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(54) **MAGNETIC MATERIAL FOR MAGNETIC REFRIGERATION APPARATUS, AMR BED, AND MAGNETIC REFRIGERATION APPARATUS**

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(57) **ABSTRACT**

There are provided a magnetic material for a magnetic refrigeration apparatus, which improves magnetic refrigeration efficiency by the wide operation temperature range of it, AMR bed using the magnetic material, and a magnetic refrigeration apparatus. The magnetic material is used for the magnetic refrigeration apparatus using a liquid refrigerant, formed by approximately uniformly blending at least two kinds of magnetic particles having different magnetic transition temperatures, and the magnetic particles exhibit an approximately spherical shape with maximum diameter of 0.3 mm or more to 2 mm or less. The AMR bed is filled with the magnetic particles.

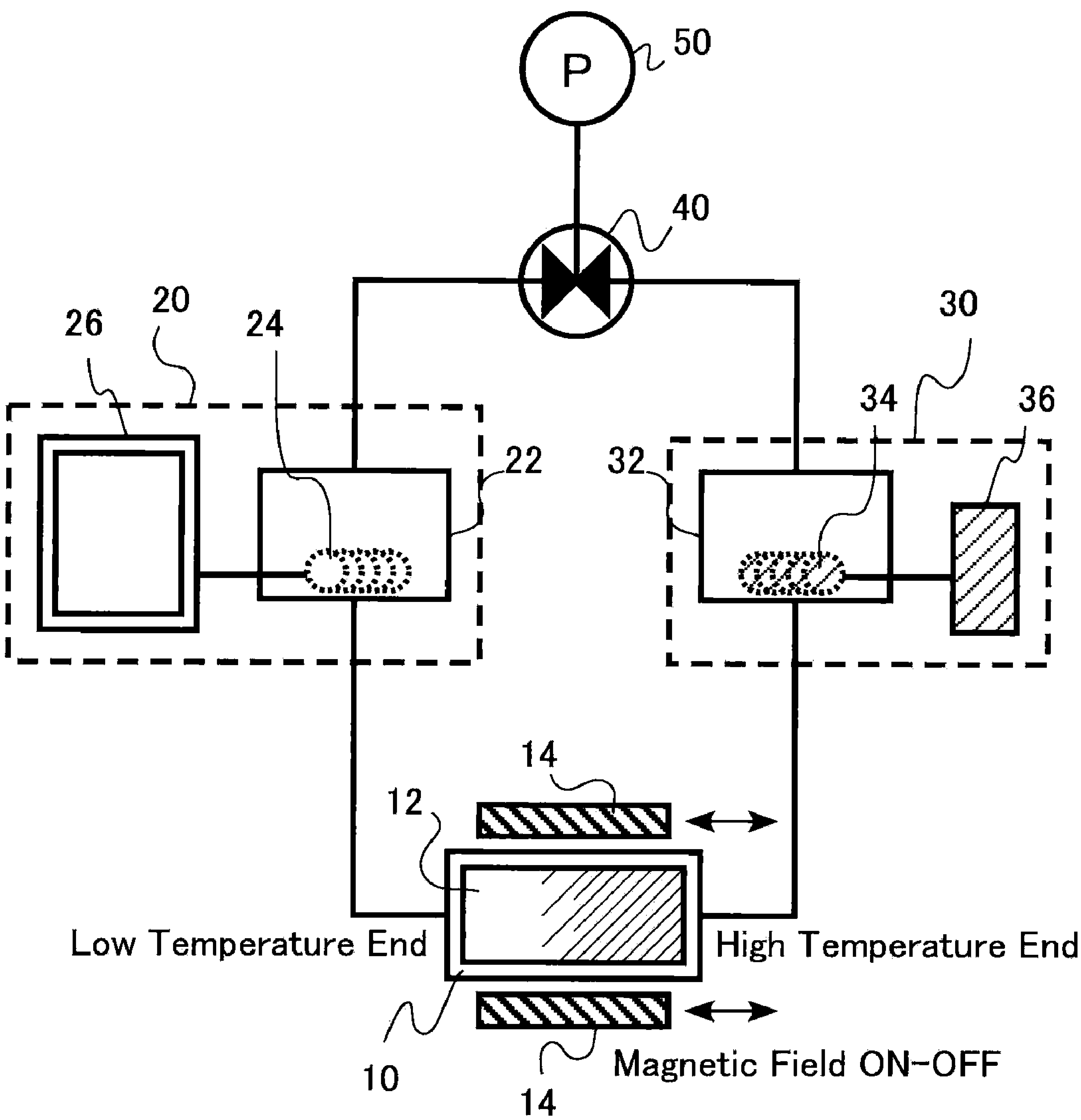


FIG.1

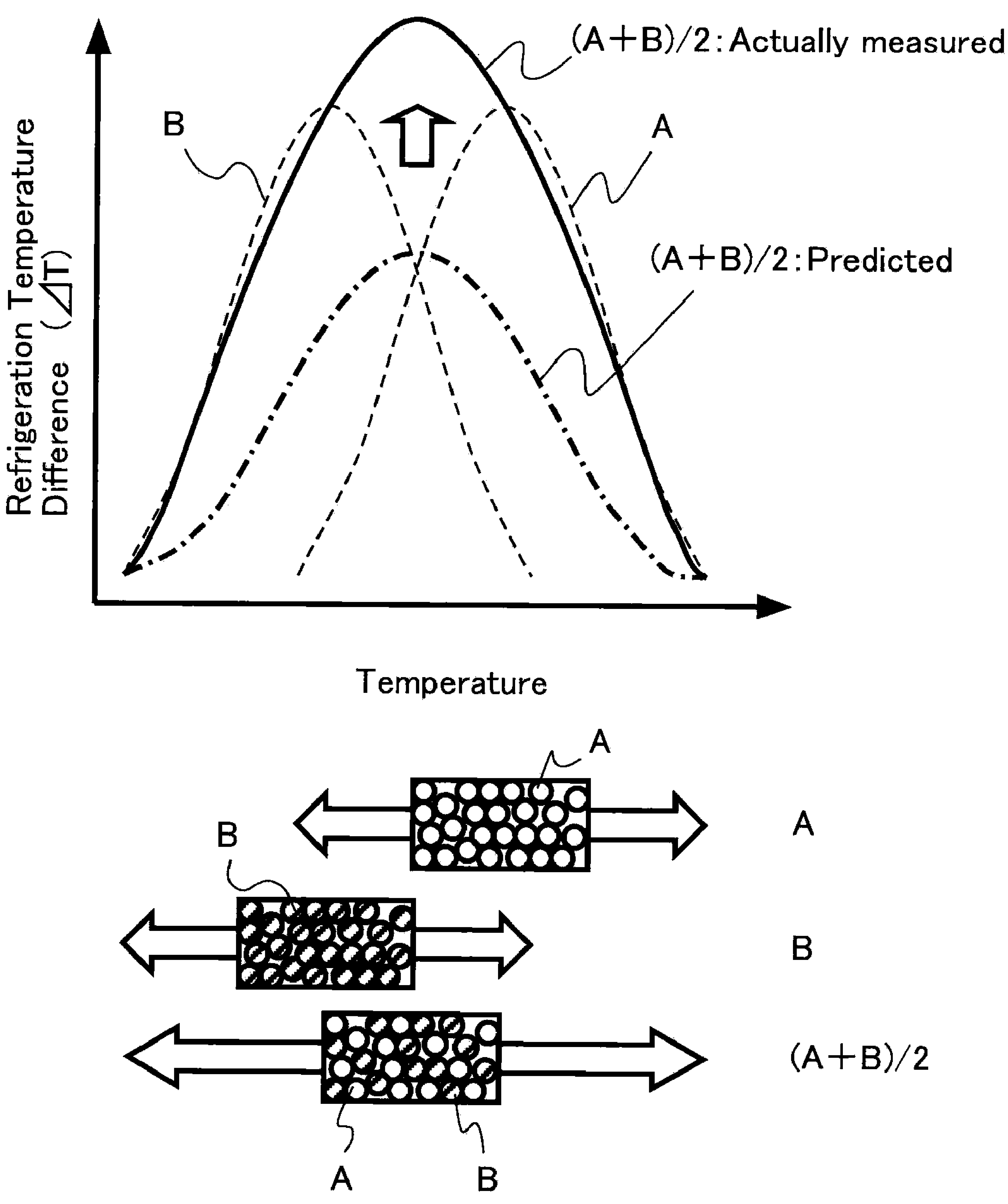

(A+B)/2: Actually measured
B
A
(A+B)/2: Predicted
Refrigeration Temperature Difference (⊿T)
Temperature
A
A
B
B
(A+B)/2
A
B

FIG.2

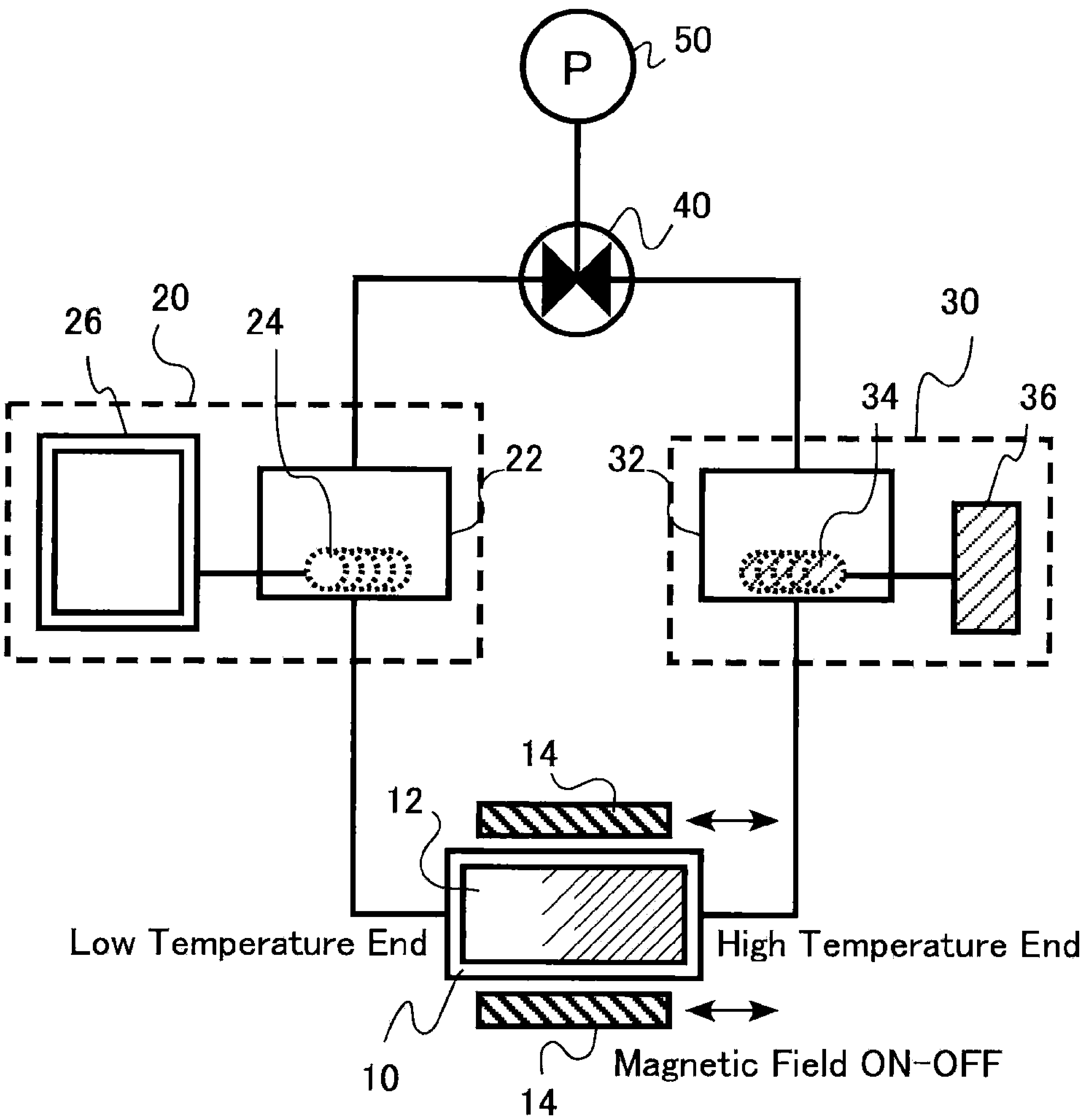

P
50
40
20
26
24
22
30
34
36
32
14
12
Low Temperature End
High Temperature End
10
14
Magnetic Field ON-OFF

FIG.3

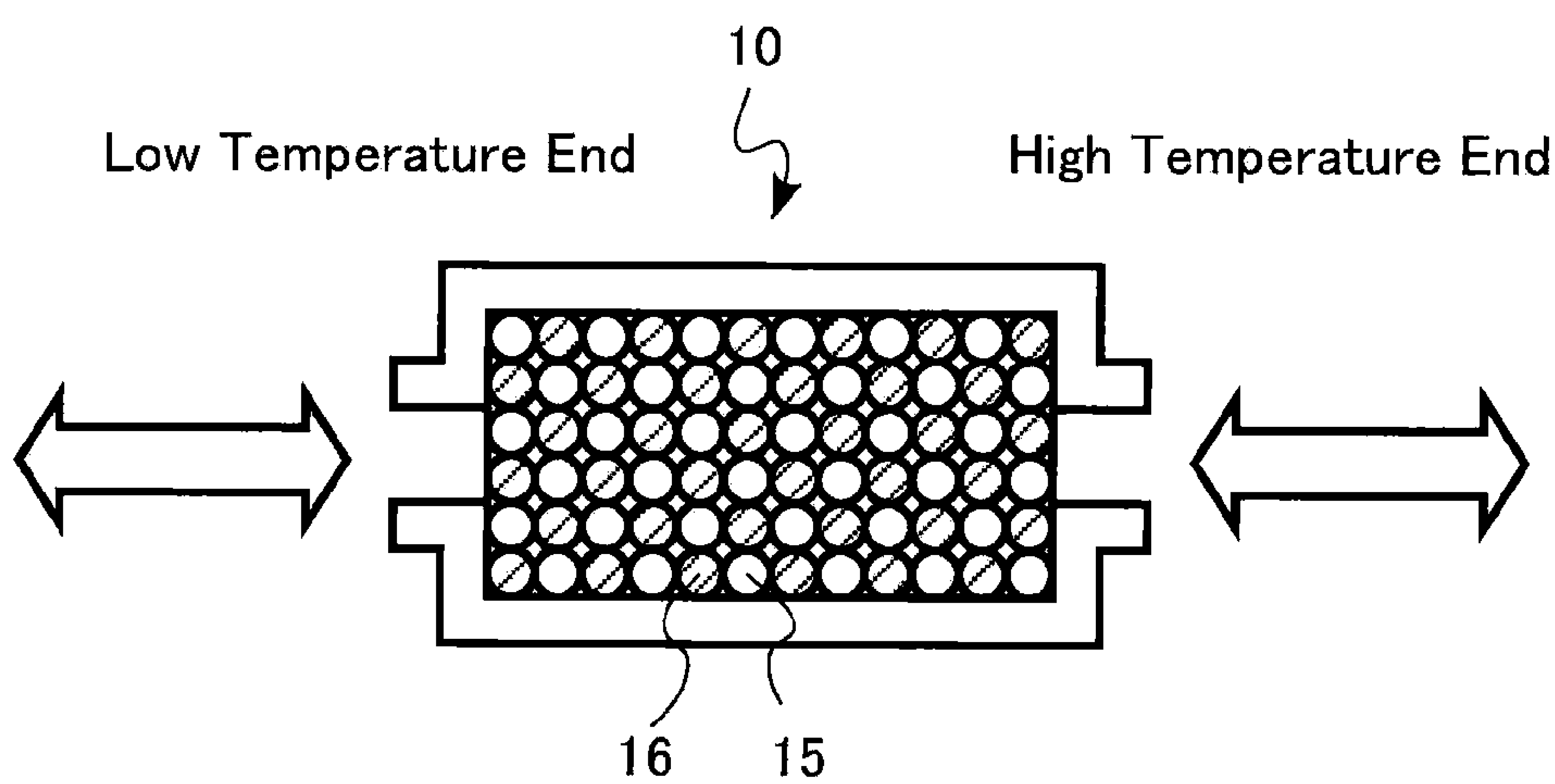

10
Low Temperature End
High Temperature End
16
15

FIG.4

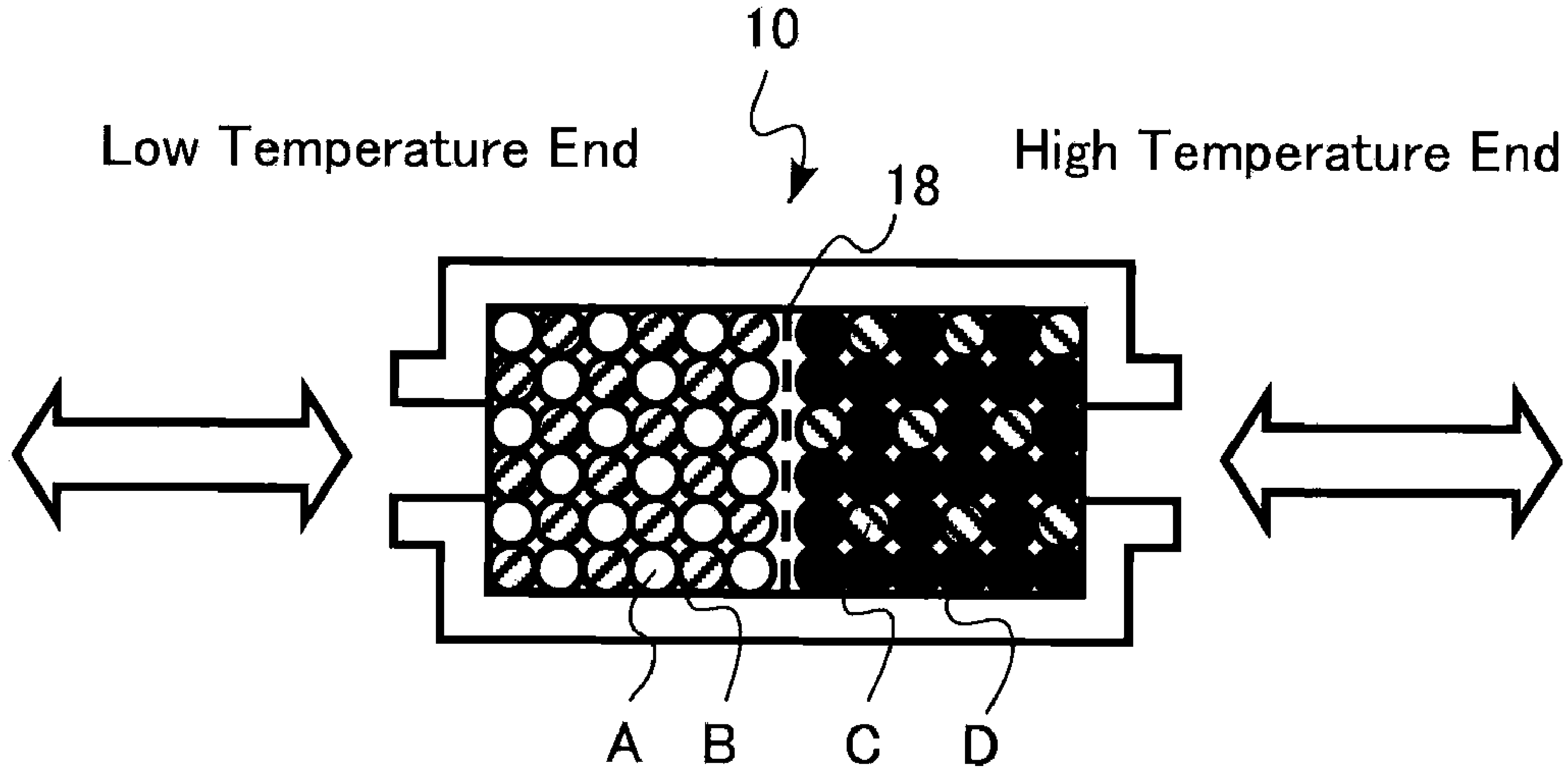

10
Low Temperature End
High Temperature End
18
A
B
C
D

FIG.5

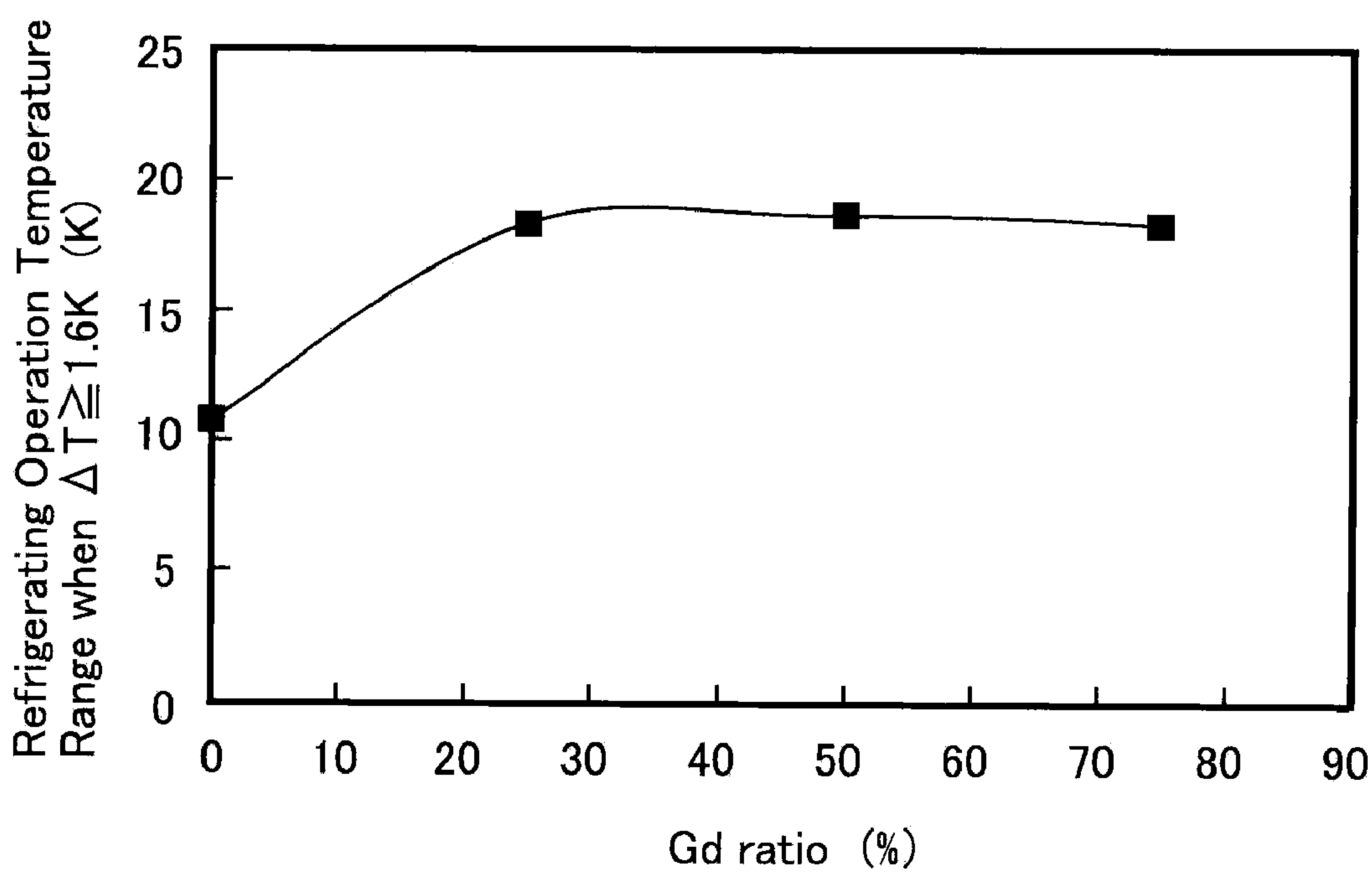
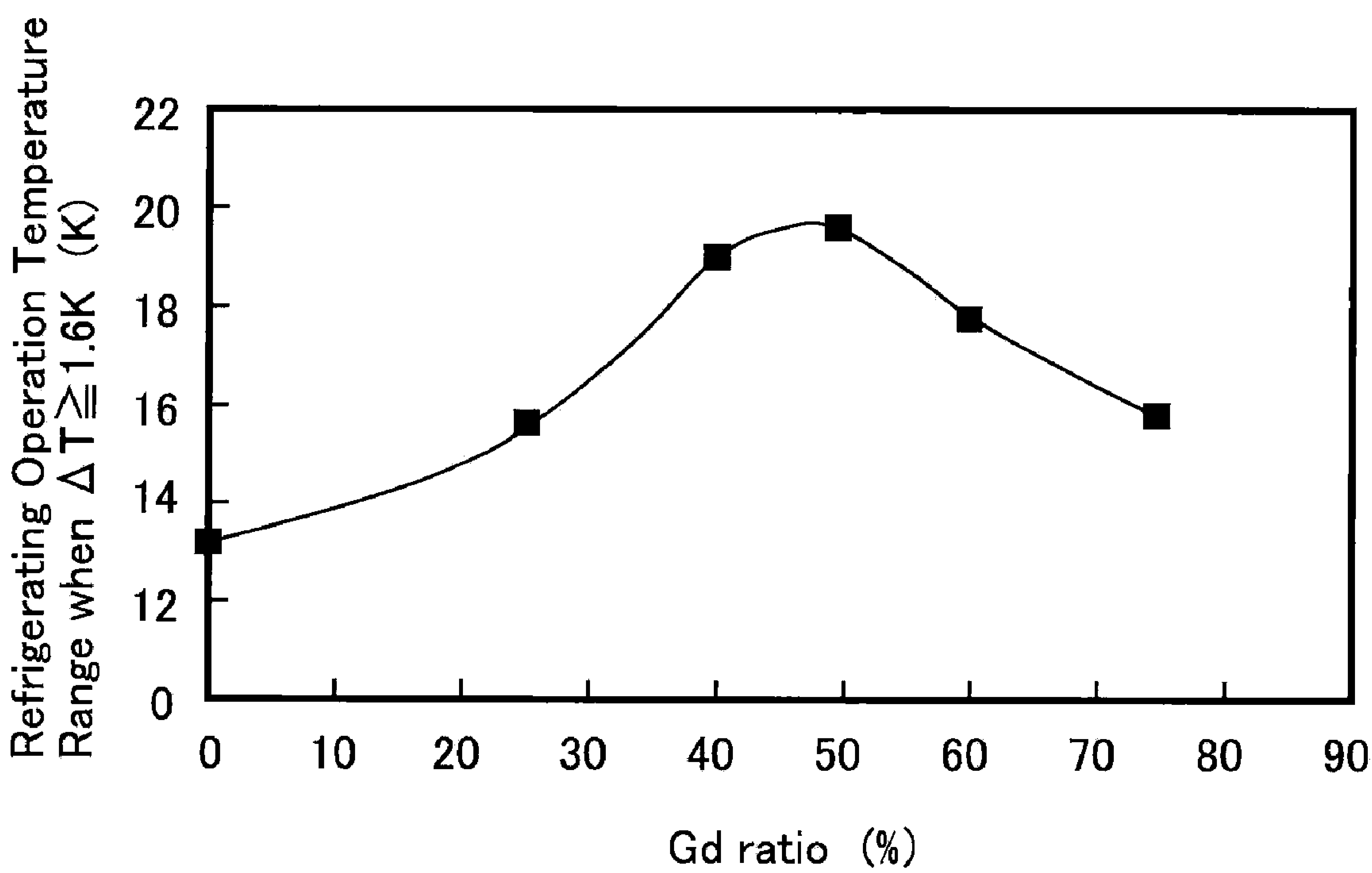

Refrigerating Operation Temperature
Range when ΔT≧1.6K (K)
25
20
15
10
5
0
0
10
20
30
40
50
60
70
80
90
Gd ratio (%)

FIG.6


Refrigerating Operation Temperature
Range when ΔT≧1.6K (K)
22
20
18
16
14
12
0
0
10
20
30
40
50
60
70
80
90
Gd ratio (%)

MAGNETIC MATERIAL FOR MAGNETIC REFRIGERATION APPARATUS, AMR BED, AND MAGNETIC REFRIGERATION APPARATUS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is based upon and claims the benefit of priority from Japanese Patent Applications No. 2008-047663, filed on Feb. 28, 2008, the entire contents of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to a magnetic material having a magnetocaloric effect and used for a magnetic refrigeration apparatus, AMR bed using the magnetic material, and the magnetic refrigeration apparatus.

BACKGROUND OF THE INVENTION

[0003] At present, a refrigeration technology in a room temperature region which closely relates to a human daily life, for example, a refrigerator, a freezer, a room air conditioner, and the like, almost employs a gas compression/expansion cycle. However, as to the gas compression/expansion cycle, a serious problem of environmental destruction is caused by specific freon gases discharged into the environment, and CFC's substitutes also have a problem of an adverse affect to the environment. From the above background, researches on the use of natural refrigerants (CO_2, ammonia, and the like) and isobutane which have little environmental risk and the like are carried out. Thus, it is required to put the refrigeration technologies, which have no environmental problems and work safety and efficiency, to practice use.

[0004] A magnetic refrigeration is one of the promising technology, in terms of environment-friendliness and high efficiency. And a magnetic refrigeration technology in a room temperature region is actively researched and developed. The magnetic refrigeration technology uses a magnetocaloric effect that Warburg discovered on iron (Fe) in 1881. The magnetocaloric effect is a phenomenon that the temperature of magnetic material changes according to changing of external magnetic field in an adiabatic state. In early 1900's, the refrigeration system using paramagnetic salts and compounds represented by $Gd_2(SO_4)_3.8H_2O$ or $Gd_3Ga_5O_{12}$, which show the magnetocaloric effect, was developed. However that system was mainly used in an ultracold temperature region around 20 K or less, and needed a high magnetic field around 10 T which is created by a superconducting magnet.

[0005] In 1970's and thereafter, researches making use of magnetic transition between a paramagnetic state and a ferromagnetic state in a ferromagnetic material have been actively carried out up to now to realize magnetic refrigeration in a high temperature region. As a result of these researches, some magnetic materials are proposed. For example, a simple substance of rare earth (Pr, Nd, Dy, Er, Tm, Gd and the like), rare earth alloys which include at least two kinds of rare earth element, such as Gd—Y, Gd—Dy, and intermetallic compounds such as RAl_2 and RNi_2 (R represents rare earth elements), GdPd, and the like.

[0006] In 1982, Barclay proposed an AMR ("Active Magnetic Regenerative Refrigeration") system as a magnetic refrigeration system for a room temperature region in the United States. The key feature of this system is to use the two effect, a magnetocaloric effect and a heat accumulation, of magnetic materials (refer to U.S. Pat. No. 4,332,135). That is, this system actively uses the lattice entropy which was conventionally considered as a disincentive.

[0007] Magnetic refrigeration is carried out by the AMR system using the following steps:

[0008] (1) A magnetic field is applied to a magnetic refrigeration working material;

[0009] (2) The magnetic refrigeration working material heat up at step (1) and this heat energy is transported to one side by a heat transfer fluid;

[0010] (3) The magnetic field removed; and

[0011] (4) The magnetic refrigeration working materials cool down at step (3) and this cold energy is transported to the other side by a heat transfer fluid.

[0012] Repeating the cycle from (1) to (4), the heat energy generated by magnetic refrigeration material is transported to one direction and then the temperature gradient is created in AMR bed. As a result, a refrigeration work is carried out by generating a large temperature difference.

[0013] In United States in 1998, Zimm, Gschneidner, Pecharsky et al succeeded in a continuous operation of a magnetic refrigeration cycle by using AMR systems with Gd (gadolinium) under the high magnetic field (5 T) generated by a superconducting magnet.

[0014] Incidentally, since the magnetocaloric effect of the magnetic refrigeration material can obtain a large effect only in the vicinity of a magnetic transition temperature, a problem arises in that the working efficiency is lowered when temperature is shifted from the magnetic transition temperature of the material. To cope with the above problem, it is proposed to increase a working temperature by filling AMR bed with magnetic materials having different magnetic transition temperatures in a layer state in accordance with a temperature difference generated in the AMR bed (JP-A 4-186802 (KOKAI)).

SUMMARY OF THE INVENTION

[0015] A magnetic material for a magnetic refrigeration apparatus using a liquid refrigerant of an embodiment of the present invention includes at least two kinds of magnetic particles having different magnetic transition temperatures and blended approximately uniformly, wherein, the magnetic particles exhibit an approximately spherical shape with a maximum diameter of 0.3 mm or more to 2 mm or less.

[0016] In AMR bed filled with a magnetic material for a magnetic refrigeration apparatus using a liquid refrigerant of an embodiment of the present invention, the magnetic material includes at least two kinds of magnetic particles having different magnetic transition temperatures and blended approximately uniformly, and the magnetic particles exhibit an approximately spherical shape with a maximum diameter of 0.3 mm or more to 2 mm or less.

[0017] A magnetic refrigeration apparatus using a liquid refrigerant of an embodiment of the present invention has AMR bed filled with a magnetic material, a magnetic field generation device for applying and removing a magnetic field to and from the magnetic material, a cooling block, a radiating block, and a refrigerant flow path connected to the AMR bed, the cooling block and the radiating block configured to circulate the liquid refrigerant, wherein the magnetic material includes at least two kinds of magnetic particles having different magnetic transition temperatures and blended approximately uniformly, and the magnetic particles exhibit an approximately spherical shape with a maximum diameter of 0.3 mm or more to 2 mm or less.

[0018] According to the present invention, there can be provided a magnetic material for a magnetic refrigeration apparatus which improves magnetic refrigeration efficiency by the wide operation temperature range of it and the magnetic refrigeration apparatus using the magnetic material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. **1** is an explanatory view showing an operation of a magnetic material for a magnetic refrigeration apparatus of a first embodiment;

[0020] FIG. **2** is a schematic view of a system of a magnetic refrigeration apparatus of a second embodiment;

[0021] FIG. **3** is a sectional view showing an arrangement of a magnetic material in AMR bed of the second embodiment;

[0022] FIG. **4** is a sectional view showing another arrangement of the magnetic material in AMR bed of a third embodiment;

[0023] FIG. **5** is a graph showing a result of measurement of a refrigerating operation temperature range of examples and comparative examples; and

[0024] FIG. **6** is a graph showing a result of measurement of the refrigerating operation temperature range of the examples and the comparative examples.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0025] The inventors have found that when at least two kinds of magnetic particles having different magnetic transition temperatures (Tc) are approximately uniformly blended and AMR bed is filled with them, a magnetic refrigeration operation temperature range can be extended without outstandingly lowering a refrigeration capability. A magnetic material for a magnetic refrigeration apparatus, AMR bed, and the magnetic refrigeration apparatus of embodiments of the present invention will be explained below referring to the drawings based on the above knowledge found by the inventors. Note that, in the specification, two kinds of magnetic particles have different magnetic transition temperatures means that the average values of the magnetic transition temperatures of respective magnetic particles are separated from each other 0.5 K or more.

First Embodiment

[0026] A magnetic material for a magnetic refrigeration apparatus of a first embodiment is a magnetic material for a magnetic refrigeration apparatus using a liquid refrigerant. At least two kinds of magnetic particles having different magnetic transition temperatures (Tc) are approximately uniformly blended. The magnetic particles exhibit an approximately spherical shape with a maximum diameter of 0.3 mm or more to 2 mm or less.

[0027] In the magnetic material of the first embodiment, two kinds of magnetic particles, for example, Gd particles having a magnetic transition temperature 293 (K) and $Gd_{95}Y_5$ particles having a magnetic transition temperature 283 (K), which is lower than that of the Gd particles, are approximately uniformly blended at a ratio of 1:1. Hereinafter, the difference between the magnetic transition temperatures of the two kinds of the magnetic particles is called a magnetic transition temperature difference (ΔTc).

[0028] The two kinds of the magnetic particles exhibit the approximately spherical shape with the maximum diameter of 0.3 mm or more to 2 mm or less. The maximum diameter of the magnetic particles can be visually measured with a calipers and the like, by direct observation under a microscope, or by a microscope photograph.

[0029] Note that it is possible to use compounds, in which Gd is combined with Y having different composition ratios, or GdR (R shows rear earth elements other than Gd, Y, i.e., Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu) as the magnetic particles in addition to $Gd_{95}Y_5$ and Gd described above. Further, for example, compounds composed of various kinds of rear earth elements and transition metal elements, NiMnGa alloys, GdGeSi alloys, $LaFe_{13}$ compounds, $LaFe_{13}H$, MnAsSb, and the like can be used.

[0030] FIG. **1** is an explanatory view showing an operation of the magnetic material for the magnetic refrigeration apparatus of the first embodiment. An upper view of FIG. **1** is a graph showing the relation between the temperature of the magnetic material and a refrigeration temperature difference (ΔT) of the magnetic material. Further, a lower view of FIG. **1** is a conceptual view showing how AMR bed is filled with magnetic materials and the magnetic refrigeration operation temperature ranges to the respective magnetic material by arrows in correspondence to a temperature axis of the upper view of FIG. **1**. Note that the refrigeration temperature difference (ΔT) means a temperature difference caused to the magnetic material when a magnetic field is repeatedly applied and removed to and from the magnetic material and used as an index of the refrigeration capability of the magnetic material.

[0031] In the upper view of FIG. **1**, when magnetic particles A and magnetic particles B, which have two kinds of different magnetic transition temperatures and the refrigeration temperature characteristics of which are shown by two broken lines, are blended, a magnetic refrigerating operation temperature is increased without outstandingly lowering the refrigeration capability as shown by a solid line (actually measured) of the upper view of FIG. **1**. In general, when the magnetic particles A and B having the two kinds of the different magnetic transition temperatures are blended, it is predicted that the refrigeration capability is lowered although the magnetic refrigerating operation temperature is increased as shown by a single-dashed line (predicted) of the upper view of FIG. **1**.

[0032] A reason why the refrigeration capability is not outstandingly lowered against prediction in the first embodiment is considered as described below. That is, at a certain temperature, a temperature change caused by application and removal of the magnetic field is determined depending on materials. Accordingly, it is considered that when all the materials are the same materials, the same temperature change ideally occurs all at once. However, when different materials exist, since dispersion occurs in the temperature change caused by application of the magnetic field, heat is transmitted between the magnetic materials. Since heat is secondarily generated and absorbed by the transmission of heat, a temperature change, which is not caused when the same kind of a material is used, occurs. As a result, it is considered that an effect of an increase of temperature, which cannot be predicted from measurement of the simple material appears. The operation temperature can be increased without outstandingly lowering the refrigeration capability by the addition of the above effect resulting from the blend.

[0033] The magnetic particles exemplified above have different magnetic transition temperatures depending on the compositions thereof. In the magnetic material of the first embodiment, a wide range of the refrigeration operation temperature can be guaranteed by appropriately combining two kinds of magnetic particles having appropriate magnetic transition temperatures. Although the example, in which the two kinds of the magnetic particles having the different magnetic transition temperatures are blended, is explained here, three kinds or more of magnetic particles may be blended.

[0034] As described above, the magnetic particles of the first embodiment exhibit the approximately spherical shape with the maximum diameter of 0.3 mm or more to 2 mm or less. It is important for the magnetic refrigeration apparatus to realize a high refrigeration capability in that a magnetic material with which the AMR bed is filled sufficiently exchanges its heat with a liquid refrigerant and realizes high heat exchange efficiency. For this purpose, it is preferable to increase the specific surface area of magnetic particles by increasing the particle diameter thereof. In contrast, when the particle diameter is too small, a refrigerant pressure loss is increased. Accordingly, the refrigeration capability of a magnetic refrigeration apparatus is improved by using the magnetic particles of the first embodiment whose maximum diameter is set to 0.3 mm or more to 2 mm or less.

[0035] As described above, the magnetic material of the first embodiment can extend the magnetic refrigeration operation temperature range without outstandingly lowering the refrigeration capability as compared with a magnetic material composed of simple magnetic particles. Further, when the magnetic material is combined with the liquid refrigerant, high heat exchange efficiency can be realized. Accordingly, the refrigeration capability of the refrigeration apparatus can be improved by filling the AMR bed with the magnetic material of the first embodiment and applying the AMR bed to the refrigeration apparatus.

[0036] Further, in the first embodiment, it is preferable to blend magnetic particles, which make use of secondary magnetic transition without hysteresis, with each other. This is because it is considered that heat is effectively transmitted between magnetic materials and an effect of suppressing a lowering of the refrigeration capability can be increased.

[0037] Note that, in the first embodiment, even if particles other than the magnetic particles for exhibiting the advantage of the first embodiment are contained as impurities in an amount of several percentages to the total weight of the magnetic material, they do not inhibit the advantage of the first embodiment.

Second Embodiment

[0038] A magnetic refrigeration apparatus of a second embodiment is a magnetic refrigeration apparatus using a liquid refrigerant. The magnetic refrigeration apparatus has AMR bed filled with a magnetic material, a magnetic field generation means (device) for applying and removing a magnetic field to and from the magnetic material, a cooling block, and a radiating block. Further, the magnetic refrigeration apparatus has a refrigerant flow path formed by connecting the AMR bed, the cooling block and the radiating block configured to circulate the liquid refrigerant. The magnetic material with which the AMR bed is filled is formed by approximately uniformly bending at least two kinds of magnetic particles having different magnetic transition temperatures, and the magnetic particles has a feature in that they exhibit an approximately spherical shape with a maximum diameter of 0.3 mm or more to 2 mm or less. Note that since the magnetic material with which the AMR bed is filled is the same as that described in the first embodiment, description of duplicate contents is omitted.

[0039] FIG. **2** is a schematic view of a system of the magnetic refrigeration apparatus of the second embodiment. The magnetic refrigeration apparatus uses, for example, water as the liquid refrigerant. The cooling block **20** is disposed to a low temperature end side of the AMR bed **10**, and the radiating block **30** is disposed to a high temperature end side thereof. A switching means **40** is interposed between the cooling block **20** and the radiating block **30** to switch a direction in which the liquid refrigerant flow. Further, a refrigerant pump **50** as a refrigerant transport means is connected to the switching means **40**. The AMR bed **10**, the cooling block **20**, the switching means **40**, and the radiating block **30** are connected by a pipe and form the refrigerant flow path for circulating the liquid refrigerant.

[0040] The AMR bed **10** is filled with the magnetic material **12** having a magnetocaloric effect. A horizontally movable permanent magnet **14** is disposed to outside of the AMR bed **10** as a magnetic field generation means. The cooling block **20** is composed of a low-temperature bath **22**, in which a low temperature side heat exchanger device **24** is disposed, and a cooling unit **26**. The low temperature side heat exchanger device **24** is thermally connected to the cooling unit **26**. In contrast, the radiating block **30** is composed of a hot bath **32**, in which a high temperature side heat exchanger device **34** is disposed, and a radiating unit **36**. The high temperature side heat exchanger device **34** is thermally connected to the radiating unit **36**.

[0041] Although the magnetic refrigeration apparatus of the second embodiment is not particularly limited, it is, for example, a home freezer/refrigerator, a home air conditioner, an industrial freezer/refrigerator, a large frozen/refrigerated warehouse, a frozen chamber for reserving and transporting a liquefied gas, and the like.

[0042] When, for example, the magnetic refrigeration apparatus is the home freezer/refrigerator, the cooling unit is a freezing/refrigerating chamber, and the radiating unit **36** is, for example, a radiation plate.

[0043] FIG. **3** is a sectional view showing an arrangement of a magnetic material in the AMR bed. As shown in the figure, the AMR bed **10** is filled with a magnetic material having the magnetocaloric effect. The magnetic material is a magnetic material formed by approximately uniformly blending two kinds of magnetic particles, for example, Gd particles **16** and $Gd_{95}Y_5$ particles **15** having a magnetic transition temperature lower than that of the Gd particles **16**. Openings are formed to both the ends of the AMR bed **10** so that a refrigerant is caused to flow in both right and left directions in the AMR bed **10**.

[0044] Next, an operation of the magnetic refrigeration apparatus of the second embodiment will be schematically explained using FIG. **2**. When the permanent magnet **14** is disposed at a position confronting with the AMR bed **10** (position shown in FIG. **2**), a magnetic field is applied to the magnetic material **12** in the AMR bed **10**. Accordingly, the magnetic material **12** having the magnetocaloric effect generates heat. At the time, the liquid refrigerant is caused to circulate in the direction from the AMR bed **10** to the radiating block **30** by the operations of the refrigerant pump **50** and the switching means **40**. Hot heat is transported to the radiating block **30** by the liquid refrigerant whose temperature is increased by the heat generated by the magnetic material **12**. Then, the liquid refrigerant flows into the hot bath **32** in the radiating block **30**, and the hot heat transported by the refrigerant is absorbed by the high temperature side heat exchanger device **34**. The absorbed hot heat is radiated to, for example, the outside air by the radiating unit **36**.

[0045] Thereafter, the permanent magnet **14** is moved from the position confronting with the AMR bed **10**, and the magnetic field applied to the magnetic material **12** is removed. When the magnetic field is removed, the magnetic material **12** absorbs heat. At the time, the liquid refrigerant is caused to circulate in the direction from the AMR bed **10** to the cooling block **20** by the operations of the refrigerant pump **50** and the switching means **40**. Cold heat is transported to the cooling block **20** by the liquid refrigerant that is cooled by the heat absorbed by magnetic material **12**. The liquid refrigerant flows into the low-temperature bath **22** in the cooling block **20**, and the cold heat transported by the refrigerant is absorbed by the low temperature side heat exchanger device **24**. The cooling unit **26** is cooled by the cold heat.

[0046] The cooling unit **26** can be continuously cooled by repeating application and removal of the magnetic field to and from the magnetic material **12** in the AMR bed **10** by repeatedly moving the permanent magnet **14**.

[0047] The magnetic refrigeration apparatus of the second embodiment can realize high heat exchange efficiency by using the magnetic material whose magnetic refrigerating operation temperature is increased without outstandingly lowering a refrigeration capability.

[0048] Note that the arrangement of the magnetic material in the AMR bed is not necessarily limited to the arrangement shown in FIG. **3**. FIG. **4** is a sectional view showing another arrangement of the magnetic material in the AMR bed. As shown in FIG. **4**, the AMR bed **10** is filled with a magnetic material, in which magnetic particles A and B having two kinds of different magnetic transition temperatures are blended, on the low temperature end side thereof. Then, the AMR bed **10** is filled with a magnetic material, in which magnetic particles C and D having two kinds of different magnetic transition temperatures are blended, on the high temperature end side thereof. The magnetic material on the low temperature end side are separated from that on the high temperature end side by, for example, a lattice-shaped partition wall **18** in which a refrigerant can flow so that they are not blended with each other.

[0049] The magnetic particles A, the magnetic particles B, the magnetic particles C, the magnetic particles D, and the blend ratio thereof are determined so that the magnetic material on the low temperature side have a refrigeration operation temperature range lower than that of the magnetic material on the high temperature side.

[0050] The magnetic refrigerating operation temperature can be more increased and a magnetic refrigeration apparatus that realizes higher heat exchange efficiency can be provided by employing the arrangement of the magnetic materials in the AMR bed shown in FIG. **4**.

[0051] Note that although the case, in which the magnetic materials in the AMR bed have a laminated structure having two layers, is shown in FIG. **4**, the magnetic refrigerating operation temperature can be more increased by providing a layered structure having three or more layers.

[0052] Further, the void ratio of the AMR bed filled with the magnetic materials is preferably 30% or more to 50% or less. In AMR bed filled with magnetic particles for a magnetic refrigeration apparatus using a liquid refrigerant, it is preferable to form a sufficient amount of void space through which a fluid flows so that the flow of the liquid refrigerant is not inhibited in the AMR bed. When the void ratio is less than 30%, since a pressure loss is excessively increased, there is a possibility that refrigeration efficiency is lowered. Further, when the void ratio exceeds 50%, since the magnetic particles that contribute to a refrigerating operation are reduced, there is possibility that a sufficient refrigeration capability cannot be obtained. Note that the void ratio is a value defined by the mass ratio of the mass of a magnetic material equivalent to the volume of AMR bed and the mass of a magnetic material with which the AMR bed is filled.

[0053] The embodiments of the present invention have been explained above referring to the specific examples. However, the above embodiments are exemplified as only examples and do not restrict the present invention. Further, in the explanation of the embodiments, although the explanation of the components in the magnetic material for the magnetic refrigeration apparatus, the AMR bed, the magnetic refrigeration apparatus, and the like, which are not directly necessary to the explanation of the present invention, is omitted, necessary components, which relate to the magnetic material for the magnetic refrigeration apparatus, the magnetic refrigeration apparatus, and the like, can be appropriately selected and used.

[0054] In addition to the above-mentioned, all the magnetic material for the magnetic refrigeration apparatus, the AMR bed, and the magnetic refrigeration apparatus, which have the components of the present invention and the design of which can be appropriately modified by persons skilled in the art, are included in the scope of the present invention. The scope of the present invention is defined by the scope of the appended claims and the scope of the equivalents thereof.

EXAMPLES

[0055] Examples of the present invention will be explained below in detail.

Example 1

[0056] AMR bed (hereinafter, called also a specimen vessel) was filled with a specimen, in which $Gd_{95}Y_5$ particles and Gd particles formed in a spherical shape and having a diameter of 0.3 mm or more to 2 mm or less were blended at a weight ratio of 3:1 (Gd ratio=25%), at a void ratio of 30% to 50%, and a refrigeration temperature difference (ΔT) was evaluated. Note that the magnetic transition temperature of the $Gd_{95}Y_5$ particles was 283 K, the magnetic transition temperature of the Gd particles was 293 K, and a magnetic transition temperature difference (ΔTc) was 10 K. The refrigeration temperature difference (ΔT) was evaluated by the following method.

[0057] The AMR bed was filled with the specimen so that the specimen did not easily move. Next, a thermocouple was inserted into the specimen vessel through a 0.8 mm ϕ hole formed to an upper lid of the vessel so that it was positioned in a central portion of the specimen vessel. Further, the specimen vessel was entirely covered with a heat insulating material and fixed to a specimen holder in a constant temperature bath. The specimen holder was located at a position at which it was possible to apply and remove a magnetic field by the operation of yoke magnet,and it was possible to adjust the internal temperature of the constant temperature bath from the outside. After the inside of the constant temperature bath was shut off from the outside, the temperature of the inside thereof was adjust, and it was waited that the inside temperature thereof was made uniform. Thereafter, the magnetic field was repeatedly applied and removed to and from the specimen by operating the yoke magnet, and ΔT was measured by a temperature difference at the time. Subsequently, after the temperature in the constant temperature bath was adjusted, ΔT at the respective temperatures of the specimen was evaluated by repeating a process of measuring the temperature dependence of ΔT by applying and removing the magnetic field to and from the specimen.

[0058] As a result of the measurement, the temperature range which satisfies $\Delta T \geqq 1.6$ K was set as the magnetic refrigeration operation temperature range of the specimen. The condition of $\Delta T \geqq 1.6$ K is a condition by which the superiority of the magnetic material is verified by the refrigeration test performance in the AMR system obtained up to that time. Table 1 shows an obtained result.

Example 2

[0059] The same evaluation as that of the example 1 was executed except that a specimen, in which $Gd_{95}Y_5$ particles and Gd particles were blended at a weight ratio of 1:1 (Gd ratio=50%), was prepared.

Example 3

[0060] The same evaluation as that of the example 1 was executed except that a specimen, in which $Gd_{95}Y_5$ particles and Gd particles were blended at a weight ratio of 1:3 (Gd ratio=75%), was prepared.

Comparative Example 1

[0061] The same evaluation as that of the example 1 was executed except that a specimen of simple $Gd_{95}Y_5$ particles was prepared.

Example 4

[0062] The same evaluation as that of the example 1 was executed except that a specimen, in which $Gd_{97}Y_3$ particles and Gd particles were blended at a weight ratio of 3:1 (Gd ratio=25%), was prepared. Note that the magnetic transition temperature of the $Gd_{97}Y_3$ particles was 287 K, the magnetic transition temperature of the Gd particles was 293 K, and a magnetic transition temperature difference (ΔTc) was 6 K.

Example 5

[0063] The same evaluation as that of the example 1 was executed except that a specimen, in which $Gd_{97}Y_3$ particles and Gd particles were blended at a weight ratio of 3:2 (Gd ratio=40%), was prepared.

Example 6

[0064] The same evaluation as that of the example 1 was executed except that a specimen, in which $Gd_{97}Y_3$ particles and Gd particles were blended at a weight ratio of 1:1 (Gd ratio=50%), was prepared.

Example 7

[0065] The same evaluation as that of the example 1 was executed except that a specimen, in which $Gd_{97}Y_3$ particles and Gd particles were blended at a weight ratio of 2:3 (Gd ratio=60%), was prepared.

Example 8

[0066] The same evaluation as that of the example 1 was executed except that a specimen, in which $Gd_{97}Y_3$ particles and Gd particles were blended at a weight ratio of 1:3 (Gd ratio=75%), was prepared.

Comparative Example 2

[0067] The same evaluation as that of the example 1 was executed except that a specimen of simple $Gd_{97}Y_3$ particles was prepared.

Example 9

[0068] The same evaluation as that of the example 1 was executed except that a specimen, in which $Gd_{98}Y_2$ particles and Gd particles were blended at a weight ratio of 3:2 (Gd ratio=40%), was prepared. Note that the magnetic transition temperature of the $Gd_{98}Y_2$ particles was 289 K, the magnetic transition temperature of the Gd particles was 293 K, and the magnetic transition temperature difference (ΔTc) was 4 K.

Example 10

[0069] The same evaluation as that of the example 1 was executed except that a specimen, in which $Gd_{98}Y_2$ particles and Gd particles were blended at a weight ratio of 1:1 (Gd ratio=50%), was prepared.

Example 11

[0070] The same evaluation as that of the example 1 was executed except that a specimen, in which $Gd_{98}Y_2$ particles and Gd particles were blended at a weight ratio of 2:3 (Gd ratio=60%), was prepared.

Example 12

[0071] The same evaluation as that of the example 1 was executed except that a specimen, in which $Gd_{98}Y_2$ particles and Gd particles were blended at a weight ratio of 1:3 (Gd ratio=75%), was prepared.

Comparative Example 3

[0072] The same evaluation as that of the example 1 was executed except that a specimen of simple $Gd_{98}Y_2$ particles was prepared.

Example 13

[0073] The same evaluation as that of the example 1 was executed except that a specimen, in which $Gd_{98.5}Y_{1.5}$ particles and Gd particles were blended at a weight ratio of 1:1 (Gd ratio=50%), was prepared. Note that the magnetic transition temperature of the $Gd_{98.5}Y_{1.5}$ particles was 290 K, the magnetic transition temperature of the Gd particles was 293 K, and the magnetic transition temperature difference (ΔTc) was 3 K.

Comparative Example 4

[0074] The same evaluation as that of the example 1 was executed except that a specimen of simple $Gd_{98.5}Y_{1.5}$ particles was prepared.

TABLE 1

Sample	Magnetic Material	Gd blending ratio (%)	Refrigerating operation temperature range (K) when ΔT ≧ 1.6K	ΔTc (K)
Example 1	$Gd_{95}Y_5$ + Gd	25	18.3	10
Example 2	$Gd_{95}Y_5$ + Gd	50	18.6	10
Example 3	$Gd_{95}Y_5$ + Gd	75	18.3	10
Comparative Example 1	$Gd_{95}Y_5$	0	10.7	—
Example 4	$Gd_{97}Y_3$ + Gd	25	15.6	6
Example 5	$Gd_{97}Y_3$ + Gd	40	19.0	6
Example 6	$Gd_{97}Y_3$ + Gd	50	19.6	6
Example 7	$Gd_{97}Y_3$ + Gd	60	17.8	6
Example 8	$Gd_{97}Y_3$ + Gd	75	15.7	6
Comparative Example 2	$Gd_{97}Y_3$	0	13.1	—
Example 9	$Gd_{98}Y_2$ + Gd	40	17.0	4
Example 10	$Gd_{98}Y_2$ + Gd	50	17.2	4
Example 11	$Gd_{98}Y_2$ + Gd	60	18.0	4
Example 12	$Gd_{98}Y_2$ + Gd	75	16.5	4
Comparative Example 3	$Gd_{98}Y_2$	0	15.9	—
Example 13	$Gd_{98.5}Y_{1.5}$ + Gd	50	20.0	3
Comparative Example 4	$Gd_{98.5}Y_{1.5}$	0	17.2	—

[0075] It is apparent from the results of the examples 1 to 3 and the comparative example 1 that the refrigeration operation temperature range of ΔT≧1.6 K, which was only 10.7 K in the simple $Gd_{95}Y_5$ particles, was increased by about 8 K by adding the Gd particles. FIG. **5** is a graph in which the results of the examples 1 to 3 and the comparative example 1 are plotted. In the examples 1 to 3 in which the magnetic transition temperature difference (ΔTc) was 10 K, when the Gd ratio was 25% to 75%, that is, when the weight ratio of first magnetic particles, which have a heaviest weight in contained magnetic materials, and second magnetic particles, which have a next heaviest weight in contained materials, was 5:5 to 3:1, a particularly wide refrigeration operation temperature range could be obtained.

[0076] It is apparent from the results of the examples 4 to 8 and the comparative example 2 that the refrigeration operation temperature range of ΔT≧1.6 K, which was only 13.1 K in the simple $Gd_{97}Y_3$ particles, was increased by about 6.5 K by adding the Gd particles. FIG. **6** is a graph in which the results of the examples 4 to 8 and the comparative example 2 are plotted. In the examples 4 to 8 in which the magnetic transition temperature difference (ΔTc) was 6 K, when the Gd ratio was 40 to 60%, that is, when the weight ratio of first magnetic particles, which have a heaviest weight in contained magnetic materials, and second magnetic particles, which have a next heaviest weight in contained materials, was 5:5 to 3:2, a particularly wide refrigeration operation temperature range could be obtained.

[0077] It is apparent from the results of the examples 9 to 12 and the comparative example 3 that the refrigeration operation temperature range of ΔT≧1.6 K, which was only 15.9 K in the simple $Gd_{98}Y_2$ particles, was increased by about 2.1 K at most by adding the Gd particles. Further, in the examples 9 to 12 in which the magnetic transition temperature difference (ΔTc) was 4 K, when the Gd ratio was 40 to 60%, that is, when the weight ratio of first magnetic particles, which have a heaviest weight in contained magnetic materials, and second magnetic particles, which have a next heaviest weight in contained materials, was 5:5 to 3:2, a particularly wide refrigeration operation temperature range could be obtained.

[0078] It is apparent from the results of the example 13 and the comparative example 4 that the refrigeration operation temperature range of ΔT≧1.6 K, which was only 17.2 K in the simple $Gd_{98}Y_2$ particles, was increased by about 2.8 K by adding the Gd particles. Further, in the example 13 in which the magnetic transition temperature difference (ΔTc) was 3 K, when the Gd ratio was 50%, that is, when the weight ratio of first magnetic particles, which have a heaviest weight in contained magnetic materials, and second magnetic particles, which have a next heaviest weight in contained materials, was 5:5, the refrigeration operation temperature range could be increased.

[0079] As described above, the advantage of the present invention is confirmed by the examples.

What is claimed is:

1. A magnetic material for a magnetic refrigeration apparatus comprising:

first magnetic particles contained in a heaviest weight; and

second magnetic particles contained in a next heaviest weight having a different magnetic transition temperature from that of the first magnetic particles,

wherein, both of the magnetic particles are blended approximately uniformly and exhibit an approximately spherical shape with a maximum diameter of 0.3 mm or more to 2 mm or less.

2. The material according to claim **1**, wherein;

the difference between the magnetic transition temperature of first and second magnetic particles is 1 K or more to less than 10 K; and

the first magnetic particles are blended with the second magnetic particles at a weight ratio from 5:5 to 3:2.

3. The material according to claim **1**, wherein the difference between the magnetic transition temperature of first and second magnetic particles is 10 K or more to 15 K or less; and

the first magnetic particles are blended with the second magnetic particles at a weight ratio from 5:5 to 3:1.

4. The material according to claim **1**, wherein the magnetic particles are Gd (gadolinium) or GdR alloys (R: rear earth elements).

5. AMR bed filled with a magnetic material for a magnetic refrigeration apparatus, wherein the magnetic material comprises first magnetic particles contained in a heaviest weight and second magnetic particles contained in a next heaviest weight having a different magnetic transition temperature from that of the first magnetic particles, and both of the magnetic particles are blended approximately uniformly and exhibit an approximately spherical shape with a maximum diameter of 0.3 mm or more to 2 mm or less.

6. The AMR bed according to claim **5**, wherein a void ratio of the AMR bed is 30% or more to 50% or less.

7. The AMR bed according to claim **5**, wherein:

the difference between the magnetic transition temperature of first and second magnetic particles is 1 K or more to less than 10 K; and the first magnetic particles are blended with the second magnetic particles at a weight ratio from 5:5 to 3:2.

8. The AMR bed according to claim **5**, wherein:

the difference between the magnetic transition temperature of first and second magnetic particles is 10 K or more to 15 K or less; and

the first magnetic particles are blended with the second magnetic particles at a weight ratio from 5:5 to 3:1.

9. The AMR bed according to claim **5**, wherein the magnetic particles are Gd (gadolinium) or GdR alloys (R: rear earth elements).

10. A magnetic refrigeration apparatus using a liquid refrigerant comprising:

AMR bed filled with a magnetic material;

magnetic field generation device for applying and removing a magnetic field to and from the magnetic material;

a cooling block;

a radiating block; and

a refrigerant flow path formed by connecting the AMR bed, the cooling block and the radiating block configured to circulate the liquid refrigerant,

wherein the magnetic material comprises first magnetic particles contained in a heaviest weight and second magnetic particles contained in a next heaviest weight having a different magnetic transition temperature from that of the first magnetic particles, and both of the magnetic particles are blended approximately uniformly and exhibit an approximately spherical shape with a maximum diameter of 0.3 mm or more to 2 mm or less.

11. The apparatus according to claim **10**, wherein:

the difference between the magnetic transition temperature of first and second magnetic particles is 1 K or more to less than 10 K; and

the first magnetic particles are blended with the second magnetic particles at a weight ratio from 5:5 to 3:2.

12. The apparatus according to claim **10**, wherein:

the difference between the magnetic transition temperature of first and second magnetic particles is 10 K or more to 15 K or less; and

the first magnetic particles are blended with the second magnetic particles at a weight ratio from 5:5 to 3:1.

13. The apparatus according to claim **10**, wherein the magnetic particles are Gd (gadolinium) or GdR alloys (R: rear earth elements).

14. The apparatus according to claim **10**, wherein a void ratio of the AMR bed is 30% or more to 50% or less.

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