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(54) **SYSTEM AND METHOD FOR REVERSE DEGRADATION OF A MAGNETOCALORIC MATERIAL**

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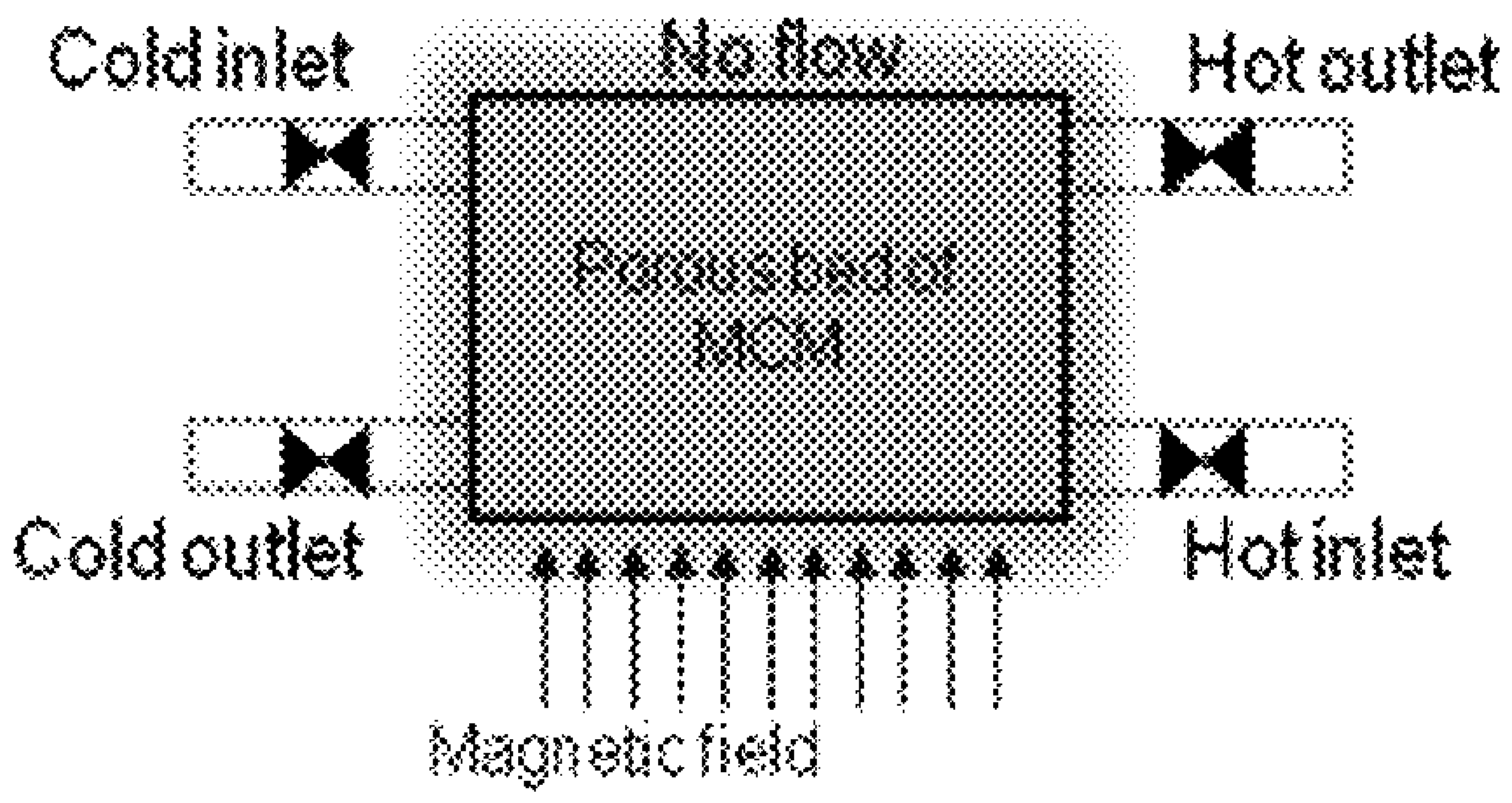
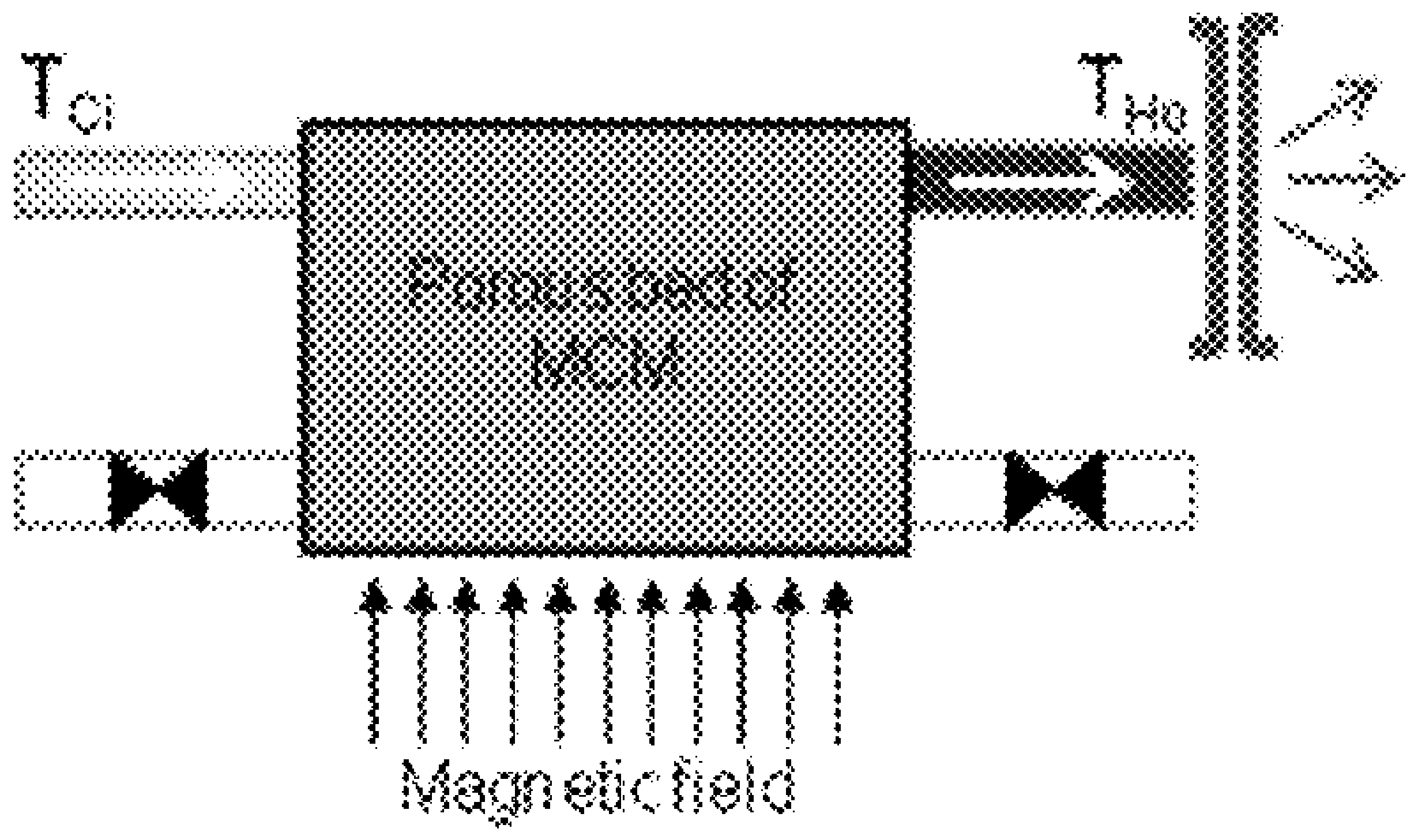
(52) **U.S. Cl.** **62/3.1**

(57) **ABSTRACT**

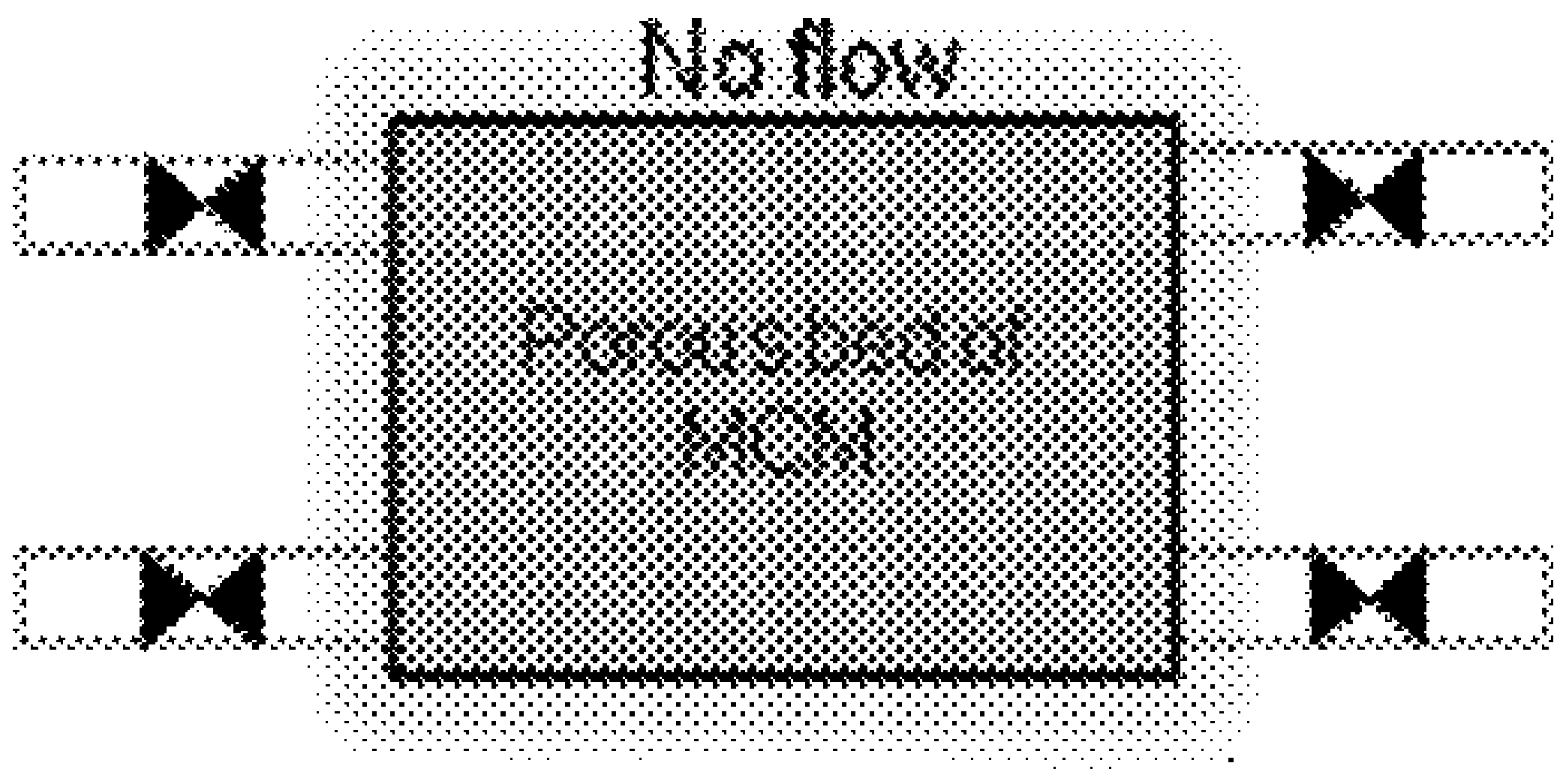
A method includes identifying at least partial degradation of a magnetocaloric material in a magnetic cooling system, wherein the magnetiocaloric material has a Curie temperature. The method also includes regenerating the magnetocaloric material by maintaining the magnetocaloric material at a regenerating temperature, wherein the regenerating temperature is different from the Curie temperature of the magnetocaloric material.



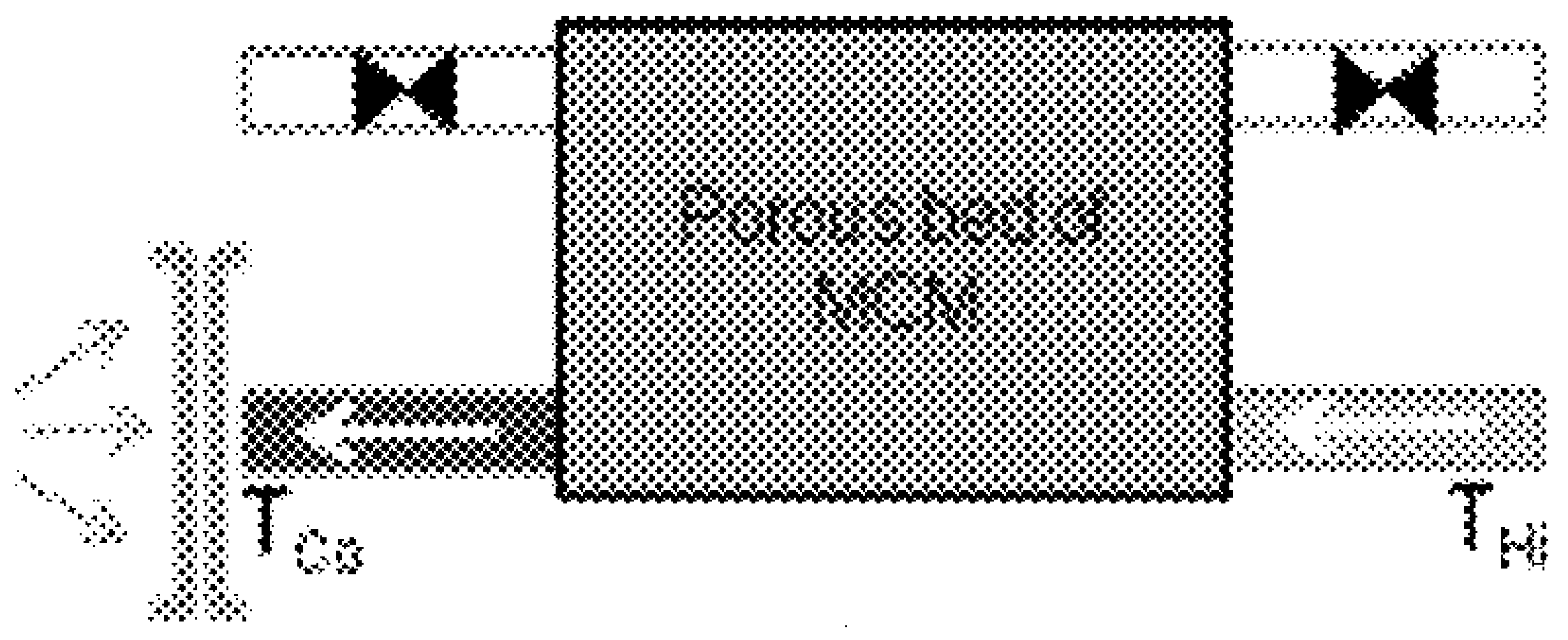
1. Magnetization



2. Cold-to-Hot Flow



3. Demagnetization



4. Hot-to-Cold Flow

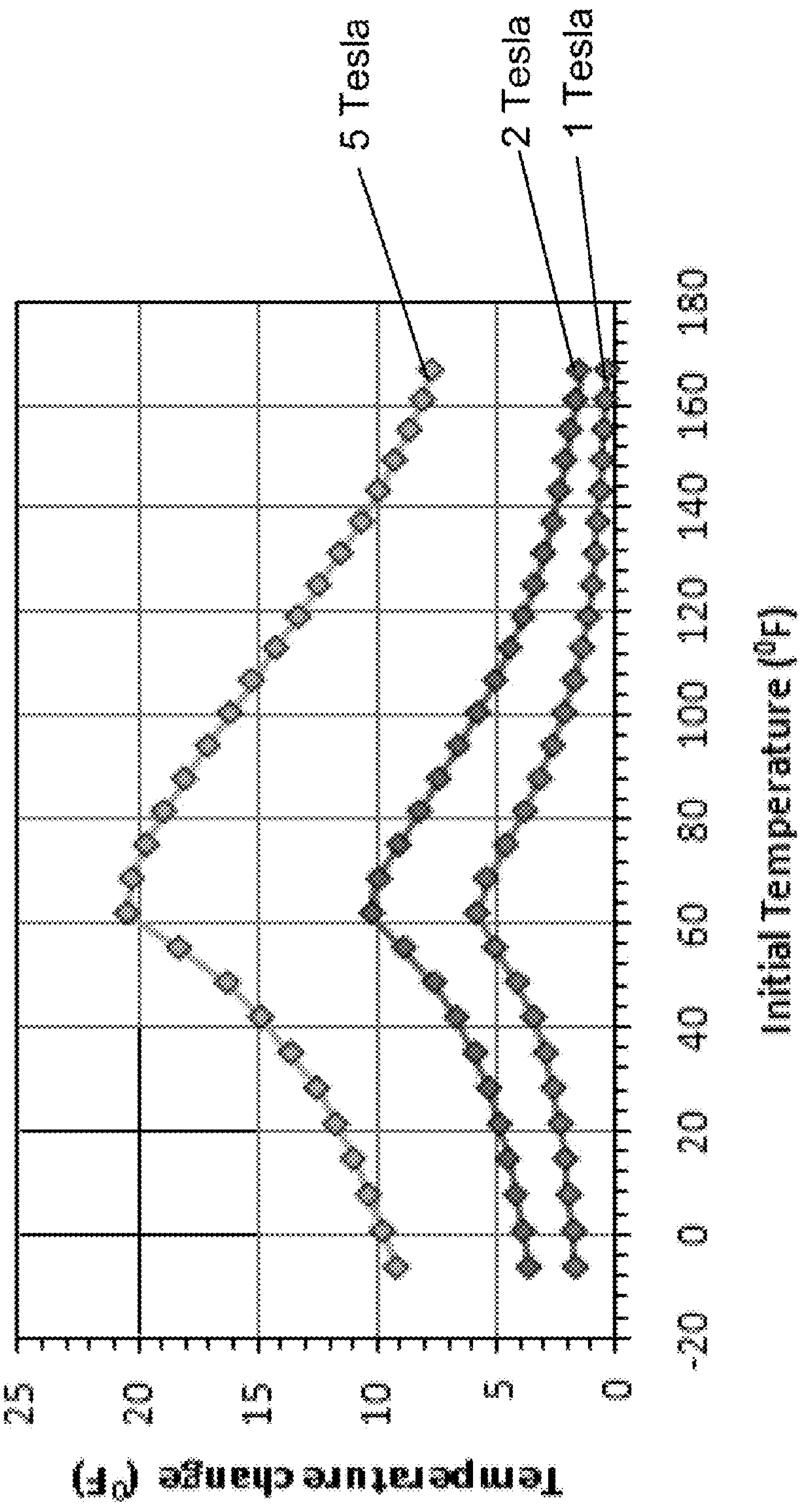

5 Tesla
2 Tesla
1 Tesla
Temperature change (°F)
0
5
10
15
20
25
Initial Temperature (°F)
-20
0
20
40
60
80
100
120
140
160
180

Fig. 1

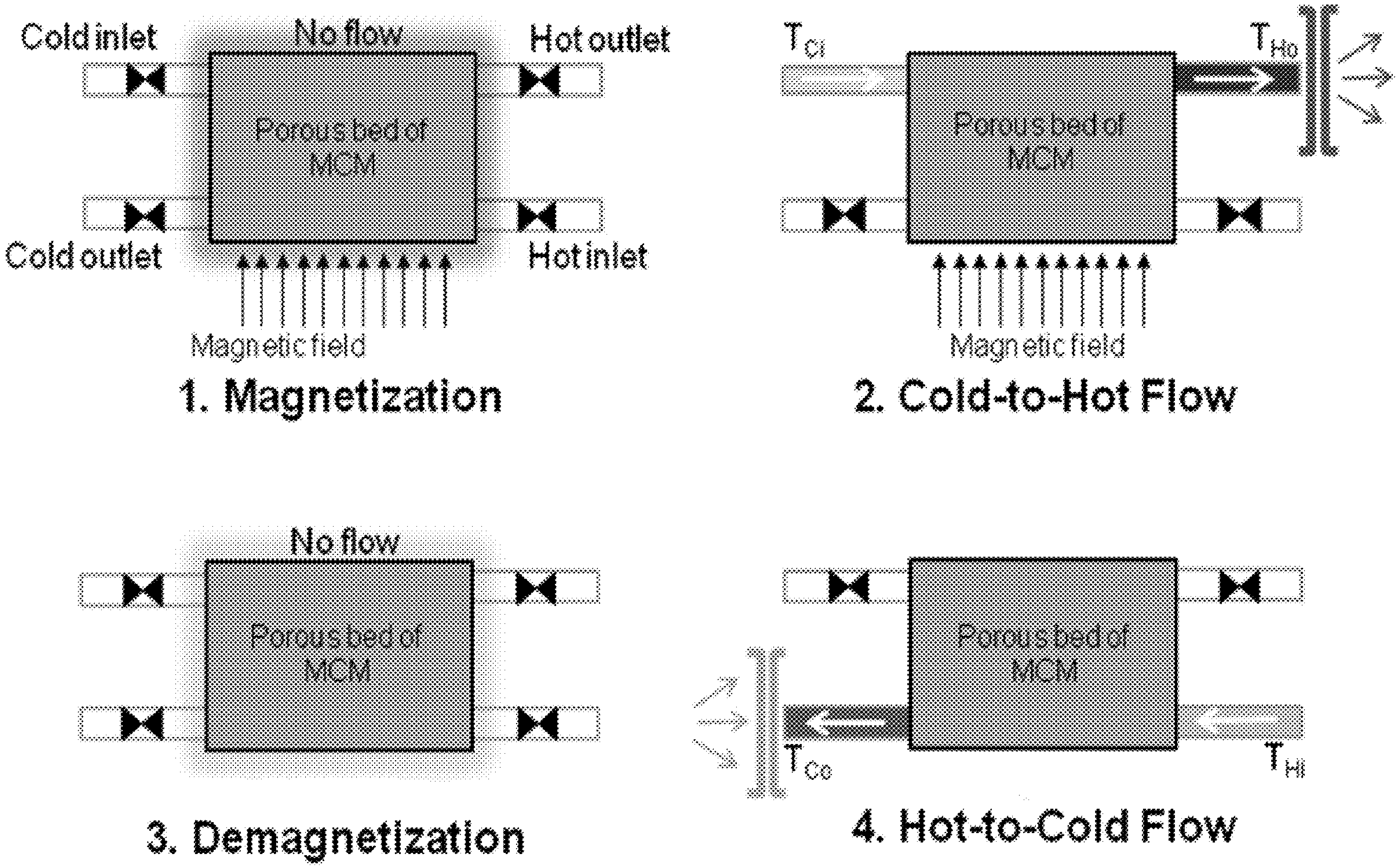

Cold inlet
No flow
Hot outlet
Porous bed of MCM
Cold outlet
Hot inlet
Magnetic field
1. Magnetization
T_{Ci}
T_{Ho}
Porous bed of MCM
Magnetic field
2. Cold-to-Hot Flow
No flow
Porous bed of MCM
3. Demagnetization
Porous bed of MCM
T_{Co}
T_{Hi}
4. Hot-to-Cold Flow

Fig. 2

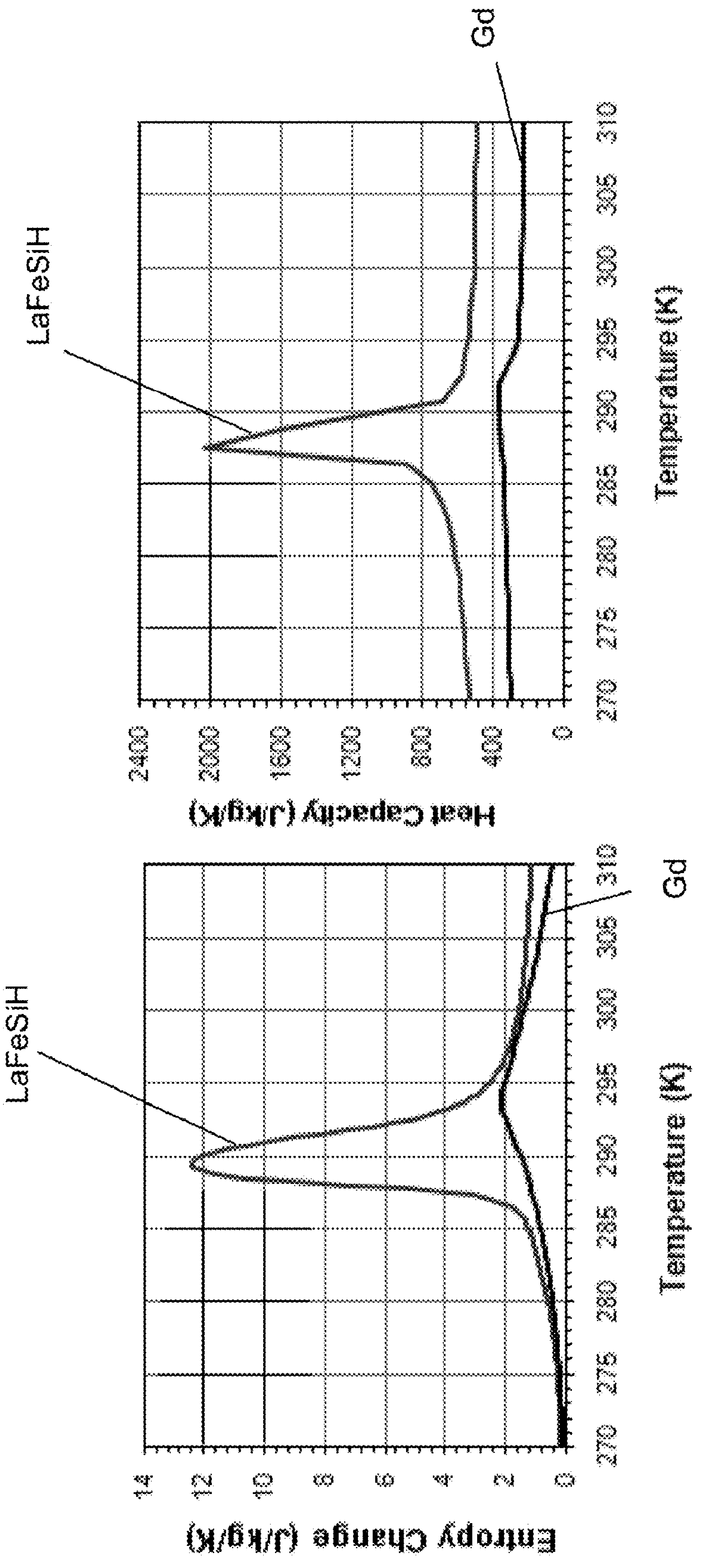

LaFeSiH
Gd
Heat Capacity (J/kg/K)
2400
2000
1600
1200
800
400
0
270
275
280
285
290
295
300
305
310
Temperature (K)
LaFeSiH
Gd
Entropy Change (J/kg/K)
14
12
10
8
6
4
2
0
270
275
280
285
290
295
300
305
310
Temperature (K)

Fig. 3

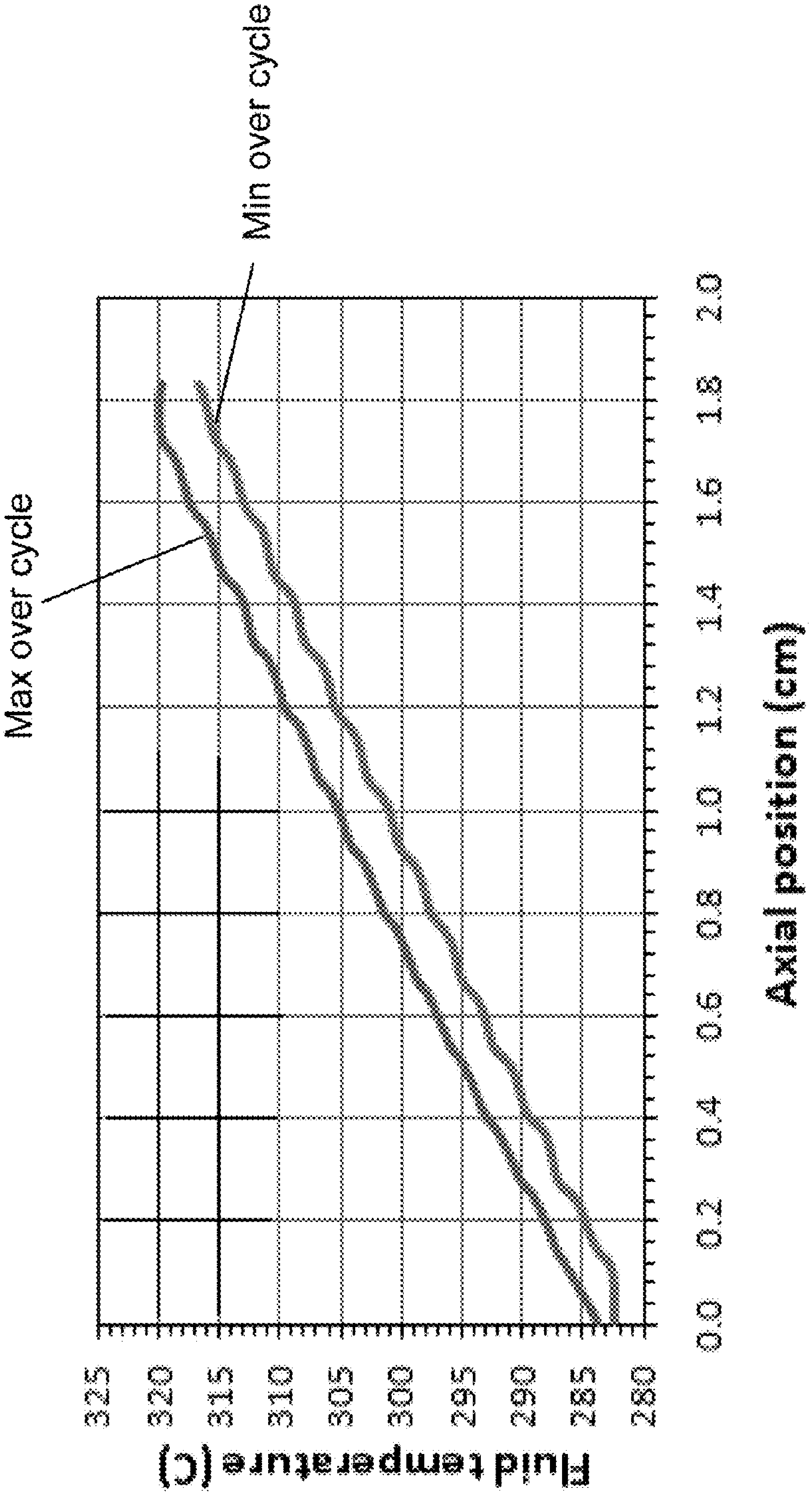

Max over cycle
Min over cycle
Fluid temperature (C)
325
320
315
310
305
300
295
290
285
280
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Axial position (cm)

Fig. 4

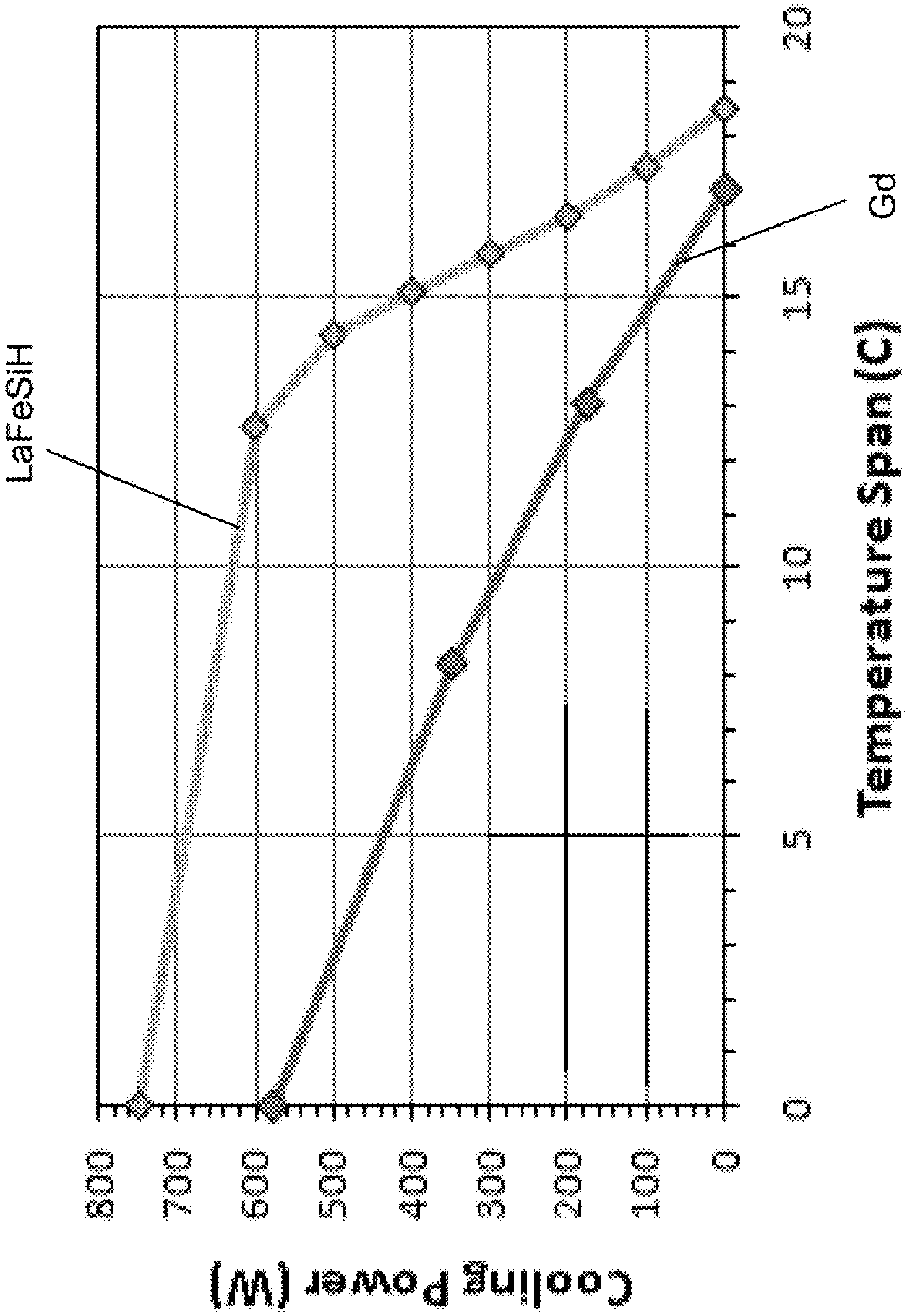

LaFeSiH
Gd
Cooling Power (W)
800
700
600
500
400
300
200
100
0
Temperature Span (C)
0
5
10
15
20

Fig. 5

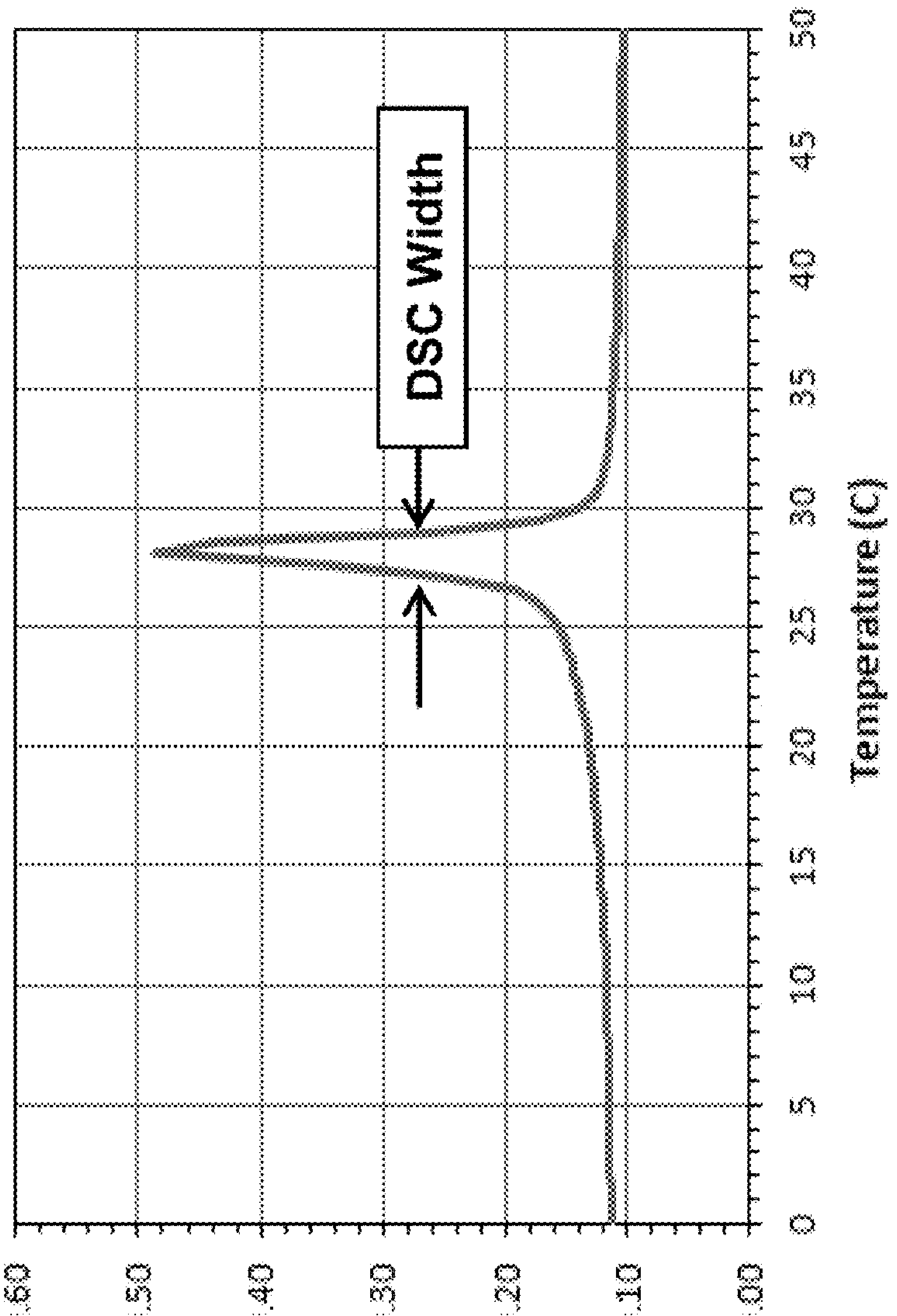

DSC Width
DSC (mw/mg)
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Temperature (C)
0
5
10
15
20
25
30
35
40
45
50

Fig. 6

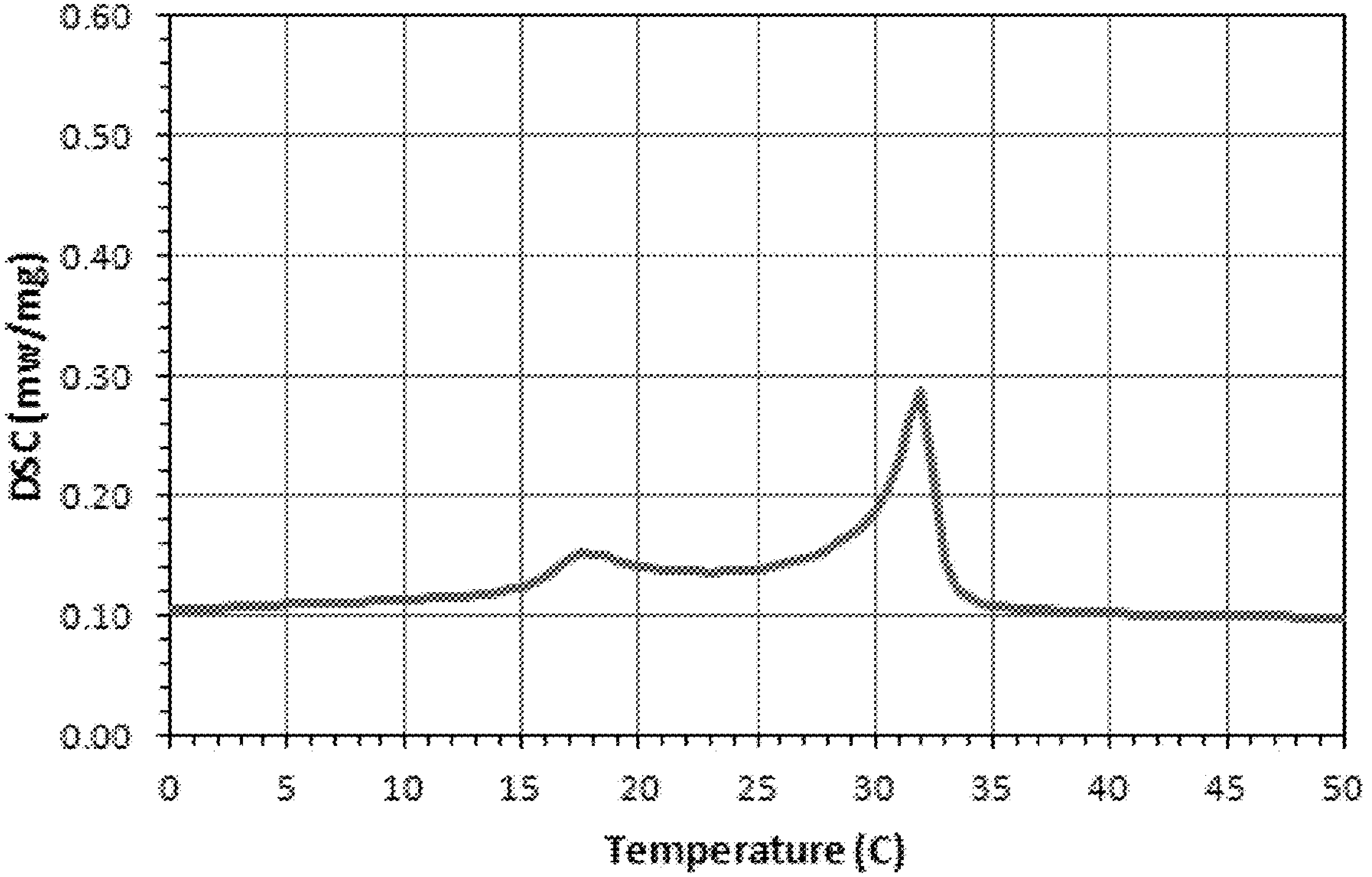

DSC (mw/mg)
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
5
10
15
20
25
30
35
40
45
50
Temperature (C)

Fig. 7

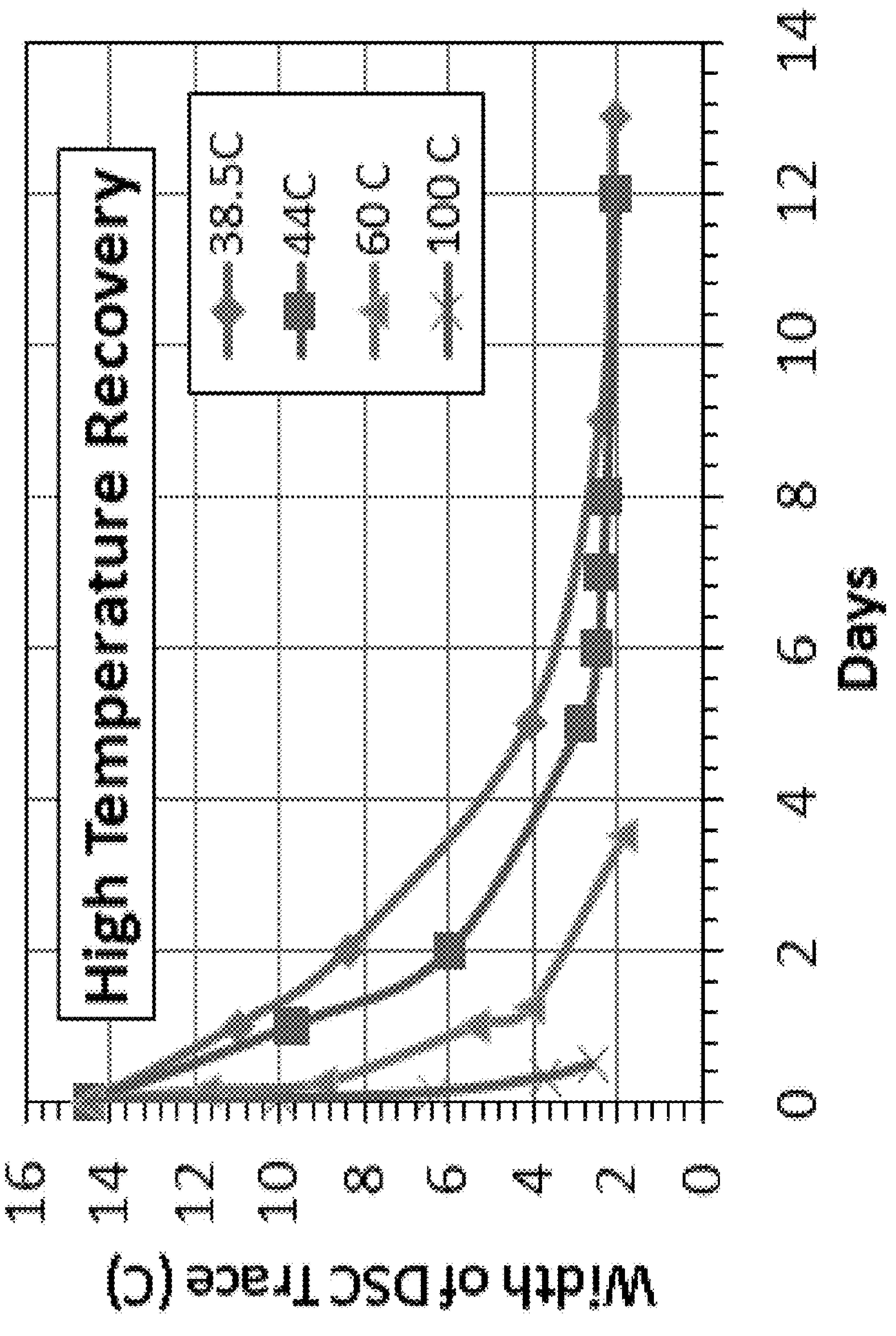

High Temperature Recovery
38.5C
44C
60 C
100 C
Width of DSC Trace (C)
16
14
12
10
8
6
4
2
0
Days
0
2
4
6
8
10
12
14

Fig. 8

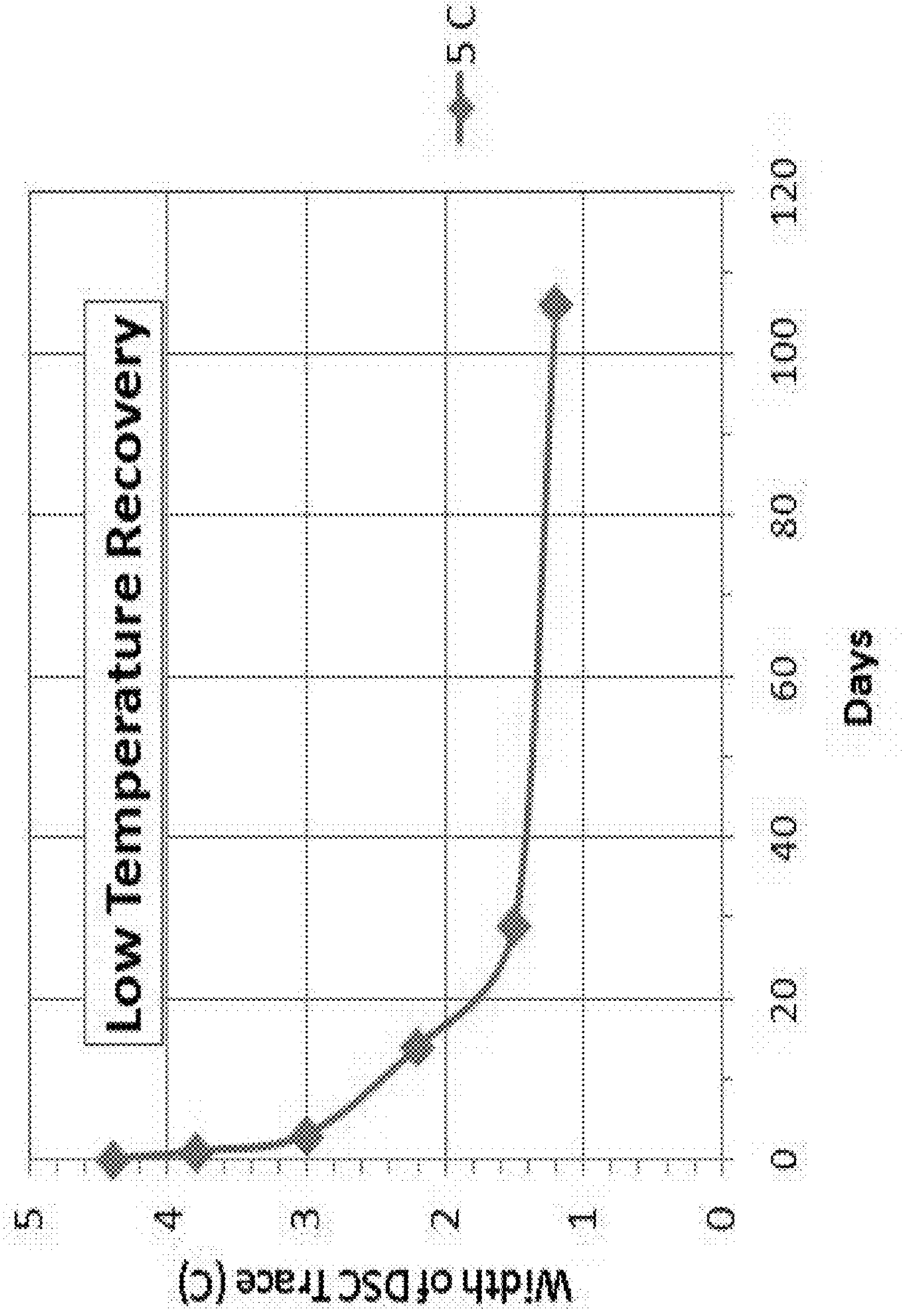

Low Temperature Recovery
Width of DSC Trace (C)
0
1
2
3
4
5
Days
0
20
40
60
80
100
120
5 C

Fig. 9

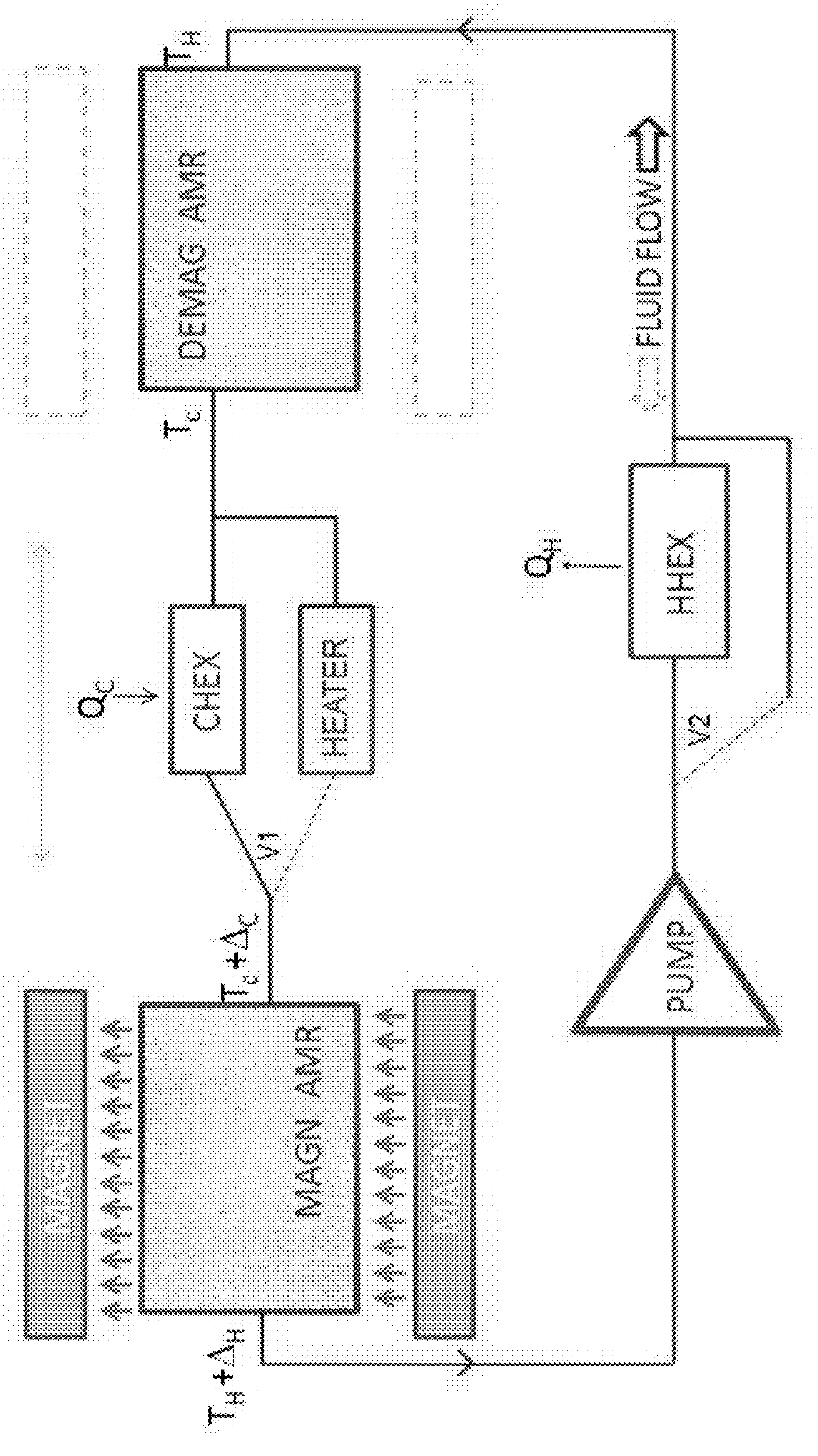

T_H
DEMAG AMR
T_c
FLUID FLOW
Q_H
HHEX
V2
Q_C
CHEX
HEATER
V1
$T_c+\Delta_c$
PUMP
MAGNET
MAGN AMR
MAGNET
$T_H+\Delta_H$

Fig. 10

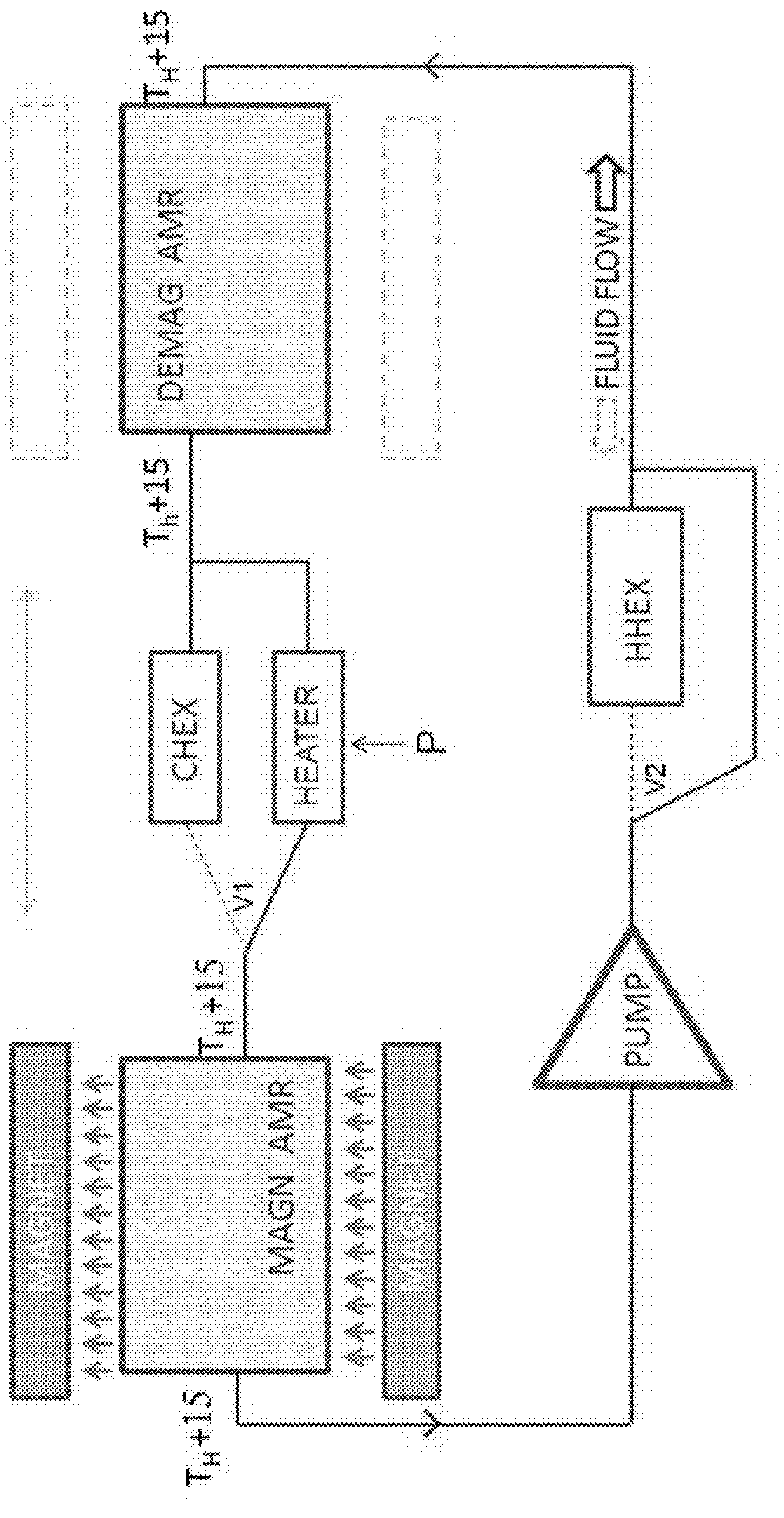
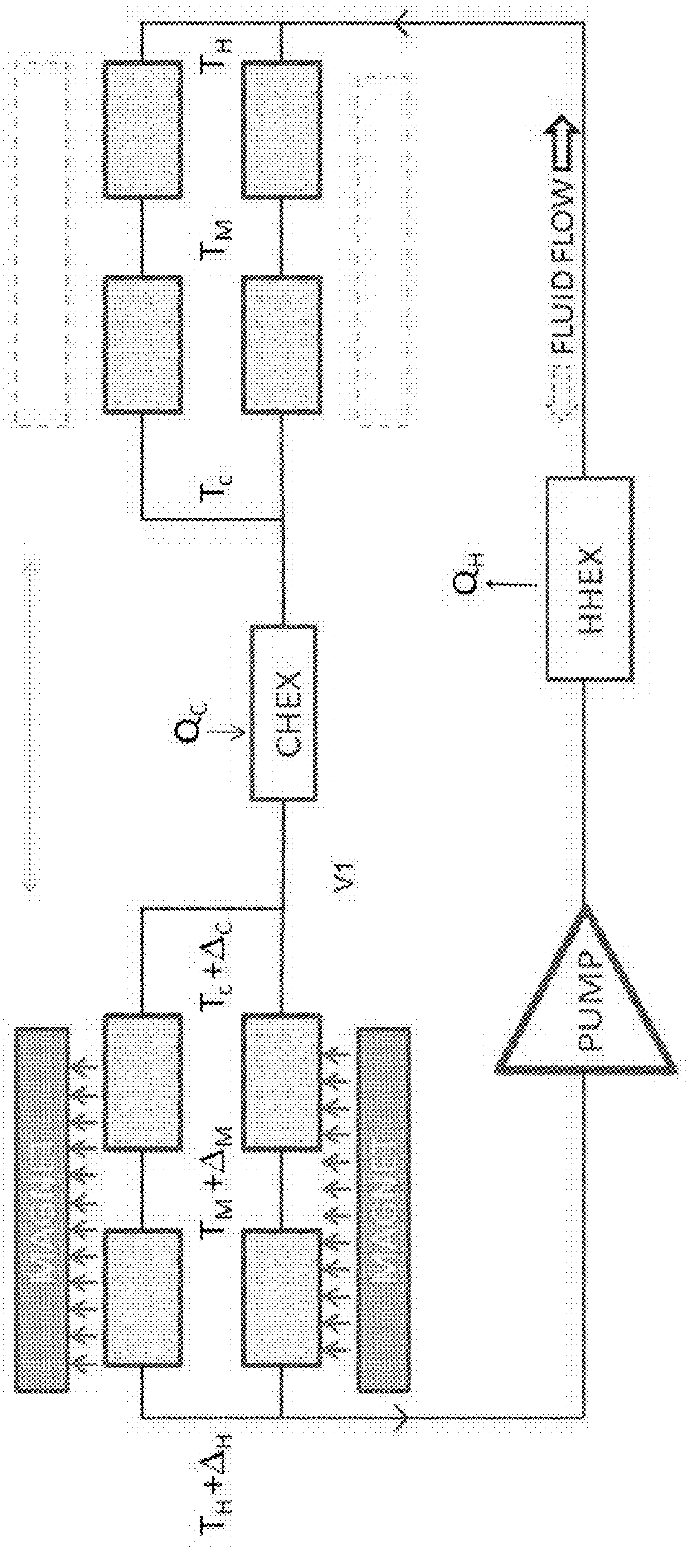

T_H+15
DEMAG AMR
T_H+15
FLUID FLOW
CHEX
HEATER
P
HHEX
V1
V2
T_H+15
MAGNET
MAGN AMR
MAGNET
PUMP
T_H+15

Fig. 11



T_H
T_M
T_c
FLUID FLOW
Q_H
HHEX
Q_C
CHEX
V1
$T_c + \Delta_C$
$T_M + \Delta_M$
$T_H + \Delta_H$
PUMP
MAGNET
MAGNET

Fig. 12

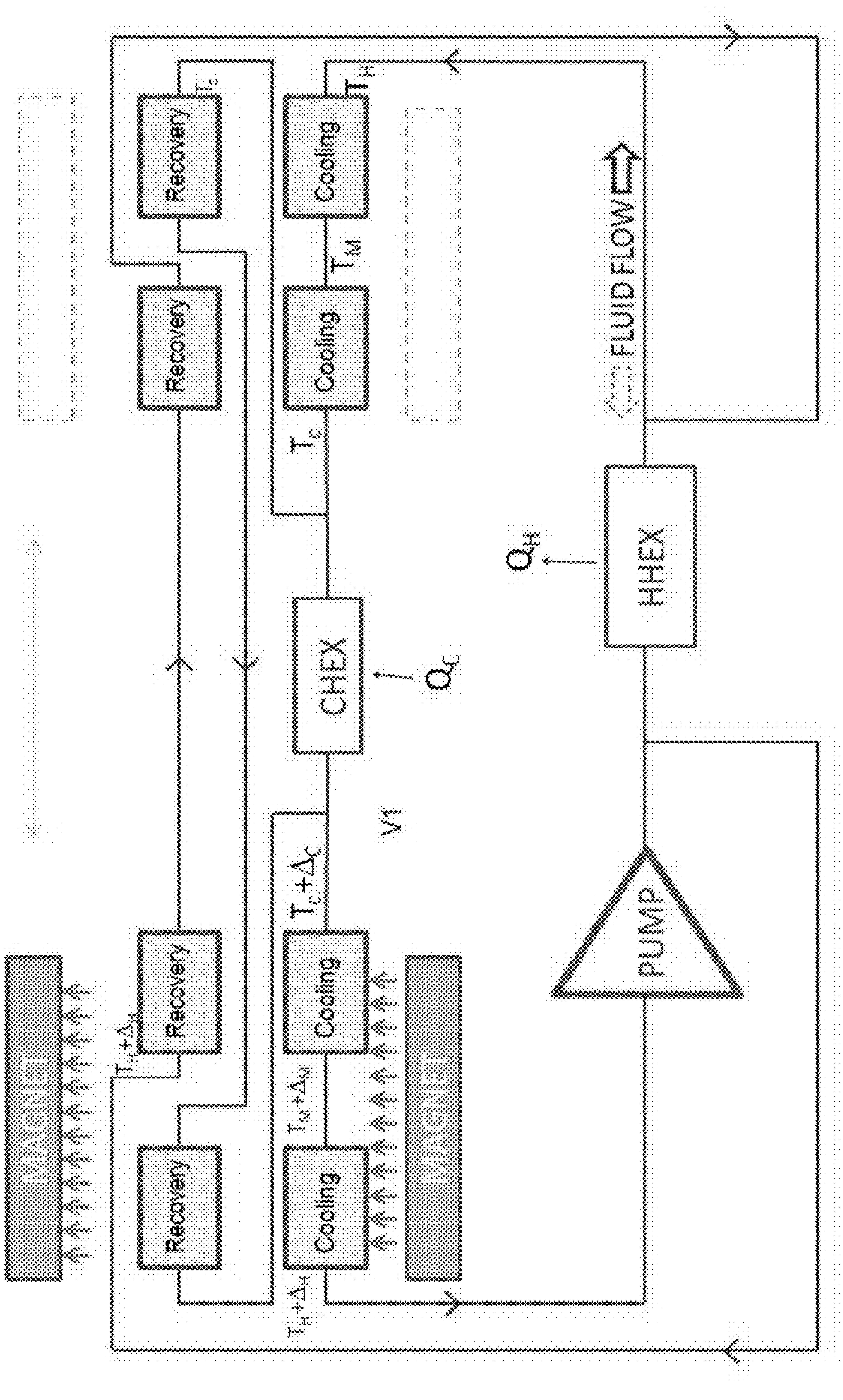

MAGNET
Recovery
Recovery
Recovery
Recovery
$T_H+\Delta_H$
T_c
Cooling
Cooling
Cooling
Cooling
MAGNET
$T_H+\Delta_H$
$T_M+\Delta_M$
$T_c+\Delta_c$
T_c
T_M
T_H
CHEX
Q_c
V1
PUMP
HHEX
Q_H
FLUID FLOW

Fig. 13

SYSTEM AND METHOD FOR REVERSE DEGRADATION OF A MAGNETOCALORIC MATERIAL

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Patent Application No. 61/509,381 filed Jul. 19, 2011, the entire disclosure of which is hereby incorporated by reference in its entirety.

BACKGROUND

[0002] The following description is provided to assist the understanding of the reader. None of the information provided or references cited is admitted to be prior art.

[0003] The strong interaction of a ferromagnetic material, such as iron, with an applied magnetic field derives from the ability of the atomic spins in the material structure to coherently align themselves with the applied field. Above a certain temperature, which is characteristic of the magnetic material and called the Curie temperature, thermal agitation prevents this coherent spin alignment, and the interaction with the applied field becomes much weaker. Above the Curie temperature, the material is paramagnetic, rather than ferromagnetic. Near the Curie temperature, the coherent alignment of atomic spins in an applied field results in a decrease in the magnetic entropy of the material. If the material is thermally isolated, so that its total entropy is conserved, this decrease in its magnetic entropy is compensated by an increase in its thermal entropy, and its temperature rises. This rise in temperature upon exposure to a magnetic field is known as the magnetocaloric effect. When the applied field is removed, the magnetic entropy rises and the thermal entropy decreases, lowering the temperature of the material.

SUMMARY

[0004] An illustrative method includes identifying at least partial degradation of a magnetocaloric material in a magnetic cooling system, wherein the magnetiocaloric material has a Curie temperature. The method also includes regenerating the magnetocaloric material by maintaining the magnetocaloric material at a regenerating temperature, wherein the regenerating temperature is different from the Curie temperature of the magnetocaloric material.

[0005] Another illustrative method includes forming at least one bed of a magnetic cooling system, wherein the at least one bed includes a magnetocaloric material, wherein the magnetocaloric material has a Curie temperature, and wherein a heat transfer fluid is configured to transfer heat to or from the magnetocaloric material in the at least one bed. The method also includes forming at least one valve of the magnetic cooling system to control a flow of the heat transfer fluid through the at least one bed and either a heater or a heat exchanger, wherein flow of the heat transfer fluid between the at least one bed and the heater regenerates the magnetocaloric material by maintaining the magnetocaloric material at a regenerating temperature, and wherein the regenerating temperature is different from the Curie temperature of the magnetocaloric material.

[0006] An illustrative apparatus includes a heat transfer fluid and a bed comprising a magnetocaloric material that has a Curie temperature. The bed is configured to allow the heat transfer fluid to transfer heat to or from the magnetocaloric material. The apparatus also includes a heater configured to maintain the magnetocaloric material at a regenerating temperature for an amount of time to regenerate the magnetocaloric material, wherein the regenerating temperature is different from the Curie temperature of the magnetocaloric material.

[0007] An illustrative system includes a first subsystem and a second subsystem. The first subsystem includes a first heat transfer fluid and a first bed having a first magnetocaloric material, wherein the first magnetocaloric material has a first Curie temperature. The first subsystem also includes a first valve configured to control whether the first subsystem operates in regeneration mode or cooling mode. The second subsystem includes a second heat transfer fluid and a second bed having a second magnetocaloric material, wherein the second magnetocaloric material has a second Curie temperature. The second subsystem also includes a second valve configured to control whether the second subsystem operates in regeneration mode or cooling mode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The foregoing and other features of the present disclosure will become more fully apparent from the following description and appended claims, taken in conjunction with the accompanying drawings. Understanding that these drawings depict only several embodiments in accordance with the disclosure and are, therefore, not to be considered limiting of its scope, the disclosure will be described with additional specificity and detail through use of the accompanying drawings.

[0009] FIG. **1** is a diagram illustrating the magnetocaloric effect in gadolinium (Gd) in accordance with an illustrative embodiment.

[0010] FIG. **2** is a diagram illustrating stages of an active magnetic regenerator cycle in accordance with an illustrative embodiment.

[0011] FIG. **3** illustrates a comparison between the isothermal entropy change in a 1.0 Tesla field (left panel) and heat capacity (right panel) of LaFeSiH and Gd in accordance with an illustrative embodiment.

[0012] FIG. **4** illustrates minimum and maximum fluid temperatures over the refrigeration cycle as functions of position in a magnetic refrigeration bed in accordance with an illustrative embodiment.

[0013] FIG. **5** is a diagram illustrating the performance of a magnetic refrigeration prototype with 5-layer LaFeSiH beds as compared to a magnetic refrigeration prototype with single-layer Gd beds in accordance with an illustrative embodiment.

[0014] FIG. **6** illustrates a differential scanning calorimetry (DSC) trace of a pristine sample of LaFeSiH in accordance with an illustrative embodiment.

[0015] FIG. **7** presents the DSC trace of the same material in FIG. **6** after being held close to its Curie temperature for over one year in accordance with an illustrative embodiment.

[0016] FIG. **8** is a diagram illustrating the recovery of age-split LaFeSiH by exposure to elevated temperatures in accordance with an illustrative embodiment.

[0017] FIG. **9** is a diagram illustrating the recovery of age-split LaFeSiH by exposure to lowered temperature in accordance with an illustrative embodiment.

[0018] FIG. **10** is a diagram of an active magnetic regenerator type refrigerator operating in cooling mode in accordance with an illustrative embodiment.

[0019] FIG. **11** is a diagram of an active magnetic regenerator type refrigerator operating in recovery mode in accordance with an illustrative embodiment.

[0020] FIG. **12** is a diagram of an active magnetic regenerator cooling system with two dual stage subsystems in accordance with a first illustrative embodiment.

[0021] FIG. **13** is a diagram of an active magnetic regenerator cooling system with two dual stage subsystems in accordance with a second illustrative embodiment.

DETAILED DESCRIPTION

[0022] In the following detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be utilized, and other changes may be made, without departing from the spirit or scope of the subject matter presented here. It will be readily understood that the aspects of the present disclosure, as generally described herein, and illustrated in the figures, can be arranged, substituted, combined, and designed in a wide variety of different configurations, all of which are explicitly contemplated and make part of this disclosure.

[0023] A magnetic refrigerator (MR) uses the magnetocaloric effect to pump heat out of a colder system and exhaust that heat to a warmer environment. The magnetocaloric effect refers to the rise in temperature of a material upon exposure to a magnetic field. When the applied field is removed, the magnetic entropy rises and the thermal entropy decreases, lowering the temperature of the material. This temperature change is shown in FIG. **1** for gadolinium (Gd), which is a magnetocaloric material with a Curie temperature of about 60° F. With this material initially at a temperature of 60° F., application of a 2-Tesla field, for example, will cause a temperature rise of 10° F. The temperature change increases as the strength of the applied field is increased.

[0024] Modern room-temperature MR systems may employ an Active Magnetic Regenerator (AMR) cycle to perform cooling. An early implementation of the AMR cycle can be found in U.S. Pat. No. 4,332,135, the entire disclosure of which is incorporated herein by reference. In one embodiment, the AMR cycle has four stages, as shown schematically in FIG. **2**. The MR system in FIG. **2** includes a porous bed of magnetocaloric material (MCM) and a heat transfer fluid, which exchanges heat with the MCM as it flows through the bed. In the figure, the left side of the bed is the cold side, while the hot side is on the right. In alternative embodiments, the hot and cold sides can be reversed. The timing and direction (hot-to-cold or cold-to-hot) of the fluid flow is coordinated with the application and removal of a magnetic field.

[0025] In the first stage of the cycle ("magnetization"), while the fluid in the bed is stagnant, a magnetic field is applied to the MCM, causing it to heat. In the second stage of the cycle ("cold-to-hot-flow"), the magnetic field over the bed is maintained, and fluid at a fixed temperature T_{Ci} (the cold inlet temperature) is pumped through the bed from the cold side to the hot side. This fluid pulls heat from each section of the bed, cooling the bed and warming the fluid as it passes to the next section of the bed, where the process continues at a higher temperature. The fluid eventually reaches the temperature T_{Ho} (the hot outlet temperature), where it exits the bed. Typically, this fluid is circulated through a hot side heat exchanger, where it exhausts its heat to the ambient environment. In the third stage ("demagnetization"), the fluid flow is terminated and the magnetic field is removed. This causes the bed to cool further. In the final stage of the cycle ("hot-to-cold-flow"), fluid at a fixed temperature T_{Hi} (the hot inlet temperature) is pumped through the bed from the hot side to the cold side in the continued absence of the magnetic field. The fluid is cooled as it passes through each section of the bed, reaching a temperature T_{Co} (the cold outlet temperature) which is the coldest temperature reached by the fluid in the cycle. Typically, this colder fluid is circulated through a cold side heat exchanger, where it picks up heat from the refrigerated system, allowing this system to maintain its cold temperature.

[0026] The time that it takes to complete execution of the four stages of the AMR cycle is called the cycle time, and its inverse is known as the cycle frequency. The "temperature span" of the MR system is defined as $T_{Hi}-T_{Ci}$, which is the difference in the inlet fluid temperatures. The AMR cycle is analogous to a simple vapor compression cycle, where gas compression (which causes the gas to heat) plays the role of magnetization, and where free expansion of the gas (which drops the gas temperature) plays the role of demagnetization. Although FIG. **2** illustrates the operation of a single-bed MR system, in alternative embodiments, multiple beds, each undergoing the same AMR cycle, may be combined in a single system to increase the cooling power, reduce the system size, or otherwise improve the implementation of the AMR cycle.

[0027] Typically, a magnetic field of 1-2 Tesla is utilized to effectively exploit the magnetocaloric effect for refrigeration. This field is usually provided by an assembly of powerful NdFeB magnets. The remanent magnetization of the highest grade of NdFeB magnets is about 1.5 Tesla. The use of a stronger field than this would improve MR performance, but to achieve fields in excess of the remanent magnetization, a large (and potentially prohibitive) increase in magnet size and weight is required. Thus, 1.5 Tesla is the field strength that provides a roughly optimum balance between MR system size and performance. As permanent magnet technology improves, magnets with remanent magnetizations greater than 1.5 Tesla may be obtained. In this case, the optimum field strength of an MR system will increase accordingly.

[0028] The permanent magnet assembly is generally the most expensive component in the MR. To make the best use of this expensive resource, the magnetocaloric material used in the MR should possess the strongest possible magnetocaloric effect. This material should also avoid the use of any toxic, reactive, or rare (and therefore expensive) constituents. The former consideration rules out the commercial use of Gd, for example, which is nontoxic, inert, and inexpensive but has a weak magnetocaloric effect. MR systems employing Gd, or other materials of comparable magnetocaloric strength, would be too large for commercial utility. Lanthanum iron silicon hydride (LaFeSiH) is one of the most promising magnetocaloric materials for use in commercial MR systems. A description of LaFeSiH can be found in an article by Fujita et al. titled "Itinerant-electron metamagnetic transition and large magnetocaloric effects in $La(Fe_xSi_{1-x})_{13}$ compounds and their hydrides," Physical Review B 67 (2003), the entire disclosure of which is incorporated by reference herein. This material has a strong magnetocaloric effect. FIG. **3**, for example, shows the two most important measures of magnetocaloric strength, the isothermal entropy change (left panel) in a 1.0 Tesla field and heat capacity (right panel) of LaFeSiH. For comparison, the same properties for Gd are also shown. Because of its greatly enhanced magnetocaloric strength, MR systems employing LaFeSiH can be much more compact than a system employing Gd. Although LaFeSiH has the rare earth metal La (Lanthanum) as a constituent, it remains inexpensive as La is one of the most abundant of these elements.

[0029] In most cooling applications, the temperature span will be substantial, typically about 30° C. (54° F.) or larger. Although the overall span supported by an MR system may be large, the temperature within a given axial section of a bed in the system will remain within a relatively narrow range over the refrigeration cycle. FIG. **4**, for example, shows the theoretical minimum and maximum fluid temperatures over the refrigeration cycle as a function of axial position in the bed for a particular MR system designed as a residential air conditioner. For this case, although the overall temperature span is 37° C., each axial position in the bed experiences a temperature variation of only ±2° C. around its mean value. If the bed is composed of a single magnetocaloric material, some regions of it will therefore be at temperatures away from its Curie temperature. These regions of the bed will undergo little entropy change and will have low heat capacity (see FIG. **3**). These regions will behave more like passive regenerators and will contribute little to the cooling power of the system. This inefficient use of bed volume can be circumvented through the use of layered beds, which greatly enhance the performance of a MR system. In a layered bed, each layer contains a magnetocaloric material with Curie temperature matched to the average temperature of that layer over the cycle. By choosing the Curie temperatures of the layer materials in this manner, every layer will have a strong entropy change during the cycle and a large heat capacity. All layers will therefore contribute actively during the refrigeration cycle, greatly improving the overall performance of the system. In addition to having a strong magnetocaloric effect, the Curie temperature of LaFeSiH can be easily controlled between ±60° C. (the range of interest for room temperature MR systems) by varying the hydrogen (H) content, making it ideal for use in a layered bed.

[0030] The advantages associated with the use of layered beds of LaFeSiH are demonstrated in FIG. **5**, which shows the measured cooling power of a prototype MR system as a function of temperature span with beds formed from 5 layers of LaFeSiH. In alternative embodiments, fewer or more layers may be used. For comparison, the figure also shows the performance of identical beds with a single layer of Gd under the same operating conditions. At a temperature span of 13° C., for example, the layered LaFeSiH beds provide over three times the cooling power of the Gd beds.

[0031] Although LaFeSiH appears to be an ideal material for use in a MR, its properties are not stable. This material has been shown to undergo a gradual deterioration of its magnetocaloric strength when it is stored at a temperature very close to its Curie point, as described in an article by A. Barcza et al. entitled "Stability and magnetocaloric properties of sintered $La(Fe,Mn,Si)_{13}H_z$ alloys", presented at the IEEE International Magnetics Conference (Taipei, Taiwan) 2011, session ED-07 (hereinafter "A. Barcza et al."), the entire disclosure of which is incorporated by reference herein. This deterioration is most readily observed in Differential Scanning calorimetry (DSC). FIG. **6** illustrates the DSC trace of a pristine sample of LaFeSiH, which has a single, sharp peak. The figure also illustrates the width of the peak in the DSC trace. For comparison, FIG. **7** shows the DSC trace of the same sample after it has been kept close to its Curie temperature for over one year. When kept at a temperature close to its Curie temperature, the DSC trace shows that the ferromagnetic to paramagnetic phase change broadens in width and declines in height. Eventually, the initially large and sharp transition of this material will split into two broad, shallow peaks ("age-splitting"), as illustrated in FIG. **7** and in A. Barcza et al. The age-splitting of the DSC trace is accompanied by a reduction in the entropy change of the material, as measured by magnetometry and as also illustrated in A. Barcza et al. The rate at which the splitting occurs depends on temperature. For LaFeSiH with a 2° C. curie point stored at 2° C., significant broadening of the peak takes about 10 days, and a split peak takes about 60 days to form. For LaFeSiH material with a 20° C. curie point stored at 20° C., a split peak develops in about 10 days. For material with a 32° C. curie point stored at 32° C., a split peak develops in about 5 days.

[0032] The ageing process for LaFeSiH appears to not depend on the synthesis method, as long as the hydrogen content is less than 1.5 per formula unit. The age-splitting process was seen in material that was arc melted, then annealed for several weeks to form the 1-13 phase, then hydrided. The age-splitting process was also seen in material that was rapidly solidified by melt spinning or atomization, and then annealed for a few hours or less to form the 1-13 phase, and then hydrided. The ageing process was seen in different samples of LaFeSiH with slightly different compositions, such as $La_{1.29}(Fe_{0.88}Si_{0.12})_{13}H_y$ and $La_{1.2}(Fe_{0.888}Si_{0.112})_{13}H_y$. The ageing process was also seen in a sample of $Pr_{0.6}La_{0.6}(Fe_{0.888}Si_{0.112})_{13}H_y$, where Pr was substituted for some of the La to increase the magnetocaloric strength. Thus, the age-splitting process will generally occur in magnetocaloric materials of the form $RE(TM_xSi_{1-x})_{13}H_y$ material (where RE represents a rare earth element such as La, Ce, Pr, or Nd, and TM represents a transition metal such as Fe, Cr, Mn, or Ni, $x<0.15$, and $y<1.5$). In an illustrative embodiment, the value of y can be between approximately 0.8 and 1.5. Alternatively, a different range of y values may be used. As discussed herein, different values of y can be used to generate magnetocaloric materials having different Curie temperatures.

[0033] When used in an MR system, the magnetocaloric material will inevitably be exposed to temperatures close to its Curie temperature. Indeed, in a layered bed, the material in a layer is selected to have a Curie temperature equal to the average temperature seen by that layer during the MR cycle. Thus, if partially hydrogenated LaFeSiH, or more generally $RE(TM_xSi_{1-x})_{13}H_y$, is used in an MR system, its magnetocaloric properties will degrade over time. In spite of its significant advantages over other magnetocaloric materials, this degradation in the magnetocaloric properties of partially hydrogenated $RE(TM_xSi_{1-x})_{13}H_y$ material could potentially preclude its use in a commercial MR system.

[0034] Applicants have discovered that when degraded $RE(TMxSi_{1-x})_{13}H_y$ material is subsequently held at a temperature away from (e.g., either a higher or a lower temperature) its Curie point, the degradation process reverses and eventually the properties of the material return to their initial condition. Moreover, Applicants have found that the recovery of the material proceeds more quickly at higher temperatures, as shown in FIG. **8**. Material (i.e., LaFeSiH) with a Curie temperature of 26.7° C. was allowed to age-split by storage at this temperature for over one year, until the width of the magnetic transition as measured by DSC reached 14° C. The original magnetic transmission as measured by DSC was 2.1° C. The degraded material was then exposed to different temperatures as shown in the figure (i.e., 38.5° C., 44° C., 60° C., and 100° C.). Exposure at 44° C. for about 6 days was sufficient to completely restore the material to its initial condition, and exposure at 60° C. for about 3 days was sufficient to completely restore the material to its initial condition. Exposure at 100° C. for less than 1 day was sufficient to obtain complete reversal of age-splitting. Applicants have also found that age-splitting degradation of $Pr_{0.5}La_{0.5}(Fe_{1-x}Si_x)_{13}H_y$ is also completely reversible by this heat treatment. Recovery of the original sharp magnetic transition of age-split LaFeSiH is also obtained by exposure to lowered temperature, although the process proceeds more slowly, as shown in FIG. **9**. The LaFeSiH material initially had a 1.2° C. wide magnetic transition, that had been widened to 4.4° C. after a 6 day hold near its 37° C. Curie point. Recovery was obtained by holding the material at 5° C. Recovery was complete after 100 days. In an illustrative embodiment, the regenerating temperature used to recover the magnetocaloric material can be less than a maximum temperature at which hydrogen may begin to leave the magnetocaloric material. The maximum temperature is approximately 180° C.

[0035] Because the age-splitting degradation can be completely reversed in a relatively simple manner, $RE(TM_xSi_{1-x})_{13}H_y$ materials can be used in suitably modified MR systems, which forms the basis of the subject matter described herein. In the usual mode of operation of an MR system with layered beds of magnetocaloric material, the material layers will remain close to their respective Curie temperatures, which will cause deterioration of the magnetocaloric material. In addition, when the system is not operating, the portion of the magnetocaloric material with Curie point near ambient temperature may also deteriorate. As such, Applicants have developed a modified MR system that is configured to hold the layers of magnetocaloric material at a temperature that differs from the Curie temperature of the magnetocaloric material to reverse whatever age-splitting degradation may have occurred and to recover their full magnetocaloric effect. The temperature at which the magnetocaloric material is held, which can be higher or lower than the Curie temperature of the magnetocaloric material, can differ from the Curie temperature by 10° C., 25° C., 50° C., 100° C., etc. depending on the desired rate of recovery, the system capacity, etc. In an illustrative embodiment, temperature at which the magnetocaloric material is held can differ from the Curie temperature by approximately 10° C.

[0036] In one illustrative embodiment, an MR system employs $RE(TM_xSi_{1-x})_{13}H_y$ as the magnetocaloric material and has a heating element plumbed into the flow system. When the MR system would otherwise be idle (e.g., a residential air conditioner at night), the heating element can be activated. The MR system would then circulate heated fluid through the magnetocaloric material, completely reversing any age-splitting that may have occurred since the last high-temperature treatment.

[0037] In the particular case of a MR system that normally absorbs heat at a cold heat exchanger (CHEX) and exhausts heat at a hot heat exchanger (HHEX), a heater can be plumbed in parallel with the cold heat exchanger. In normal cooling mode, flow is directed through the CHEX and the HHEX, as shown in FIG. **10**. As illustrated in FIG. **10**, an AMR type refrigerator is operating in cooling mode, including one or more demagnetized beds providing cooling to a cold heat exchanger in thermal contact with the load to be cooled. One or more magnetized beds are rejecting heat to a hot heat exchanger. In one embodiment, each bed comprises layers of RE(TMxSi1-x)13Hy with Curie points approximately ranging from Tc to Th, where Th>Tc.

[0038] FIG. **11** illustrates an AMR type refrigerator operating in recovery mode. In one embodiment, a heater in series with the beds heats the beds to more than 10 C above the highest Curie point of the material in the beds, and the heat exchangers are bypassed. When the recovery mode is started, a valve switches flow away from the cold heat exchanger and redirects the flow to the heater, as shown in FIG. **11** and discussed in more detail below. A second valve may be added to switch flow away from the hot heat exchanger when in recovery mode (also see FIG. **11**). These two valves thermally isolate the MR system so it may be heated to a temperature approximately 10° C. higher than the Curie point of all magnetocaloric materials in the system using a relatively small amount of heater power. If either the magnet motion or fluid flow reversal is suspended during the recovery mode, operation of the AMR cycle is suspended, which reduces the amount of heater power required to stay in recovery mode. Because magnet motion and fluid flow reversal utilize additional electrical power, suspending these operations also reduces the amount of power consumed by the system while in recovery mode.

[0039] In an alternative embodiment, in addition to having a heating element, a cooling system can include two independent MR subsystems. The first MR subsystem can provide cooling as in FIG. **10**, while simultaneously the beds of the second subsystem undergo heat treatment as in FIG. **11**, to reverse age-splitting. After a certain duration under these operating conditions (e.g., 1 hour, 2 hours, 4 hours, 12 hours, etc.), the MR subsystems can be switched, with the second subsystem providing cooling, and the first subsystem undergoing heat treatment. Under periods of peak cooling demand, both MR subsystems could provide cooling power. In another alternative embodiment, the system can incorporate more than two subsystems, with some subsystems providing cooling power while the remaining subsystems undergo heat treatment.

[0040] In another alternative embodiment, the cooling system can have two stages, with each stage containing layered AMR beds. The cold stage can have Curie temperatures ranging from T_c to T_m, while the hot stage can have Curie temperatures ranging from T_m to T_h, where $T_h>T_m>T_c$. In an air conditioner implementation, T_c may have a value of 10° C., T_m may have a value of 25° C., and T_h may have a value of 40° C. In alternative embodiments and/or implementations, different temperature values may be used. When recovery of the hot stage magnetocaloric material is desired, the cold stage can operate in cooling mode, generating a cold outlet fluid stream with temperature near T_c. This cold fluid, instead of flowing through the cold side heat exchanger, can be directed through the hot stage to bring the hot stage temperature near T_c. Because T_c is well below all Curie temperatures in the hot stage, exposure to this temperature would reverse any age-splitting in the hot stage. Similarly, when recovery of the cold stage magnetocaloric material is desired, the hot stage can operate in cooling mode and can therefore generate a hot outlet fluid stream with a temperature near T_h. This hot fluid, instead of flowing through the hot side heat exchanger, can be directed through the cold stage, bringing its temperature to approximately T_h. Because this temperature is well above all Curie temperatures in the cold stage, exposure to this temperature would reverse any age-splitting of the cold stage material.

[0041] In another alternative embodiment, the system can include two independent MR subsystems, with each subsystem having two stages, a hot stage and a cold stage as in the above-described embodiment. When maximum cooling power is desired, both subsystems can be run in parallel, with each providing cooling, as shown in FIG. **12**. In FIG. **12**, the stages connected to the pump and hot HEX have LaFeSiH as the magnetocaloric material with Curie points ranging from Th to Tm. The stages connected to the cold HEX have LaFeSiH MCM with Curie points ranging from Tm to Tc. In an illustrative embodiment, the MCM with Curie point at Tm is at the end of the bed that is connected to another bed. When less cooling power is needed, one subsystem could be run in cooling mode, while the other subsystem could be run in recovery mode to restore the performance of its magnetocaloric material as shown in FIG. **13**. In this figure, the lower subsystem is providing cooling power, while the upper subsystem is in recovery mode. At least a portion of the cold outlet fluid stream emerging from the demagnetized beds of the lower subsystem is diverted into the hot stage beds of the upper subsystem. Simultaneously, part of the hot outlet fluid stream of the magnetized beds of the lower subsystem is diverted to the cold stage beds of the upper subsystem. This embodiment can also be modified to incorporate more than two subsystems, with some subsystems providing cooling power while the remaining subsystems undergo heat treatment. Each subsystem in this generalized case could have two stages as described above.

[0042] In another alternative embodiment, the possibly multiple beds of a magnetic refrigeration system can be designed to be easily removable and replaceable from the system. Beds that have been degraded from age-splitting can then be removed and replaced with pristine beds. In a separate device that can be physically remote from the magnetic refrigeration system, the degraded beds can be returned to pristine condition through exposure to temperatures sufficiently far from the Curie temperatures of all the layers they contain. This device, for example, could be a simple flow loop with a heater, capable of circulating fluid at an elevated temperature through the degraded beds, or an oven for holding the beds at an elevated temperature. Once restored to pristine condition, these beds can then be re-installed in the magnetic refrigeration system.

[0043] Any of the operations described herein can be performed by a computing system that includes a processor, a memory, a transmitter, a receiver, a display, a user interface, and/or any other computer components known to those of skill in the art. Any type of computing system known to those of skill in the art may be used. In one embodiment, any of the operations described herein can be coded into instructions that are stored on a computer-readable medium. A computing system can be utilized to execute the instructions such that the operations are performed.

EXAMPLES

[0044] To verify the effect on magnetic refrigerator performance of the age-splitting degradation, and to verify that elevated temperature treatment was effective at reversing this degradation, the beds of a magnetic refrigerator were packed with five layers of $La(Fe_{0.885}Si_{0.115})H_y$ material, with each layer having a different value of y and therefore a different Curie point. The Curie points of the layers were initially 8° C., 11° C., 15° C., 18° C. and 21° C. The machine was tested under a standard set of operating conditions, where the cycle frequency was 3.33 Hz, the flow rate was 6 lit/min, the hot inlet temperature was 25° C., and the cooling load, provided by an electrical heater, was 400 watts. Before operation as a MR, the LaFeSiH in the beds was suffused with 35° C. aqueous fluid for 80 hours to bring the material to its initial state. The temperature span of the machine with pristine material under the standard operating conditions was found to be 13.4° C. The machine was then left in a non-operating state at an ambient temperature of 22° C. for ten days. In this state, the materials with Curie temperatures of 18° C. and 21° C. would be expected to undergo age-splitting degradation, and indeed, the temperature span of the machine after this 10-day treatment under the standard operating conditions dropped to only 2.9° C. The LaFeSiH MCM was then suffused with 50° C. aqueous fluid for 19 hours to bring the material to its initial state, and then the temperature span of the machine in AMR mode at the standard condition of a cooling load of 400 watts and a hot inlet temperature of 25° C. was measured to be 13.2° C. Thus bringing the LeFeSiH MCM to a temperature more than 10° C. above the Curie point of the material for 19 hours was able to restore the performance of the MCM after a substantial reduction in performance that occurred when the MCM was kept close to its Curie point for ten days.

[0045] The herein described subject matter sometimes illustrates different components contained within, or connected with, different other components. It is to be understood that such depicted architectures are merely exemplary, and that in fact many other architectures can be implemented which achieve the same functionality. In a conceptual sense, any arrangement of components to achieve the same functionality is effectively "associated" such that the desired functionality is achieved. Hence, any two components herein combined to achieve a particular functionality can be seen as "associated with" each other such that the desired functionality is achieved, irrespective of architectures or intermedial components. Likewise, any two components so associated can also be viewed as being "operably connected", or "operably coupled", to each other to achieve the desired functionality, and any two components capable of being so associated can also be viewed as being "operably couplable", to each other to achieve the desired functionality. Specific examples of operably couplable include but are not limited to physically mateable and/or physically interacting components and/or wirelessly interactable and/or wirelessly interacting components and/or logically interacting and/or logically interactable components.

[0046] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0047] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (e.g., bodies of the appended claims) are generally intended as "open" terms (e.g., the term "including" should be interpreted as "including but not limited to," the term "having" should be interpreted as "having at least," the term "includes" should be interpreted as "includes but is not limited to," etc.). It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases "at least one" and "one or more" to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or "an" limits any particular claim containing such introduced claim recitation to inventions containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (e.g., "a" and/or "an" should typically be interpreted to mean "at least one" or "one or more"); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should typically be interpreted to mean at least the recited number (e.g., the bare recitation of "two recitations," without other modifiers, typically means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (e.g., "a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to "at least one of A, B, or C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (e.g., "a system having at least one of A, B, or C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B."

[0048] The foregoing description of illustrative embodiments has been presented for purposes of illustration and of description. It is not intended to be exhaustive or limiting with respect to the precise form disclosed, and modifications and variations are possible in light of the above teachings or may be acquired from practice of the disclosed embodiments. It is intended that the scope of the invention be defined by the claims appended hereto and their equivalents.

What is claimed is:

1. A method comprising:

identifying at least partial degradation of a magnetocaloric material in a magnetic cooling system, wherein the magnetiocaloric material has a Curie temperature; and

regenerating the magnetocaloric material by maintaining the magnetocaloric material at a regenerating temperature, wherein the regenerating temperature is different from the Curie temperature of the magnetocaloric material.

2. The method of claim **1**, wherein the regenerating temperature differs from the Curie temperature by at least five degrees Celcius.

3. The method of claim **1**, wherein the regenerating temperature differs from the Curie temperature by at least ten degrees Celcius.

4. The method of claim **1**, wherein the magnetocaloric material includes hydrogen, wherein the regenerating temperature is below a maximum temperature, and wherein the maximum temperature is a temperature at which at least a portion of the hydrogen will begin to leave the magnetocaloric material.

5. The method of claim **1**, wherein the magnetocaloric material comprises $RE(TM_xSi_y)_{13}H_z$, where RE is a rare earth element and TM is a transition metal.

6. The method of claim **1**, further comprising suspending an active magnetic regenerator cycle of the magnetic cooling system while the magnetocaloric material is maintained at the regenerating temperature.

7. The method of claim **1**, further comprising:

removing the magnetocaloric material from the magnetic cooling system such that the magnetocaloric material is maintained at the regenerating temperature remote from the magnetic cooling system; and

replacing the magnetocaloric material with a regenerated magnetocaloric material.

8. The method of claim **1**, wherein regenerating comprises reversing age splitting of the magnetocaloric material.

9. A method comprising:

forming at least one bed of a magnetic cooling system, wherein the at least one bed includes a magnetocaloric material, wherein the magnetocaloric material has a Curie temperature, and wherein a heat transfer fluid is configured to transfer heat to or from the magnetocaloric material in the at least one bed;

forming at least one valve of the magnetic cooling system to control a flow of the heat transfer fluid through the at least one bed and either a heater or a heat exchanger, wherein flow of the heat transfer fluid between the at least one bed and the heater regenerates the magnetocaloric material by maintaining the magnetocaloric material at a regenerating temperature, and wherein the regenerating temperature is different from the Curie temperature of the magnetocaloric material.

10. The method of claim **9**, wherein flow of the heat transfer fluid between the at least one bed and the heat exchanger cools the magnetocaloric material.

11. The method of claim **9**, wherein the at least one bed comprises a plurality of layers, wherein each layer of the at least one bed includes a distinct magnetocaloric material having a distinct Curie temperature, and wherein the distinct Curie temperature of the distinct magentocaloric material in a given layer is an average temperature of the given layer during an active magnetic regenerator cycle.

12. An apparatus comprising:

a heat transfer fluid;

a bed comprising a magnetocaloric material that has a Curie temperature, wherein the bed is configured to allow the heat transfer fluid to transfer heat to or from the magnetocaloric material; and

a heater configured to maintain the magnetocaloric material at a regenerating temperature for an amount of time to regenerate the magnetocaloric material, wherein the regenerating temperature is different from the Curie temperature of the magnetocaloric material.

13. The apparatus of claim **12**, wherein the heater is configured to heat the bed via the heat transfer fluid.

14. The apparatus of claim **12**, wherein the regenerating temperature is greater than the Curie temperature.

15. The apparatus of claim **12**, wherein the bed comprises a plurality of magnetocaloric materials having distinct Curie temperatures, and wherein the regenerating temperature is greater than a largest of the distinct Curie temperatures.

16. The apparatus of claim **12**, wherein the heater is remote from the bed, and wherein the bed is configured to be temporarily removed from the apparatus for regeneration by the heater.

17. A heat transfer system comprising:

a first subsystem comprising:

a first heat transfer fluid;

a first bed having a first magnetocaloric material, wherein the first magnetocaloric material has a first Curie temperature; and

a first valve configured to control whether the first subsystem operates in regeneration mode or cooling mode; and

a second subsystem comprising:

a second heat transfer fluid;

a second bed having a second magnetocaloric material, wherein the second magnetocaloric material has a second Curie temperature; and

a second valve configured to control whether the second subsystem operates in regeneration mode or cooling mode.

18. The heat transfer system of claim **17**, wherein:

the first valve is configured to control the first subsystem to operate in the cooling mode and the second valve is configured to control the second subsystem to operate in the regenerating mode during a first period of time; and

the first valve is configured to control the first subsystem to operate in the regenerating mode and the second valve is configured to control the second subsystem to operate in the cooling mode during a second period of time.

19. The heat transfer system of claim **17**, wherein the first valve is configured to control the first subsystem to operate in the cooling mode and the second valve is configured to control the second subsystem to operate in the cooling mode during a given period of time.

20. The heat transfer system of claim **17**, wherein:

the first bed comprises a first plurality of layers, wherein each layer of the first bed includes a distinct magnetocaloric material having a distinct Curie temperature, and wherein the first subsystem comprises a cold stage such that the distinct Curie temperatures of the distinct magnetocaloric materials in the first plurality of layers are in a range between T_c and T_m; and

the second bed comprises a second plurality of layers, wherein each layer of the second bed includes a distinct magnetocaloric material having a distinct Curie temperature, and wherein the second subsystem comprises a hot stage such that the distinct Curie temperatures of the distinct magnetocaloric materials in the second plurality of layers are in a range between T_m and T_h, wherein $T_h>T_m>T_c$.

21. The heat transfer system of claim **20**, wherein the first heat transfer fluid is at a temperature of T_c when the cold stage operates in the cooling mode, and wherein at least one of the first valve and the second valve direct the first heat transfer fluid at the temperature of T_c through the hot stage to regenerate the hot stage.

22. The heat transfer system of claim **20**, wherein the second heat transfer fluid is at a temperature of T_h when the hot stage operates in the cooling mode, and wherein at least one of the first valve and the second valve direct the second heat transfer fluid at the temperature of T_h through the cold stage to regenerate the cold stage.

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