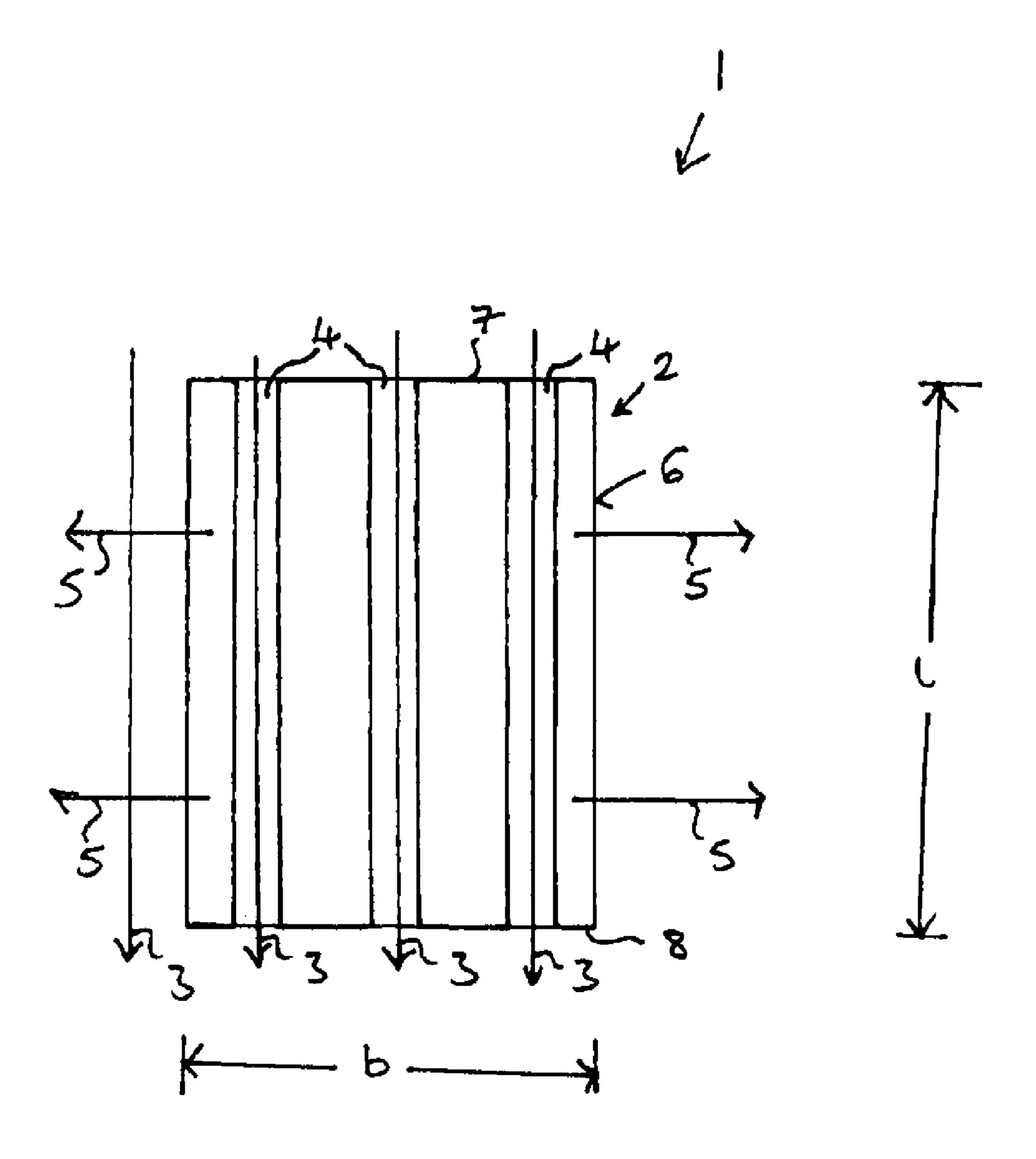
(51) Int. Cl. *F28F 7/00* 

F28F 7/00 (2006.01) B21D 53/02 (2006.01)

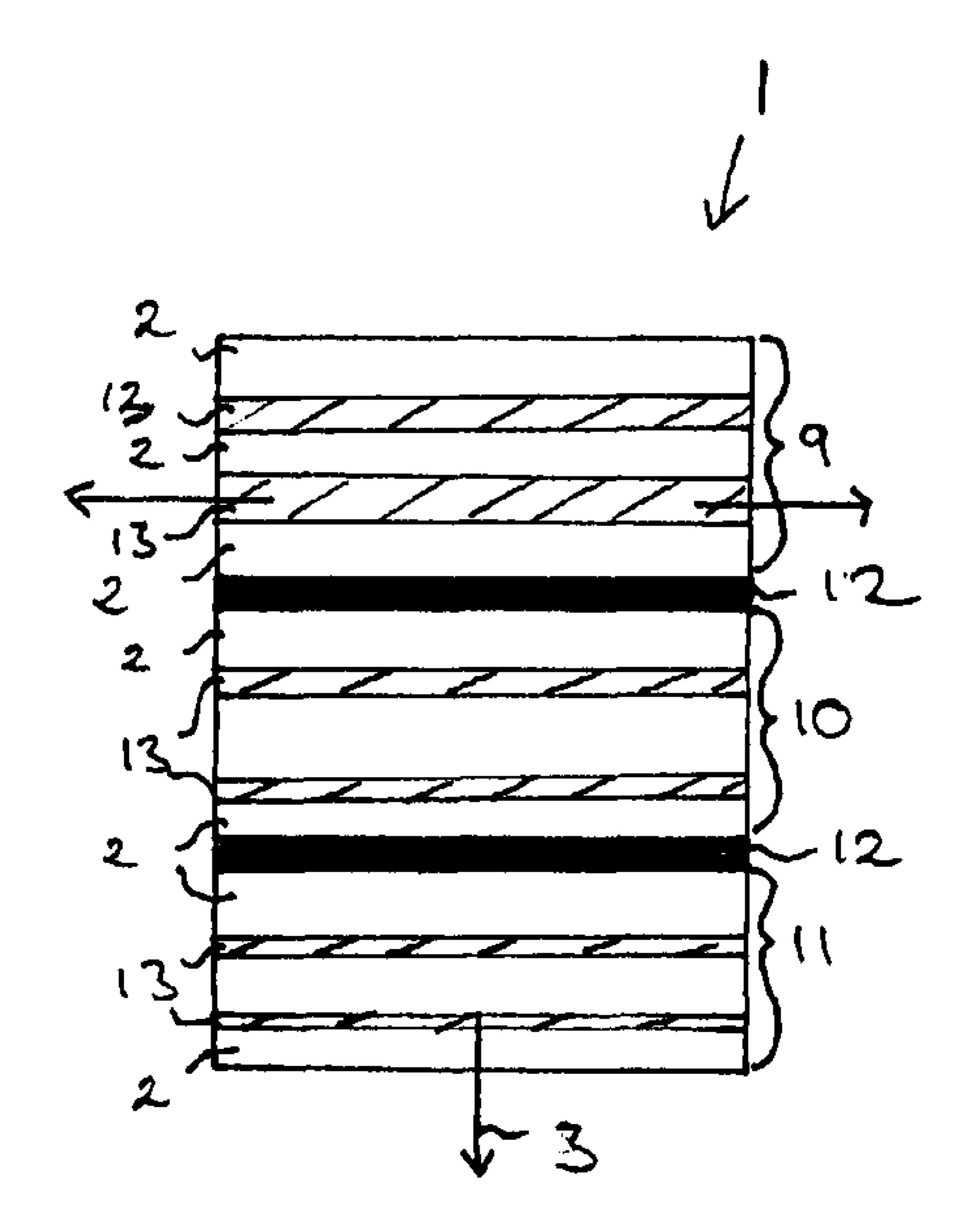
(57) ABSTRACT

An article (1) for magnetic heat exchange extends in a first direction (3) and in a second direction (5) generally axially perpendicular to said first direction (3). The article (1) comprises at least one magnetocalorically active phase (2). The average thermal conductivity of the article (1) is anisotropic.

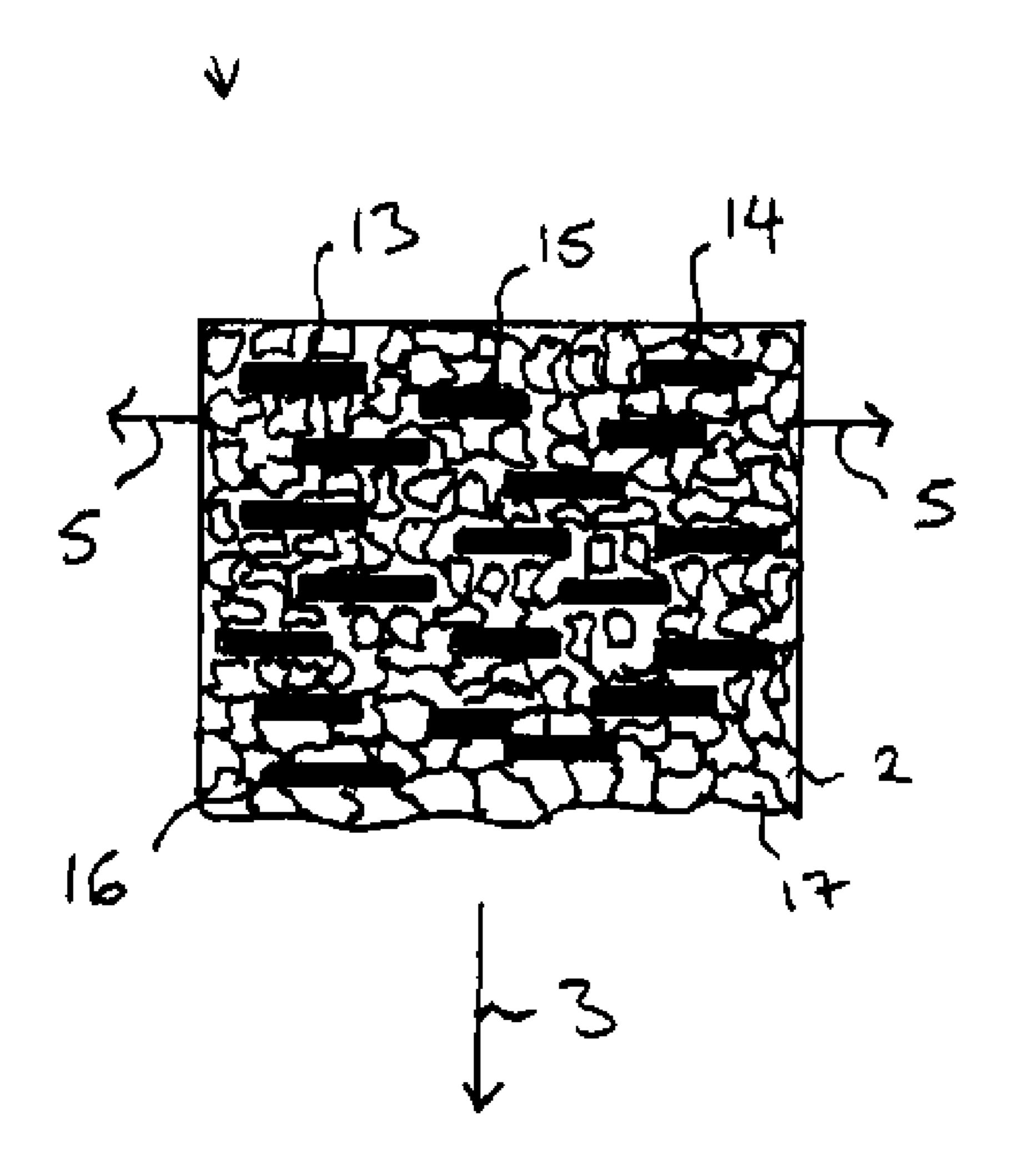




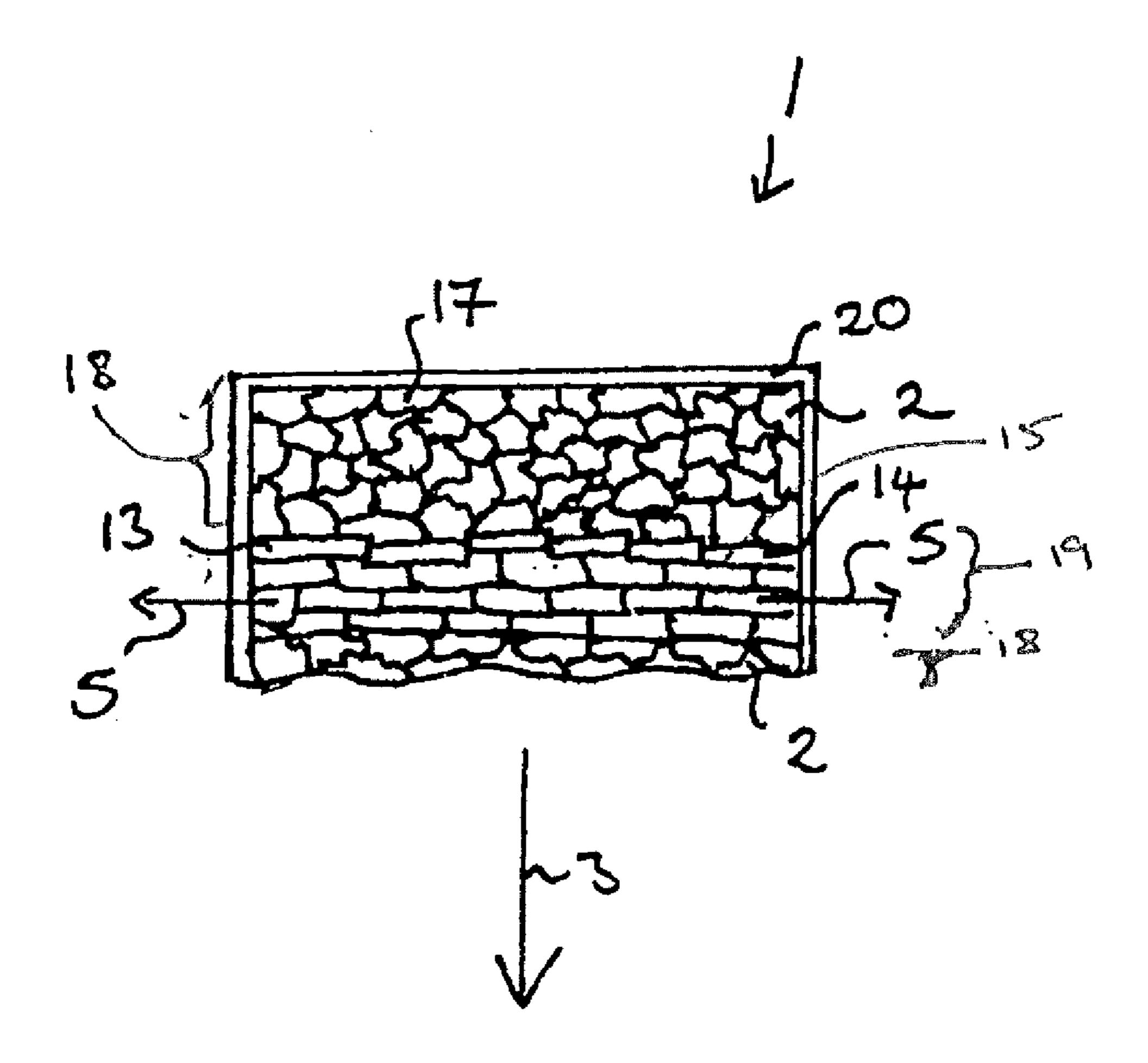
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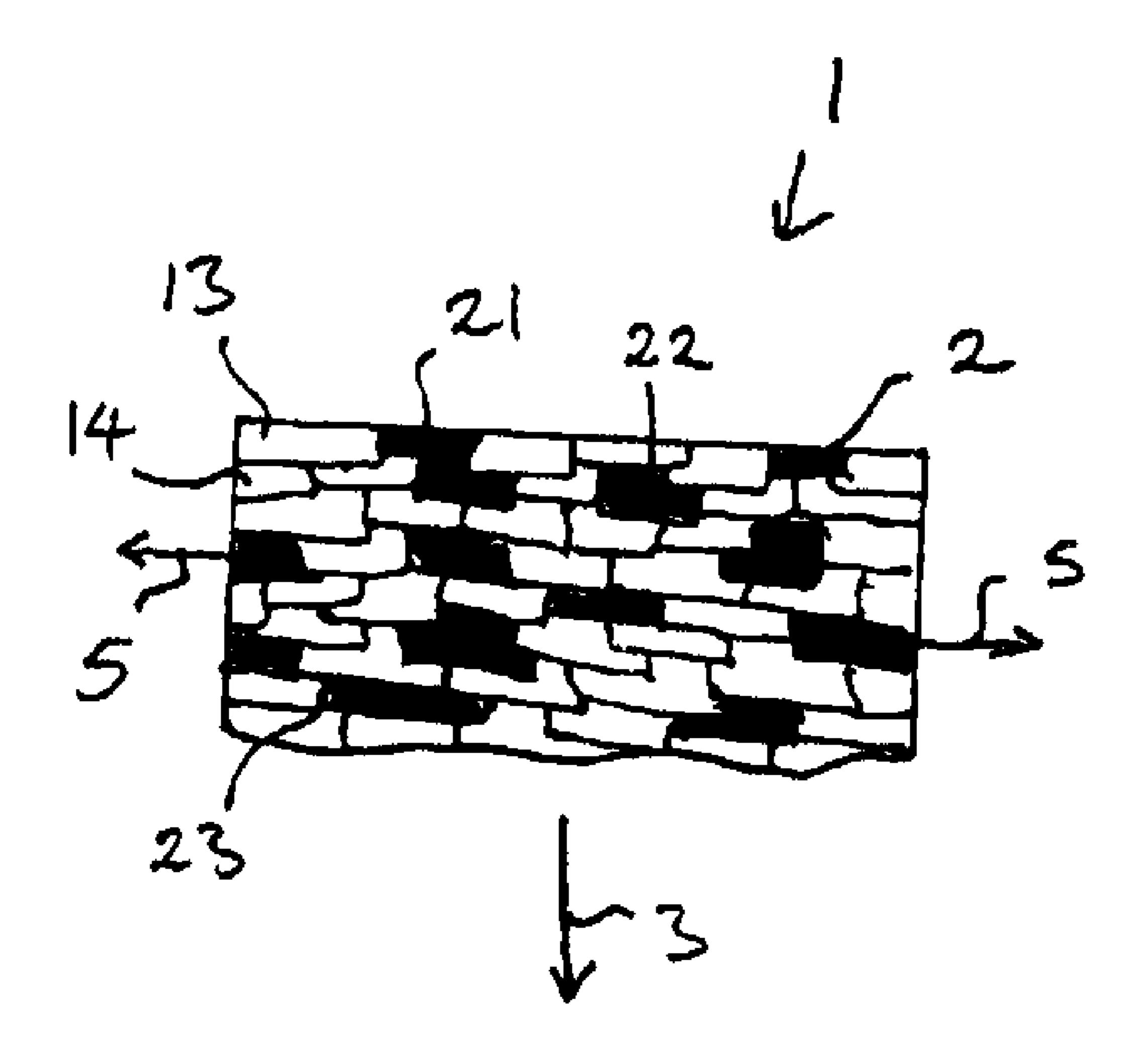


Fig. 5

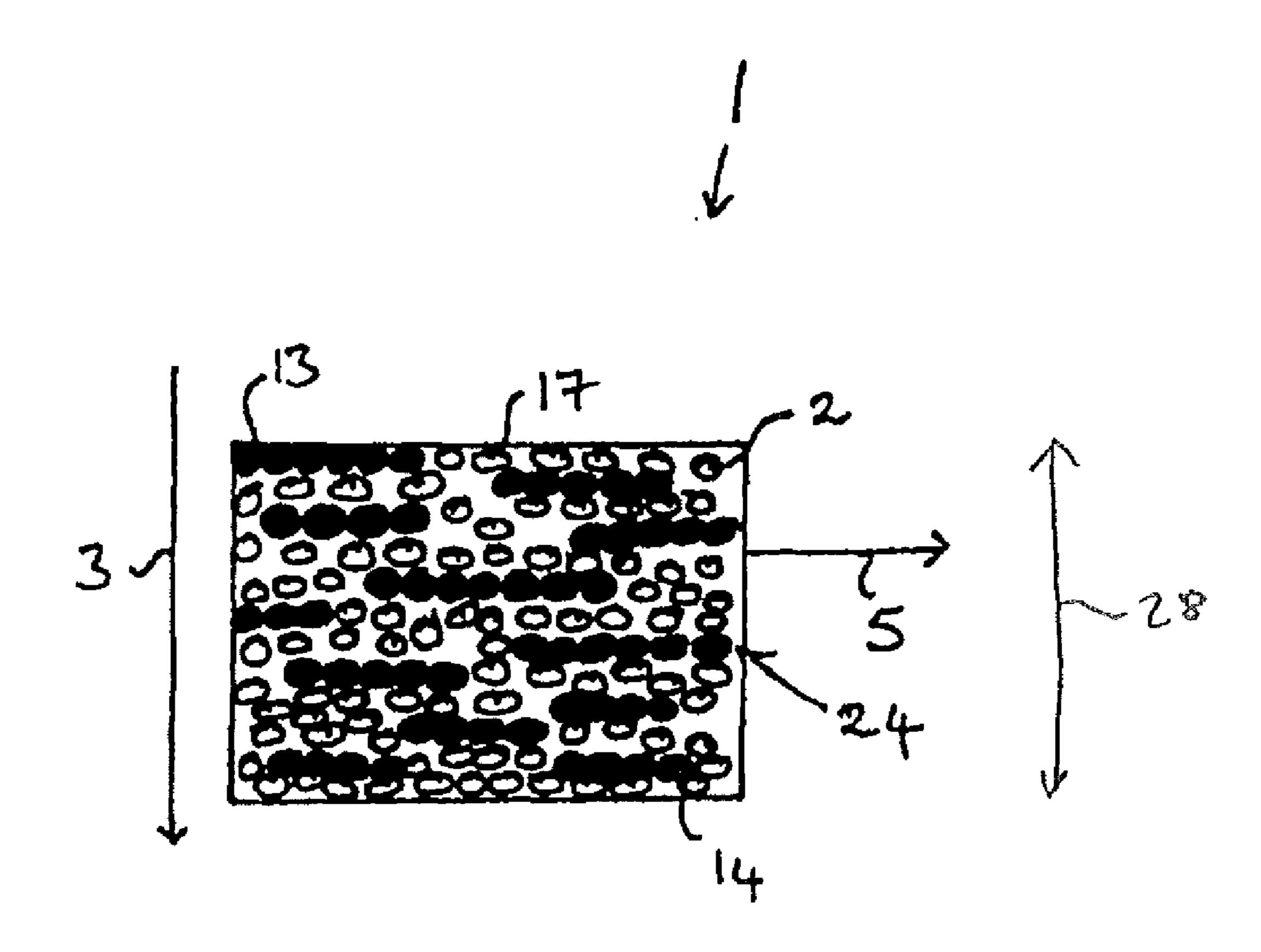
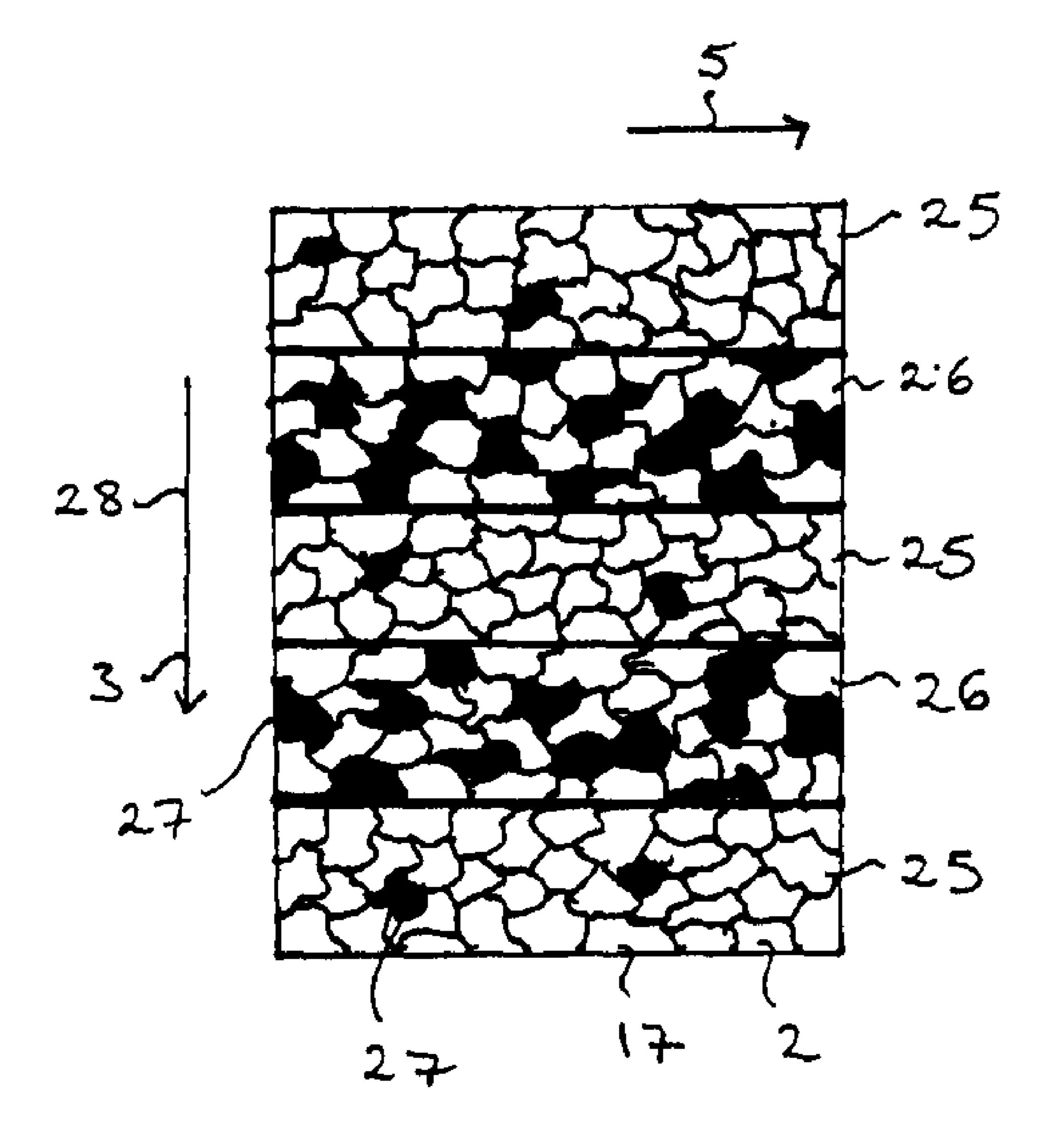


Fig. 6





#### ARTICLE FOR MAGNETIC HEAT EXCHANGE AND METHOD FOR MANUFACTURING AN ARTICLE FOR MAGNETIC HEAT EXCHANGE

#### **BACKGROUND**

[0001] 1. Field

[0002] Disclosed herein is an article for magnetic heat exchange and methods for manufacturing an article for magnetic heat exchange.

[0003] 2. Description of Related Art

[0004] The magnetocaloric effect describes the adiabatic conversion of a magnetically induced entropy change to the evolution or absorption of heat. By applying a magnetic field to a magnetocaloric material, an entropy change can be induced which results in the evolution or absorption of heat. This effect can be harnessed to provide refrigeration and/or heating.

[0005] In recent years, materials such as  $La(Fe_{1-a}Si_a)_{13}$ ,  $Gd_5(Si, Ge)_4$ , Mn (As, Sb) and MnFe(P, As) have been developed which have a Curie Temperature,  $T_c$ , at or near room temperature. The Curie Temperature translates to the operating temperature of the material in a magnetic heat exchange system. Consequently, these materials are suitable for use in applications such as building climate control, domestic and industrial refrigerators and freezers as well as automotive climate control.

[0006] Magnetic heat exchange technology has the advantage that magnetic heat exchangers are, in principle, more energy efficient than gas compression/expansion cycle systems. Furthermore, magnetic heat exchangers are environmentally friendly as chemicals such as chlorofluorocarbons (CFC) which are thought to contribute to the depletion of ozone levels are not used.

[0007] Consequently, magnetic heat exchanger systems are being developed in order to practically realise the advantages provided by the newly developed magnetocaloric materials. Magnetic heat exchangers, such as that disclosed in U.S. Pat. No. 6,676,772, typically include a pumped recirculation system, a heat exchange medium such as a fluid coolant, a chamber packed with particles of a magnetic refrigerant working material which displays the magnetocaloric effect and a means for applying a magnetic field to the chamber.

[0008] However, further improvements are desirable to enable a more extensive application of magnetic heat exchange technology.

#### **SUMMARY**

[0009] Disclosed herein are embodiments of an article for magnetic heat exchange which can be reliably and cost effectively manufactured. Also disclosed herein are embodiments of methods by which the article may be produced.

[0010] A particular embodiment relates to an article for magnetic heat exchange. The article extends in a first direction and in a second direction generally axially perpendicular to said first direction and comprises at least one magnetocalorically active phase. The average thermal conductivity of the article is anisotropic.

[0011] The article may be used as the magnetic refrigerant or magnetic working medium of a magnetic heat exchange system. Providing the article with an anisotropic average thermal conductivity has the advantage that heat generated within the article due to the magnetocaloric effect can be conducted to the surface of the article anisotropically. The heat exchange between the article and a cooling or heat exchange medium which surrounds the article may be anisotropic as well. As used herein, the terms "coolant" or "coolant"

medium" and "heat exchange medium," are used interchangeably irrespective of whether the article is used to supply heat to, or remove heat from, the heat exchange medium or working fluid.

[0012] The article may be arranged in the magnetic heat exchange system so that the most efficient thermal transfer occurs in directions perpendicular to the direction of coolant medium flow and so that the least efficient thermal transfer occurs in the direction of the coolant medium flow. This arrangement enables a more efficient heat exchange. Heat generated by the magnetocaloric effect within the article can be conducted efficiently in directions perpendicular to the coolant medium flow to the surface of the article where the heat is transferred to the coolant and carried by the coolant medium away from the article in the coolant flow direction. [0013] The poorer thermal conductivity of the article in the direction of the coolant flow hinders the transfer of the heat initially conducted away from the article back into the article and in the opposite direction to the coolant medium flow. Overall, the cooling efficiency of the article for magnetic heat exchange is improved by providing the article with an anisotropic average thermal conductivity.

#### BRIEF DESCRIPTION OF DRAWINGS

[0014] Embodiments disclosed herein will now be explained with reference to the accompanying drawings, which are intended to illustrate, but not limit, the scope of the appended claims.

[0015] FIG. 1 is a schematic diagram that illustrates a side view of an embodiment of an article for magnetic heat exchange,

[0016] FIG. 2 is a schematic diagram that illustrates a cross-sectional view of the article of FIG. 1,

[0017] FIG. 3 is a schematic diagram that illustrates a cross-sectional view of an article for magnetic heat exchange having a microstructure according to a first embodiment disclosed herein,

[0018] FIG. 4 is a schematic diagram that illustrates a cross-sectional view of an article for magnetic heat exchange having a microstructure according to a second embodiment disclosed herein,

[0019] FIG. 5 is a schematic diagram that illustrates a cross-sectional view of an article for magnetic heat exchange having a microstructure according to a third embodiment disclosed herein,

[0020] FIG. 6 is a schematic diagram that illustrates a cross-sectional view of an article for magnetic heat exchange having a microstructure according to a fourth embodiment disclosed herein, and

[0021] FIG. 7 is a schematic diagram that illustrates a cross-sectional view of an article for magnetic heat exchange having a microstructure according to a fifth embodiment disclosed herein.

## DETAILED DESCRIPTION OF THE SPECIFIC EMBODIMENTS

[0022] A magnetocalorically active material is defined herein as a material which undergoes a change in entropy when it is subjected to a magnetic field. The entropy change may be the result of a change from ferromagnetic to paramagnetic behaviour, for example. The magnetocalorically active material may exhibit, in only a part of a temperature region, an inflection point at which the sign of the second derivative of magnetization with respect to an applied magnetic field changes from positive to negative.

[0023] A magnetocalorically passive material is defined herein as a material which exhibits no significant change in entropy when it is subjected to a magnetic field.

[0024] In an embodiment, the average thermal conductivity of the article in the first direction is less than the average thermal conductivity of the article in the second direction. In operation, the article is arranged with the first direction generally parallel to the coolant medium flow to produce the most efficient heat transfer.

[0025] In an embodiment, the article comprises a first length extending in said first direction and a cross-sectional area extending in said second direction, the cross-sectional area having a second length. The average thermal conductivity measured over the first length of the article is less than the average thermal conductivity measured over the second length of the article and, therefore, in the plane of the cross-sectional area. Again, in operation the first length of the article is arranged generally parallel and the second direction generally perpendicular to the flow direction of the coolant medium.

[0026] The anisotropy in the average thermal conductivity of the article can be provided in a number of ways. For example, in some embodiments, the article further comprises a magnetocalorically passive phase having a thermal conductivity which is greater than the thermal conductivity of the magnetocalorically active phase.

[0027] The anisotropic average thermal conductivity of the article may be produced by various arrangements of the magnetocalorically active phase and the magnetocalorically passive phase within the article. The thermal conductivity anisotropy may be produced at a microscopic level, (i.e., by microscopic anisotropy), that is, the arrangement of the individual grains or particles of the magnetocalorically passive phase and/or magnetocalorically active phase which results in anisotropy in thermal conductivity. Alternatively, the thermal conductivity anisotropy may be produced macroscopically, that is, due to arrangements of members consisting essentially of one of the magnetocalorically active and passive phases.

[0028] In an embodiment, the magnetocalorically passive phase comprises a plurality of grains having, on average, a preferred orientation. Preferred orientation is used to describe an anisotropic arrangement and/or distribution of grains within the article. For example, even in embodiments where the individual grains may be generally spherical in shape and, therefore, individually have no preferred orientation. However, the spherical grains may be aligned in one or more rows or in a matrix of rows and columns and, therefore, have a preferred, i.e. physically anisotropic, arrangement within the article.

[0029] This anisotropic arrangement provides an article with an average anisotropic thermal conductivity in the case that the thermal conductivity of the magnetocalorically passive phase is different from thermal conductivity of the magnetocalorically active phase even if the magnetocalorically active phase is randomly arranged within the article. If the thermal conductivity of the magnetocalorically passive phase is greater than the thermal conductivity of the magnetocalorically active phase, then the average thermal conductivity of the article in the long direction of the row or in the plane of the matrix of the grains of the magnetocalorically passive phase is greater than that in directions perpendicular to the long direction of the row or in the plane of the matrix of the grains of the magnetocalorically passive phase. The article as a whole then has an anisotropic average thermal conductivity.

[0030] In an embodiment, the magnetocalorically passive phase comprises a plurality of grains, each having an elongate form with a long direction and at least one short direction generally perpendicular to the long direction.

[0031] To produce thermal anisotropy at a microscopic level, the grains of the magnetocalorically passive phase may be arranged in the article with a preferred orientation and/or a preferred texture.

[0032] "Preferred orientation" is a term used to describe the physical arrangement of the grains within the article. "Preferred texture" is a term used to describe grains which are arranged within the article such that they have, on average, a preferred crystallographic orientation. It is, therefore, possible that the grains have both a preferred orientation and a preferred texture.

[0033] In the case of grains having an elongate form arranged with a preferred texture, the average thermal conductivity of the article in the long direction of the grains is higher than the average thermal conductivity of the article in the short direction of the grains.

[0034] A thermally anisotropic article may be provided by arranging the plurality of elongate grains of the magnetocalorically passive phase in the article so that on average their long direction extends generally perpendicular to the first direction of the article. The plurality of elongate grains of the magnetocalorically passive phase may be arranged in the article so that on average their short direction extends generally parallel to the first direction of the article. These arrangements provide an article with an average thermal conductivity which is higher in directions perpendicular to the first direction and lower in directions parallel to the first direction.

[0035] In operation, the article is arranged so that the long direction of the grains is orientated generally perpendicular to the coolant medium flow direction and the short direction of the grains is orientated generally parallel to the coolant medium flow. This arrangement discourages heat flow through the article in directions opposite to the coolant medium flow.

[0036] In an embodiment, the magnetocalorically active phase comprises a plurality of grains arranged in the article with, on average, a preferred orientation. In this case, the term "preferred orientation" is again used to denote an anisotropic arrangement of grains within the article.

[0037] In a further embodiment, the magnetocalorically active phase comprises a plurality of grains arranged in the article with a preferred texture and, in a further embodiment, also with a preferred orientation. In an embodiment, the magnetocalorically active phase comprises a plurality of grains, each having an elongate form with a long direction and at least one short direction generally perpendicular to the long direction. The grains may be fibre-like or plate-like, for example.

[0038] To produce an article with thermal anisotropy at the microscopic level, the grains of the magnetocalorically active phase may be arranged in the article so that on average the long direction of the grains extends generally perpendicular to the first length of the article. The grains of the magnetocalorically active phase may also be arranged in the article so that on average the short direction of the grains extends generally parallel to the first length of the article.

[0039] This arrangement provides an article with an average thermal conductivity which is higher in directions of the

article parallel to the long direction of the grains and with an average thermal conductivity which is lower in the short direction of the grains.

[0040] In some embodiments, both the magnetocalorically passive phase and the magnetocalorically active phase are arranged within the article with a preferred orientation and/or preferred texture. The grains of the two phases may be intimately mixed so as to provide thermal anisotropy at a microscopic level.

[0041] In other embodiments, only the magnetocalorically active phase has a preferred orientation and/or texture or elongate grains to provide an article with an anisotropic average thermal conductivity. The article may comprise a magnetocalorically passive phase which has no preferred texture. The magnetocalorically active phase may be distributed with a preferred orientation and/or texture among the grains of the magnetocalorically passive phase. Alternatively, the magnetocalorically active phase may be distributed without a preferred orientation and/or texture among grains of the magnetocalorically passive phase having a preferred orientation and/or texture. The magnetocalorically passive phase may provide a matrix in which the grains of the magnetocalorically active phase are arranged. In such an embodiment, the article can be described as a composite.

[0042] An article for magnetic heat exchange may also be provided with an anisotropic average thermal conductivity by arranging materials of different thermal conductivity at a macroscopic level. In an embodiment, the article comprises a plurality of first layers consisting essentially of the magnetocalorically active phase interleaved with a plurality of second layers consisting essentially of the magnetocalorically passive phase.

[0043] In another embodiment, the article comprises only magnetocalorically active phases and no substantial portion of magnetocalorically passive phases. In this sense, phase is used to denote a solid body and exclude gases and air. The term "no substantial portion" is defined as less than 10 vol %.

[0044] In this embodiment, an average anisotropic thermal conductivity is achieved by an anisotropic distribution of the density of the article. In particular, the density of the article varies macroscopically. This is provided in one embodiment by at least one first layer consisting essentially of a magnetocalorically active phase and having a first density and at least one second layer consisting essentially of the magnetocalorically active phase and having a second density, the first density being greater than the second density.

[0045] The first layer with the greater density has a greater thermal conductivity than the second layer with a lower density. Therefore, the average thermal conductivity of the article in directions perpendicular to the plane of the layers is lower than the average thermal conductivity of the article in directions parallel to the plane of the layers. The article, therefore, has an anisotropic average thermal conductivity.

[0046] The density of the at least one first layer and the at least one second layer may be adjusted to the desired average value by controlling the porosity of the respective layer. The at least one first layer may comprise a first average porosity and the at least one second layer may comprise a second average porosity, the second average porosity is greater than the first average porosity. This provides a first layer with a greater density than the second layer and an article with an anisotropic average thermal conductivity.

[0047] In a further embodiment, the at least one first layer and the at least one second layer are arranged in a stack,

wherein adjacent layers are in physical contact with one another. The adjacent layers may be connected to their immediate neighbour by a layer of an adhesive material or be directly connected to each other by sintering of material of the adjacent layers, for example.

[0048] The first layers and the second layers have a thickness which extends generally parallel to the first direction of the article and a plane of a lateral area extending generally in the second direction of the article (e.g., perpendicularly to the first direction of the article). Each layer is built up from a plurality of layers of grains or particles of the respective phase.

[0049] In operation, the article is arranged so that the cross-sectional or lateral area of the layers extends in a planar fashion in directions that are generally perpendicular to the coolant flow direction and the thickness of the layers extends generally parallel to the coolant flow direction. The thermal conductivity of the magnetocalorically passive phase is, preferably, greater than the thermal conductivity of the magnetocalorically active phase in this arrangement of the article in order that the average thermal conductivity of the article in the coolant flow direction is less than the average thermal conductivity of the article in directions perpendicular to the coolant flow direction.

[0050] In another embodiment, the article comprises a plurality of active layers, each active layer comprising a magnetocalorically active material having a  $T_c$  which is different from the  $T_c$  of the magnetocalorically active material in an adjacent layer. In a further embodiment, the magnetocalorically active material of each of the layers is selected, along with the order in which the materials are arranged, in order that the  $T_c$  progressively increases from one end of the article to the other.

[0051] The use of articles comprising a plurality of magnetocalorically active materials having different  $T_c$ 's, has the advantage that the operating range of the heat exchanger in which the article is used is increased. The Curie temperature  $T_c$  translates to the operating temperature and, since a range of  $T_c$ 's are provided, the operating range of the heat exchanger is increased. This enables the heat exchanger to provide cooling and/or heating over a wider operating temperature range and to provide cooling and/heating from a starting temperature to a smaller/larger lowermost/uppermost temperature, respectively, than that possible using magnetocalorically active material having a single  $T_c$ .

[0052] In a further embodiment, the article further comprises at least one thermal barrier comprising a thermal conductivity which is less than the thermal conductivity of the magnetocalorically active phase.

[0053] The thermal barrier hinders thermal transfer from the region of the article on one side to the region of the article on the other side of the thermal barrier. The thermal barrier can be arranged so that thermal transfer in the direction of the coolant medium flow is hindered, thus further improving the efficiency of the magnetic heat exchange.

[0054] In a further embodiment, the article comprises a plurality of thermal barriers arranged at intervals along the first direction of the article. If a plurality of portions with differing T, are provided, the thermal barrier may be arranged between adjacent portions.

[0055] The magnetocalorically active phase may be one or more of Gd, a  $La(Fe_{1-b}Si_b)_{13}$ -based phase, a  $Gd_5(Si, Ge)_4$ -based phase, a Mn(As, Sb)-based phase, a MnFe(P, As)-based phase, a Tb—Gd-based phase, a (La, Ca, Pr, Nd, Sr)MnO<sub>2</sub>-

based phase, a Co—Mn—(Si, Ge)-based phase and a Pr<sub>2</sub>(Fe, Co)<sub>17</sub>-based phase. These basic compositions may further comprise further chemical elements which may substitute partially or in full for the listed elements. These phases may also comprise elements which are accommodated at least in part interstitially within the crystal structure, for example, hydrogen. These phases may also include impurity elements and small amounts of elements such as oxygen.

[0056] In a further embodiment, the grains of the magnetocalorically active phase comprise a corrosion protection coating. This corrosion protection coating may comprise one or more metals, alloy, polymers, ceramics or inorganic compounds. The metal may be Al, Cu or Sn and the alloy may comprise one or more of Al, Cu and Sn. An inorganic corrosion protection coating may be provided by a phosphate, for example a zinc phosphate. The corrosion protection coating may be applied to increase the working life of the magnetocalorically active phase since the corrosion and degradation of the magnetocalorically active material into non-magnetocalorically active phases is at least slowed, or even prevented entirely, over the working lifetime of the magnetocalorically active material, due to the corrosion protection coating.

[0057] The article may further comprise an effective porosity. The term "effective porosity" is used herein to describe a porosity of the article which has a measurable effect on the efficiency of the magnetic heat exchange.

[0058] The effective porosity comprises at least one channel within the body of the article which extends from a first side of the article to a second side of the article. The porosity may be in the range of 10 vol. % to 60 vol. % based upon the total volume of the article.

[0059] The effective porosity may be provided in the form of a series of interconnected channels in flow communication with each other forming a hollow network of skeleton type structure within the body of the article. The heat exchange fluid or coolant can then flow through the hollow network from one side of the article to the other.

[0060] The effective porosity may be provided by loosely compacting the powder from which the article or a portion thereof is formed, or by loosely compacting the powder followed by sintering, to form in each case a body with a density of less than 100% such that the unoccupied volume provides an interconnected hollow network though which the heat exchange medium can flow.

[0061] These embodiments of a article having an effective porosity have the additional advantage that the surface area of the article is increased. The coolant is in contact with inner surfaces, that is the surfaces of the interconnected channels that provide the effective porosity, and which are positioned within the body of the article, as well as with the overall outer surface of the article. Thus, the contact area between the article and the heat exchange fluid is increased. Consequently, the efficiency of the magnetic heat exchange may be further increased.

[0062] The article may further comprise at least one channel different from the interconnected channels that provide effective porosity. The channel may be provided in the form of a through-hole which is surrounded by the article or may be provided in the form of a channel in an outer surface of the article. One or more channels have the advantage of increasing the surface area of the article which can further improve the heat exchange efficiency between the article and the coolant. The channel may be formed by extrusion or profile rolling, for example.

[0063] In a further embodiment, the channel can be adapted to direct the flow of the coolant. The position of the channel is determined by the design of the heat exchange system in which the article is to operate. The channel may be adapted to direct the flow of the coolant with reduced or, optimally, minimum turbulence in order to increase the efficiency of the heat exchange.

[0064] The article may be a component of a heat exchanger, a cooling system, an air conditioning unit for a building or a vehicle, in particular an automobile, or a climate control device for a building or an automobile. The climate control device may be used as a heater in winter and as a cooler in summer by reversing the direction of the fluid coolant or heat exchanger medium. This is particularly advantageous for automobiles and other vehicles as the space available within the chassis for accommodating the climate control system is limited by the design of the vehicle.

[0065] The article may also comprise an outer protective coating. The outer protective coating may comprise a metal, an alloy or a polymer. The material of the outer protective coating may be chosen so as to be chemically, as well as mechanically, stable during the lifetime operation of the article in the heat exchange medium. If the coating is applied to the finished article, it is not subjected to higher temperatures, for example during sintering, or working of the article. In this case, a polymer with a relatively low decomposition temperature or melting temperature may be used.

[0066] The heat exchange medium or working fluid used to exchange heat with the article may comprise ethanol or glycol, mixtures of water, ethanol or glycol or an alternative material with a high thermal conductivity in order to increase the efficiency of the heat exchange between the heat exchange medium and the article. In some circumstances, the heat exchange medium may be corrosive to the magnetocalorically active material and/or the magnetocalorically passive material of the matrix. Therefore, an additional outer protective coating may be used to provide additional protection.

[0067] The article according to one of these embodiments may be used as a component of a heat exchanger, a refrigeration system, a climate control device, an air-conditioning unit, or an industrial, commercial or domestic freezer. The article is arranged so that the first direction of the article is arranged generally parallel to the direction of heat flow during operation.

[0068] The invention also provides methods of manufacturing an article for magnetic heat exchange. In an embodiment, a magnetocalorically active phase is provided and a magnetocalorically passive phase comprising a plurality of particles are provided. The magnetocalorically active phase and the magnetocalorically passive phase are assembled and compacted to form an article. A preferred orientation, that is, a preferred physical arrangement, of at least a plurality of grains of the magnetocalorically passive phase, on average, is produced.

[0069] In an embodiment, a precursor of a magnetocalorically active phase is provided and a magnetocalorically passive phase comprising a plurality of particles are provided. The precursor of the magnetocalorically active phase and the magnetocaloritally passive phase are assembled and compacted to form an article. A preferred orientation of the plurality of grains of the magnetocalorically passive phase is produced. In this embodiment, the article is reaction sintered, wherein the magnetocalorically active phase forms from the precursor.

[0070] The article is provided with an anisotropic thermal conductivity due to the preferred orientation of the magneto-calorically passive phase since the thermal conductivity of the plurality of grains of the magnetocalorically passive phase is higher in the longer direction of the grains than in the shorter direction. As previously discussed, the grains may also have, on average, a preferred texture of crystallographic orientation.

[0071] The preferred orientation may be produced at least in part by the compaction process or may be produced in part or entirely in a separate method step which may take place before or after compaction.

[0072] In an embodiment, the compaction is carried out so as to induce preferred orientation of at least the grains of the magnetocalorically passive phase and/or at least the grains of the magnetocalorically active phase

[0073] In an embodiment, the average preferred orientation of at least the plurality of grains of the magnetocalorically passive phase is produced at least in part by applying a magnetic field. This method may be used when the magnetocalorically passive phase is ferromagnetic, for example, comprises Fe or FeSi.

[0074] A magnetic field may also be used to provide a preferred orientation of particles of the magnetocalorically active phase if the magnetocalorically active phase is in the ferromagnetic state. If the magnetocalorically active phase is ferromagnetic at temperatures below its Curie Temperature, the magnetic field may be applied at a temperature below the Curie temperature of the magnetocalorically active phase in order to magnetically align the particles so that at least some of the particles have the preferred orientation.

[0075] The magnetic field may be applied before the compaction is carried out so as to provide a preferred orientation of the particles of the magnetocalorically passive phase and/or magnetocalorically active phase. This preferred orientation is maintained during compaction and in the compacted article.

[0076] The compaction may be carried out so as to induce a preferred texture in at least the magnetocalorically passive phase. If the particles of the magnetocalorically passive phase have anisotropic dimensions, the compaction may be carried out by arranging the compaction direction so that it is generally perpendicular to the long direction of the grains, or, in the case of plate-like grains, generally perpendicular to the plane of the plate. A degree of preferred orientation may also be provided by shaking the powder in directions perpendicular to the compaction direction before the compaction is carried out. This encourages plate-like grains to take on a stratified structure before compaction.

[0077] The compaction is carried out so that the grains of the magnetocalorically passive phase are on average orientated with their long direction perpendicular to the first direction of the article. This produces an article with a higher average thermal conductivity in directions perpendicular to the first direction and a lower average thermal conductivity in the first direction.

[0078] In an embodiment, the average preferred orientation of at least the plurality of grains of the magnetocalorically passive phase and/or of the magnetocalorically active phase is produced at least in part by mechanical deformation of the article after the compaction. The mechanical deformation may be carried out by one of more of rolling, swaging, drawing and extruding.

[0079] In an embodiment, the magnetocalorically active phase and the magnetocalorically passive phase are assembled by intimately mixing the magnetocalorically active phase and the magnetocalorically passive phase with one another. This method produces an article with an anisotropic thermal conductivity produced on a microscopic scale. [0080] In a further embodiment, the magnetocalorically active phase and the magnetocalorically passive phase are assembled by alternately arranging layers consisting essentially of the magnetocalorically active phase interleaved with layers consisting essentially of the magnetocalorically passive phase. This method produces an article with an anisotropic average thermal conductivity on a macroscopic scale.

[0081] In an embodiment, additionally one or more of a lubricant, an organic binder and a dispersant are added to the assembled magnetocalorically active phase and magnetocalorically passive phase. These additives can help to increase the density of the article.

[0082] The assembled magnetocalorically active phase and magnetocalorically passive phase may be compacted by one or more of rolling and pressing. Rolling may be used to produced a long length article in which the thermal conductivity in directions along the length of the article and across its breadth is greater than the thermal conductivity in a direction across its thickness. Such articles can be arranged in a laminated stack. Pressing may be used to produce an article in which the thermal conductivity is greater across the breadth of the article than along its length as the long direction of the magnetocalorically passive phase are orientated generally perpendicularly to the length of the article.

[0083] In a further embodiment, the article is heated during compaction. A heat treatment may be used to further compact the article as well as sinter the grains together. If precursor is used, the heat treatment is carried out under conditions selected so that the magnetocalorically active phase is formed from the precursor.

[0084] A heat treatment during compaction may also be used to further increase the degree of texture of the grains due to reorientation of the grains as well as grain growth in a preferred direction, advantageously the long direction of the grains.

[0085] In a further embodiment, a magnetic field is applied during compaction so as to magnetically orientate the grains of the magnetocalorically passive phase and/or active phase so that on average their long direction is oriented generally perpendicular to the first direction of the article. Heat may also be applied at the same time. This method may be used when the magnetocalorically passive phase comprises a soft magnetic material such as Fe or FeSi or when the magnetocalorically active phase has already formed and is ferromagnetic during the pressing process.

[0086] A method of manufacturing an article without a magnetocalorically passive phase and with an average anisotropic thermal conductivity is also provided. In this method, at least one first plate consisting essentially of a magnetocalorically active phase and having a first density and at least one second plate consisting essentially of a magnetocalorically active phase and having a second density is provided. The first density of the first plate is greater than the second density of the second plate. The first plate and the second plate are arranged in a stack to provide an article for magnetic heat exchange.

[0087] The first and the second plates have differing average thermal conductivities due to their differing densities. A

higher density provides a higher average thermal conductivity. Therefore the average thermal conductivity in the stack direction, that is perpendicular to the plane of the plates is lower than the average thermal conductivity in the plane of the plates.

[0088] In an embodiment, the first plate and the second plate are arranged so that they are in physical contact with one another.

[0089] In a further embodiment, the first plate comprises a first porosity and the second plate comprises a second porosity, the second porosity being greater than the first porosity. This provides a first plate with a greater density than the second plate.

[0090] The first plate and/or the second plate may be produced by compacting particles of a magnetocalorically active phase or precursor of a magnetocalorically active phase.

[0091] The conditions of the compaction are adjusted so as to produce a lower porosity in the first plate than in the second plate. For example, the compaction pressure and, if used, temperature, can be increased to lower the porosity and increase the density of the plate. Conversely, the compaction pressure and, if used, temperature, can be decreased to increase the porosity and decrease the density of the plate.

[0092] In a further embodiment, a plurality of first plates and a plurality of second plates are provided. The plurality of first plates and the plurality of second plates are interleaved with one another in a stacking direction of the article. The article produced has a multi-layer or stratified structure.

[0093] In a particular embodiment, after the article is compacted or after the article has been produced, an outer protective coating may be applied to the article. The outer protective coating may be for example, applied by dipping, spraying or electro-deposition.

[0094] FIG. 1 illustrates a side view of an article 1 for magnetic heat exchange which comprises a magnetocalorically active phase 2 which, in this particular embodiment, consists essentially of a La(Fe<sub>1-a-b</sub>Co<sub>a</sub>Si<sub>b</sub>)<sub>13</sub>-based phase with a Curie Temperature,  $T_c$ , of 20° C. The article 1 provides the magnetic refrigerant working component of a non-illustrated magnetic heat exchange system which further includes a pumped recirculation system, a heat exchange medium, such as a fluid coolant, and means for applying a magnetic field to the chamber.

[0095] The article 1 has a first length 1 and a second length b extending generally perpendicularly to the first length 1. The direction of the coolant flow is indicated in FIG. 1 by the arrows 3. Depending on whether the heat exchange system is used to provide refrigeration or to provide heating, the coolant may flow in two opposing directions. In operation, the first length 1 of the article 1 is arranged so that it extends in the coolant flow direction 3 and the second length b is arranged so that it extends generally perpendicularly to the coolant flow direction 3. In the view illustrated in FIG. 1, the coolant direction is from top to bottom. The article 1 is also provided with a plurality of channels 4 in its outer surface which extend in the direction of the coolant flow 3 and increase the surface area of the article 1 so as to improve the effectiveness of the heat transfer from the article 1 to the coolant.

[0096] According to the invention, the article 1 has an anisotropic average thermal conductivity. In particular, the average thermal conductivity of the article in the direction of the coolant flow 3 is lower than the average thermal conduc-

tivity of the article 1 in directions perpendicular to the coolant flow 3, indicated by the arrows 5, in which the second length b of the article 1 extends.

[0097] This arrangement enables the magnetically induced heat produced by the magnetocalorically active phase 2 within the article 1 to be conducted efficiently to the outer surfaces 6 of the article 1 in the direction of the arrows 5 and from there to the coolant while at the same time preventing conduction of the magnetically induced heat within the article in directions opposing the coolant flow direction 3. This prevents a type of internal short circuit within the article 1 in which heat carried from the cold end 7 to the hot end 8 by the coolant is simply conducted back to the cold end 7 by the article 1 itself.

[0098] FIG. 2 illustrates a cross-sectional view of the article 1 of FIG. 1. The cross-sectional view of FIG. 2 illustrates that the article 1 has a layered structure and comprises three active portions 9, 10, 11, each comprising a magnetocalorically active phase 2. Each of the three active portions 9, 10, 11 comprises a magnetocalorically active phase having a different  $T_c$  such that the  $T_c$  of each active portion increases in the direction of coolant flow 3. Each active portion 9, 10, 11 is separated from its neighbour by a thermal barrier 12 which further prevents thermal conductivity between adjacent portions 9, 10, 11 of the article 1.

[0099] Each portion 9, 10, 11 further comprises a magnetocalorically passive phase 13 which has a greater thermal conductivity than the thermal conductivity of the magnetocalorically active phase 2. The anisotropic average thermal conductivity of the article 1 is provided by providing the grains 14 of the magnetocalorically passive phase 13 in a layered type arrangement. The layered arrangement may be provided microscopically, as illustrated in FIGS. 3 and 5, or macroscopically, as illustrated in FIGS. 2 and 4. Arrangements including a combination of both microscopic and microscopic layering may also be used.

[0100] In the embodiment illustrated in FIG. 3, the magnetocalorically passive phase 13 comprises a plurality of grains 14 having a general plate-like form and for illustrative purposes only illustrated in the drawing as black shaded, filled rectangular plates. The plate-like grains 14 have a long direction 15 and a short direction 16 which is arranged generally perpendicularly to the long direction 15. The plate-like grains 14 are arranged within the article 1 such that on average the long direction 15 extends in directions parallel to the second length b of the article 1 and generally perpendicular to the coolant flow direction 3. The short direction 16 of the grains 14 extends on average generally parallel to the first length 1 of the article and parallel to the coolant flow direction 3.

[0101] The plurality of grains 14 of the magnetocalorically passive phase 13 are arranged within the article such that they have a preferred orientation and/or preferred texture. Preferred orientation is used to denote the physical arrangement of the grains and preferred texture is used to denote the crystallographic orientation of the grains. Due to this preferred orientation and/or texture, the average thermal conductivity of the article 1 in directions perpendicular to the coolant flow direction 3 is higher than the average thermal conductivity of the article 1 in directions parallel to the coolant flow direction 3.

[0102] The grains 17 of the magnetocalorically active phase 2 are, in this embodiment, generally isotropic in comparison to the grains 14 of the magnetocalorically passive phase 13 and for illustrative purposes only are illustrated in

the drawing as open, white areas of variable outline. The grains 17 of the magnetocalorically active phase 2 are illustrated in FIG. 3 as distributed among the grains 14 of the magnetocalorically passive phase 13 and forming a matrix therefore. Alternatively, the magnetocalorically passive phase 13 may provide the matrix of the article 1 and act as a binder for the grains 17 of the magnetocalorically active phase 2. The embodiment illustrated in FIG. 3 provides an article 1 comprising anisotropic average thermal conductivity due to the distribution of the grains 14 of the magnetocalorically passive phase 13 on the microscopic scale.

[0103] In the second embodiment illustrated in FIG. 4, the grains 14 of the magnetocalorically passive phase 13 also have a generally plate-like form. The grains 14 are also arranged in the article 1 with a preferred orientation such that their long direction 15 extends in directions generally parallel to the second length b of the article 1 and in directions generally perpendicular to the coolant flow direction 3.

[0104] In the second embodiment of FIG. 4, as in the embodiment of FIG. 2, the anisotropic thermal conductivity of the article 1 is provided by a layered structure in which layers 18 consisting essentially of a magnetocalorically active phase 2 are interleaved with layers 19 consisting essentially of a magnetocalorically passive phase 13. In the embodiment illustrated in FIG. 4, the anisotropic average thermal conductivity of the article 1 is provided macroscopically.

[0105] A single layer 19 of a magnetocalorically passive phase 13 sandwiched between two layers 18 of magnetocalorically active phase 2 are illustrated in FIG. 4, although any number of layers can be provided. The stacked arrangement of layers 18, 19 is built up in the direction of the first length 1 of the article 1.

[0106] The magnetocalorically passive phase 13 may be a metal and in some embodiments, is magnetic. A magnetic magnetocalorically passive phase 13 has the advantage that the grains 14 can be aligned magnetically to produce the preferred orientation.

[0107] The article 1 may also comprise an outer coating 20 in order to protect the article 1 and, in particular, the magnetocalorically active phase 2, from corrosion by the environment and, in particular, by the coolant.

[0108] The article 1 of FIG. 3 may be fabricated by intimately mixing a powder of a magnetocalorically active phase 2 and a powder of a magnetocalorically passive phase 13 and compacting the resulting mixture. The preferred orientation of the grains 14 of the magnetocalorically passive phase 13 may occur at least partly as a result of settling of the powder in the mould in which the powder mixture is compacted. The preferred orientation of the grains 14 may also be induced by the compaction process. The direction of pressure exerted during the compaction process is generally perpendicular to the long direction 16 of the plate-like grains 14 so that the plate-like grains 14 are encouraged to lie with their long direction perpendicular to the direction of compaction. Furthermore, the plate-like grains 14 may slide over one another so increasing the degree of preferred orientation.

[0109] The degree of preferred orientation and/or texture may also be increased by applying heat during the compaction process. The heat may encourage sintering of the grains which, given a preferred growth direction, can further increase the anisotropy of the plate-like grains and the degree of preferred orientation.

[0110] The preferred orientation of the grains may also be at least in part produced by alignment processes which take

place before or after compaction. The preferred orientation may also be achieved substantially separate from the compaction process.

[0111] In a further embodiment, the magnetocalorically passive phase may be provided by a magnetic material and a magnetic field applied so as to induce preferred orientation in the desired direction within the article 1. The magnetic field may be applied before and/or during compaction. Furthermore, a heat treatment may also be applied at the same time as the magnetic field.

[0112] The article 1 may also be fabricated by reaction sintering. In this embodiment, precursor of the magnetocalorically active phase is provided. The precursor consists of non-magnetocalorically active phases in amounts to produce the magnetocalorically active phase when they react with one another. The precursor may be intimately mixed with the magnetocalorically passive phase to produce an anisotropically thermally conductive article at a microscopic scale. The precursor of the magnetocalorically active phase may also be provided as a discreet layer or layers within a macroscopically layered arrangement similar to that illustrated in FIG. 4. After or during compaction, the article is heated so as to reaction sinter the precursor and form the magnetocalorically active phase.

[0113] The preferred orientation of the magnetocalorically passive phase may also be achieved by other methods known in the art. For example, the magnetocalorically passive phase could be subjected to a rolling treatment or may be provided as a thin layer with a preferred orientation.

[0114] If an outer coating is provided, the coating may be applied to the article after compaction and any heat treatment process. The coating may be applied by e.g., dipping, spraying or electroplating.

[0115] In a further embodiment, illustrated in FIG. 5, the magnetocalorically active phase 2 also comprises grains 21 having an elongate form. For illustrative purposes only, the grains 21 of the magnetocalorically active phase 2 are shaded black and the grains 14 of the magnetocalorically passive phase 13 are left unshaded. In this embodiment, the magnetocalorically active phase 2 is also arranged in the article 1 with a preferred orientation such that the long direction 22 of the grains 21 extends in directions generally perpendicular to the coolant flow direction 3 and the short direction 23 of the grains 21 extends in the direction of the coolant flow 3.

[0116] FIG. 6 illustrates an embodiment of an article 1 for use as the working component of a magnetic heat exchange system according to a fourth embodiment.

[0117] The article 1 of the fourth embodiment comprises a plurality of grains 17 of a magnetocalorically active phase 2 and a plurality of grains 14 of a magnetocalorically passive phase 13. For illustrative purposes only, the grains 17 are unshaded and the grains 14 are shaded black. On average, each of the grains 14 and/or 17 has a shape which is generally isotropic (e.g., generally spherical). In this embodiment, the article 1 has anisotropic thermal conductivity due to the preferred orientation of the isotropically-shaped grains 14 of the magnetocalorically passive phase 13.

[0118] The generally spherical grains 14 of the magneto-calorically passive phase 13 comprises a ferromagnetic material, in this case iron. The grains 14 are arranged in a plurality of rows or chains 24 having a long direction which extends in directions generally parallel to the second direction 5 and perpendicular to the coolant flow direction 3 of the article 1. The chains 24 are arranged in a series of layers arranged one

above the other in the stack direction 28 which is parallel to the coolant flow direction 3. The grains 17 of the magnetocalorically active phase 2 are arranged between the chains 24 of the magnetocalorically passive phase 13 and also have a degree of preferred orientation. The preferred orientation of the magnetocalorically active phase 2 is produced as a result of the pre-formation of a preferred orientation in the magnetocalorically passive phase 13.

[0119] The thermal conductivity of the magnetocalorically passive phase 13 is greater than the thermal conductivity of the magnetocalorically active phase 2. The article 1, therefore, has on average an anisotropic thermal conductivity. In particular, the thermal conductivity of the article 1 is greater in the second direction 5 than in the coolant flow direction 3. [0120] The article 1 of the fourth embodiment illustrated in FIG. 6 is fabricated by intimately mixing particles of the magnetocalorically active phase 2 and particles of the magnetocalorically passive phase 13 and placing these in a compaction vessel such as a die. A magnetic field is applied in the second direction 5 which causes the ferromagnetic particles of the magnetocalorically passive phase 13 to align themselves in the direction of the applied magnetic field to create the plurality of chains 24.

[0121] The preferred orientation of the grains 17 of the magnetocalorically active phase 2 occurs due to the restriction of the movement of the particles of the magnetocalorically active phase 2 within the article 1 due to the pre-formation of the aligned chains 24 of the particles of the magnetocalorically passive phase 13.

[0122] In a further embodiment, the magnetocalorically active phase 2 is ferromagnetic at temperatures below its Curie temperature. Therefore, if the magnetic field is applied to the powder mixture at temperatures below the Curie temperature of the magnetocalorically active phase 2, a preferred orientation of the particles of the magnetocalorically active phase 2 in the direction of the applied magnetic field can also be achieved.

[0123] FIG. 7 illustrates an article 1' for use as the working component of a magnetic heat exchange system according to a fifth embodiment.

[0124] The article 1' of the fifth embodiment consists essentially of one or more magnetocalorically active phases 2. For purposes of illustration, these phases are depicted as unshaded areas. The article 1' of the fifth embodiment is free from magnetocalorically passive phases. The anisotropic average thermal conductivity of the article 1' is provided, in this embodiment, by an anisotropic distribution of the density of the article 1' and, in particular, and anisotropic distribution of the porosity of the article 1'.

[0125] The article 1' of the fifth embodiment includes a plurality of layers of which five are illustrated in FIG. 7. Three first layers 25 have a relatively low porosity and two second layers 26, which are arranged between adjacent first layers 25, include a higher degree of porosity than that of the first layers 25. In the illustration of FIG. 7, the pores 27 are indicated by the black shaded regions.

[0126] The pores have a lower thermal conductivity than the magnetocalorically active phase 2. Therefore, the second layers 26 have a lower average thermal conductivity than the first layers 25. This provides an article 1' with an average thermal conductivity measured from end to end of the article in the coolant flow direction 3 which is less than the average thermal conductivity measured from the side face to side face of the article 1' in the second direction 5.

[0127] The multilayer or laminated article 1' of the fifth embodiment may be fabricated by stacking a plurality of layers of differing densities or porosities together. In particular, layers 25 having a higher density are interleaved with layers 26 having a lower density. The layers 25, 26 are stacked directly on top of one another in the stack direction 28 so that each layer is in physical contact with its immediate neighboring layer. The layers 25, 26 may be fixedly attached to their neighbour by an adhesive.

[0128] The article 1' of the fifth embodiment may be fabricated by first fabricating a plurality of first layers 25 in the form of plates or foils having a first density. A plurality of second layers 26 in the form of plates or foils may be fabricated having a second density which is lower than the first density.

[0129] The first layers 25 and second layers 26 are stacked alternately on top of one another joining each layer 25, 26 to the underlying one to produce article 1'.

[0130] The plates or foils which form layers 25, 26 may be fabricated by compacting particles of a magnetocalorically active phase which then form grains of magnetocalorically active phase 2. The density of the plates and foils can be adjusted by adjusting the compaction conditions. For example, the compaction pressure and, if a heat treatment is used, the temperature and time of the heat treatment may be increased to achieve a higher density in the plate or foil.

[0131] The article 1' of the fifth embodiment may also further comprise an outer protective coating, thermal barrier layers, a corrosion protection coating covering the grains of the magnetocalorically active phase as described in connection with the previous embodiments.

[0132] The invention having been described with reference to certain specific embodiments, it will be understood that these specific embodiments are provided in order to illustrate, and not limit, the scope of the appended claims.

- 1. An article for magnetic heat exchange, the comprising: at least one magnetocalorically active phase, wherein the article extends in a first direction and in a second direction generally perpendicular to the first direction, and wherein the average thermal conductivity of the article is anisotropic such that the average thermal conductivity in the first direction differs from the average thermal conductivity in the second direction.
- 2. The article according to claim 1, wherein the average thermal conductivity of the article in the first direction is less than the average thermal conductivity of the article in the second direction.
- 3. The article according to claim 1 wherein the first direction corresponds to the thickness of the article, and the second direction corresponds to a direction in a plane of a lateral area extending generally perpendicular to the first direction, and wherein the average thermal conductivity measured over the thickness of the article is less than the average thermal conductivity measured in a direction in the plane of a lateral area of the article.
  - 4. The article according to claim 1, further comprising:
    - a magnetocalorically passive phase having a thermal conductivity which is greater than a thermal conductivity of the magnetocalorically active phase.
- 5. The article according to claim 4, wherein the magnetocalorically passive phase comprises a plurality of grains having, on average, a preferred orientation.

- 6. The article according to claim 5, wherein
- the plurality of grains of the magnetocalorically passive phase comprise an elongate form having a long direction, and a short direction generally perpendicular to the long direction.
- 7. The article according to claim 5, wherein
- at least some of the plurality of grains of the magnetocalorically passive phase are arranged in the article with a preferred texture.
- 8. The article according to claim 6, wherein
- the plurality of grains of the magnetocalorically passive phase are arranged in the article so that on average their long direction extends generally perpendicular to the first direction of the article.
- 9. The article according to claim 5, wherein
- the plurality of grains of the magnetocalorically passive phase are arranged in the article so that on average their short direction extends generally parallel to the first direction of the article.
- 10. The article according to claim 1, wherein
- the magnetocalorically active phase comprises a plurality of grains arranged in the article with, on average, a preferred orientation.
- 11. The article according to claim 10, wherein the plurality of grains of the magnetocalorically active phase have, on average, a preferred texture.
  - 12. The article according to claim 10, wherein
  - the magnetocalorically active phase comprises a plurality of grains, each having an elongate form with a long direction and a short direction generally perpendicular to the long direction.
  - 13. The article according to claim 12, wherein
  - the grains of the magnetocalorically active phase are arranged in the article so that on average the long direction of the grains extends generally perpendicular to the first direction of the article.
  - 14. The article according to claim 13, wherein
  - the grains of the magnetocalorically active phase are arranged in the article so that on average the short direction of the grains extends generally parallel to the first direction of the article.
- 15. The article according to claim 10, wherein the grains of the magnetocalorically active phase comprise a corrosion protection coating disposed thereon.
- 16. The article according to claim 15, wherein the corrosion protection coating comprises a metal, an alloy, a polymer, a ceramic, or an inorganic compound.
- 17. The article according to claim 15, wherein the corrosion protection coating comprises Al, Cu, Sn, or a phosphate.
  - 18. The article according to one claim 4, wherein
  - the magnetocalorically active phase is disposed in a plurality of first layers interleaved with a plurality of second layers containing the magnetocalorically passive phase.
  - 19. The article according to claim 1, wherein
  - the magnetocalorically active phase comprises at least one first layer having a first density, and at least one second layer having a second density, wherein the first density is greater than the second density.
- 20. The article according to claim 19, wherein the at least one first layer has a first average porosity and the at least one second layer has a second average porosity, wherein the second average porosity is greater than the first average porosity.

- 21. The article according to claim 18, wherein the at least one first layer and the at least one second layer are arranged in a stack, wherein adjacent layers are in physical contact with one another.
- 22. The article according to claim 18, wherein the first layers and the second layers each have a thickness extending generally parallel to the first direction of the article and a lateral area extending generally in the second direction of the article.
  - 23. The article according to claim 1, wherein
  - the article comprises two or more active portions arranged along the first direction, each portion comprising a magnetocalorically active phase having a different Curie temperature T<sub>c</sub>.
  - 24. The article according to claim 23, wherein
  - the  $T_c$  of the active portions increases in the first direction of the article.
  - 25. The article according to claim 1, further comprising: at least one thermal barrier having a thermal conductivity which is less than the thermal conductivity of the magnetocalorically active phase.
  - 26. The article according to claim 25, wherein
  - a plurality of thermal barriers are arranged at intervals along the first direction of the article.
- 27. The article according to claim 23, and further comprising
  - a thermal barrier having a thermal conductivity which is less than the thermal conductivity of the magnetocalorically active phase, that is arranged between adjacent active portions.
- 28. The article according to claim 1, wherein the magnetocalorically active phase comprises one or more of Gd, a La(Fe<sub>1-b</sub>Si<sub>b</sub>)<sub>13</sub>-based phase, a Gd<sub>5</sub>(Si, Ge)<sub>4</sub>-based phase, a Mn(As, Sb)-based phase, a MnFe(P, As)-based phase, a Tb—Gd-based phase, a (La, Ca, Pr, Nd, Sr)MnO<sub>3</sub>-based phase, a Co—Mn—(Si, Ge)-based phase and a Pr<sub>2</sub>(Fe, Co)<sub>17</sub>-based phase.
- 29. The article according to claim 4, wherein the magnetocalorically passive phase comprises one or more of the elements, Al, Cu, Ti, Mg, Zn, Sn, Bi or Pb.
- 30. The article according to claim 4, wherein the magnetocalorically passive phase comprises a soft magnetic material.
- 31. The article according to claim 30, wherein the soft magnetic material comprises one or more of Fe, FeSi, Co, or Ni.
- 32. The article according to claim 1, further comprising at least one channel in a surface of the article.
- 33. The article according to claim 32, wherein the channel is adapted to direct the flow of a heat exchange medium.
- 34. The article according to claim 1, further comprising an outer protective coating.
- 35. The article according to claim 34, wherein the outer protective coating comprises a polymer or a metal or an alloy.
- 36. A heat exchanger, comprising the article according to claim 1.
- 37. A refrigeration system, comprising the heat exchanger according to claim 36.
- 38. An industrial, commercial, or domestic freezer comprising the refrigeration system according to claim 37.
- 39. A method of manufacturing an article for according to claim 4, comprising:
  - providing a magnetocalorically active phase or a precursor of a magnetocalorically active phase,
  - providing a magnetocalorically passive phase comprising a plurality of particles,
  - assembling the magnetocalorically active phase or the precursor of a magnetocalorically active phase and the magnetocalorically passive phase,

- compacting the magnetocalorically active phase or the precursor of a magnetocalorically active phase and the magnetocalorically passive phase to form an article having an average preferred orientation of at least the plurality of grains of the magnetocalorically passive phase in the article.
- **40**. The method according to claim **39**, wherein the compacting comprises inducing a preferred orientation of at least the grains of the magnetocalorically passive phase.
- 41. The method according to claim 39 wherein the compacting comprises inducing a preferred orientation of at least the grains of the magnetocalorically active phase.
- 42. The method according to claim 39, wherein the average preferred orientation of at least the plurality of grains of the magnetocalorically passive phase or at least the plurality of grains of the magnetocalorically active phase, or both, is produced at least in part by applying a magnetic field to the magnetocalorically passive phase or to the magnetocalorically active phase or to both.
  - 43. The method according to claim 42, wherein the magnetic field is applied before the compacting.
  - 44. The method according to claim 42, wherein the magnetic field is applied at a temperature less than the Curie Temperature of the magnetocalorically active phase.
  - 45. The method according to claim 39, wherein
  - the particles of the magnetocalorically passive phase have on average anisotropic dimensions and the compaction is carried out so that the grains of the magnetocalorically passive phase are on average orientated such that the grains have a long direction perpendicular to the first direction of the article.
- 46. The method according to claim 39, wherein the average preferred orientation of at least the plurality of grains of the magnetocalorically passive phase is produced at least in part by mechanical deforming the article after the compacting.
- 47. The method according to claim 46, wherein the mechanical deforming comprises one of more of rolling, swaging, drawing or extruding.
- 48. The method according to claim 39 wherein the assembling of the magnetocalorically active phase and the magnetocalorically passive phase comprises intimately mixing the magnetocalorically active phase and the magnetocalorically passive phase with one another.
- 49. The method according to claim 39 wherein the assembling of the magnetocalorically active phase and the magnetocalorically passive phase comprises alternately arranging layers consisting essentially of the magnetocalorically active phase and layers consisting essentially of the magnetocalorically passive phase.
  - **50**. The method according to claim **39** wherein the compacting of the magnetocalorically active phase and the magnetocalorically passive phase comprises rolling or pressing.
  - 51. The method according to claim 42, wherein
  - the applying of the magnetic field during compaction magnetically orientates the grains of the magnetocalorically passive phase so that on average the grains have a long direction that is oriented generally perpendicular to the first direction of the article.

- **52**. The method according to claim **42**, wherein
- the applying of the magnetic field during compaction magnetically orientates the grains of the magnetocalorically active phase so that on average the grains have a long direction that is oriented generally perpendicular to the first direction of the article.
- 53. A method of manufacturing an article for magnetic heat exchange, comprising:
  - providing at least one first plate consisting essentially of a magnetocalorically active phase and having a first density,
  - providing at least one second plate consisting essentially of a magnetocalorically active phase and having a second density, the first density of the first plate being greater than the second density of the second plate,
  - arranging the first plate and the second plate in a stack.
  - 54. The method according to claim 53, wherein
  - the first plate and the second plate are arranged so that they are in physical contact with one another.
  - 55. The method according to claim 53, wherein
  - the first plate has a first porosity and the second plate has a second porosity, the second porosity being greater than the first porosity.
  - 56. The method according to claim 53, wherein
  - the providing of the at least one first plate comprises compacting particles of a magnetocalorically active phase or particles of a precursor of a magnetocalorically active phase.
  - 57. The method according to claim 53, wherein
  - the providing of the at least one second plate comprises compacting particles of a magnetocalorically active phase or particles of a precursor of a magnetocalorically active phase.
  - **58**. The method according to claim **57**, wherein the compacting is conducted so as to produce a lower porosity in the first plate than in the second plate.
  - 59. The method according to claim 58, wherein the providing of at least one first plate and the providing of at least one second plate comprises providing a plurality of first plates and a plurality of second plates are inter-
  - leaved with one another in a stacking direction of the article.

    60. The method according to claim 39, further comprising
- adding
  - one or more of a lubricant, an organic binder or a dispersant are to the assembled magnetocalorically active phase or the magnetocalorically passive phase or both.
- 61. The method according to claim 39, further comprising heating the article during the compacting.
- **62**. The method according to claim **61**, wherein the heating forms a
  - magnetocalorically active phase from the precursor.
- 63. The method according to claim 39, further comprising applying an outer protective coating to the article.
  - **64**. The method according to claim **63**, wherein applying the outer protective coating comprises dipping, spraying or electro-deposition.
- 65. A climate control device comprising the heat exchanger according to claim 36.
- 66. An air conditioning system comprising the climate control device according to claim 65.

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