**Title:** CHEMICAL HEAT ACCUMULATOR AND METHOD FOR PRODUCING THE SAME

**Abstract:** A chemical heat accumulator (100) is provided, the chemical heat accumulator including a chemical heat storage material structure (21) that includes a granular chemical heat storage material and has a polyhedral structure, and a structure restriction member (30) that accommodates the chemical heat storage material structure and restricts each face of the accommodated chemical heat storage material structure at least at a portion of the face. A method for producing a chemical heat accumulator is also provided.

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CHEMICAL HEAT ACCUMULATOR AND METHOD FOR PRODUCING THE SAME

Technical Field
[0001] The present invention relates to a chemical heat accumulator including a chemical heat storage material that absorbs and releases heat, and a method for producing the chemical heat accumulator.

Background Art
[0002] Chemical heat storage materials are substances that can absorb and release heat by utilizing chemical reactions and are widely known conventionally, and the use of chemical heat storage materials has been studied in various fields.
[0003] For example, a chemical heat storage material including quick lime having a large number of pores as a main body has been disclosed, and it is said that, by having a large number of pores, the volume expansion in the process of the change from quick lime into hydrated lime is absorbed as compared with a conventional chemical heat storage material that does not have any surplus spaces such as holes and, as a result, destruction of particles or powderization does not occur (see, for example, Japanese Patent Application Laid-Open (JP-A) No. 1-225686).
[0004] Further, a chemical heat storage capsule in which a chemical heat storage material in the form of powder is filled at a predetermined proportion into a cylindrical body of a porous body, and a heat storage device in which a reactor filled with such heat storage capsules is connected to a heat supply device have been disclosed (see, for example, Japanese Patent Application Publication (JP-B) Nos. 6-80394 and 6-80395). In a heat storage system, it is also important to conduct heat exchange by passing heat to the outside of the system along with the reaction. In the case of filling in and encapsulating particles a cylindrical body, thermal rate limitation may easily occur due to the increase in the resistance of heat conduction caused by the filling into capsules, complication of contact routes depending on the distance between the particles, and the like.

SUMMARY OF INVENTION

Technical Problem
[0005] In a system using a chemical heat storage material, however, in a case in which, as described above for example, calcium hydroxide is used as a chemical storage material,
during operation of the system, the following reversible reaction is repeated between calcium oxide and calcium hydroxide. In this process, the volume of each particle expands or shrinks by several tens of percents.

[0006] \[ \text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca(OH)}_2 \]

[0007] Therefore, as per the conventional technique described above, by using particles having pores, it is expected that destruction of particles may be suppressed to a certain degree; however, in actual fact, the volume change is large, and the reality is that the influences of volume expansion or shrinkage cannot be absorbed only by means of having pores. For this reason, there is the problem that destruction of the particles used in the chemical heat storage material may be caused by the repeated changes in volume.

[0008] The present invention is made in consideration of the foregoing, and it is an object of the invention to provide a chemical heat accumulator in which a chemical heat storage material is restricted in order to limit the volume change of the chemical heat storage material and also to prevent the chemical heat material structure (molded body) from collapsing in conjunction with the volume change, thereby stably carrying out a reversible reaction that undertakes heat storage and heat release, and a method of producing the chemical heat accumulator.

Solution to Problem

[0009] The present inventors have found that when, for example, using a chemical heat storage material structure, the chemical heat storage material structure being a molded body of a chemical heat storage material that repeatedly changes in volume due to expansion and shrinkage accompanying binding or desorption of a heat storing/releasing reaction medium, the phenomenon whereby the chemical heat storage material structure collapses and is not capable of maintaining the initial form due to large volume change (expansion difference) follows from a certain level of volume change and can be suppressed by means of limiting (restricting) significant expansion and shrinkage exceeding this level, thereby preventing collapse and maintaining form. Therefore, the present invention has been made based on this knowledge.

[0010] The first aspect of the invention provides a chemical heat accumulator.

Embodiments of the chemical heat accumulator according to the first aspect of the invention include the followings.

<1> According to the first aspect of the invention, a chemical heat accumulator is provided, the chemical heat accumulator including a chemical heat storage material structure that includes a granular chemical heat storage material and has a polyhedral structure, and a
structure restriction member that accommodates the chemical heat storage material structure and restricts each face of the accommodated chemical heat storage material structure at least at a portion of the face.

[0011] In the first aspect of the invention, by bringing each face of plural faces (for example, 6 faces in the case of a hexahedron) possessed by the chemical heat storage material structure in contact with a structure restriction member (for example, wall faces in the interior of the hollow of the structure restriction member in which the chemical heat storage material structure is accommodated) at least at a portion of the face, to be in a state of restricting the space where the chemical heat storage material can expand or shrink, remarkable change in volume of the chemical heat storage material structure is limited and the distance between the particles inside the structure is maintained at an appropriate distance. Specifically, at the time of expansion in volume accompanying binding with a heat storing/releasing reaction medium (for example, water in the case of using a metal hydroxide such as Ca (OH)$_2$), excessive expansion in volume is restricted, and in the chemical heat storage material structure that has once expanded and contacted with the structure restriction member, a state in which the contact faces are adhered to the inner walls of the structure restriction member is formed, and thus, at the time of shrinkage in volume due to desorption of the heat storing/releasing reaction medium, a phenomenon in which the chemical heat storage material structure is pulled by the inner walls which causes excessive shrinkage is restricted.

In this manner, collapse of the chemical heat material structure which is a molded substance is prevented. With the suppression of collapse, heat conduction routes which depend on the distance between the particles can be ensured, a low heat resistance can be obtained, thermal rate limitation is cancelled, and therefore, a chemical heat storage system having a high thermal efficiency can be constructed.

[0012] In the present invention, the term "restriction" means that remarkable expansion and shrinkage when using the chemical heat storage material structure or the like is limited. Specifically, it means that a state, in which the change in volume of the chemical heat storage material structure is limited at predetermined faces, is formed in the chemical heat storage material structure, to an extent necessary for suppressing the collapse of the chemical heat storage material structure which is caused by the difference between the shrinkage of the chemical heat storage material structure due to desorption (for example, dehydration) of a heat storing/releasing reaction medium (for example, water) and the expansion of the chemical heat storage material structure accompanying binding (for example, hydration) of the heat storing/releasing reaction medium. It is preferable that the chemical heat storage material structure is accommodated in the structure restriction member in a state such that the
true density ratio of the chemical heat storage material structure is within the range of from 45% to 63%.

[0013] <2> Embodiments of the chemical heat accumulator according to the first aspect of the invention includes a chemical heat accumulator described in the item <1>, wherein the structure restriction member has a hollow portion having a form which is the same as or homothetic to the form of the polyhedral structure of the chemical heat storage material structure, the chemical heat storage material structure is accommodated in the hollow portion, and each face of the accommodated chemical heat storage material structure is restricted by an inner walls of the hollow portion.

[0014] Since the form of the hollow portion of the structure restriction member that restricts expansion and shrinkage of the chemical heat storage material structure is the same as or homothetic to the form of the chemical heat storage material structure, in a case in which change in volume is caused in the chemical heat storage material structure, the entire structure surfaces (for example, in the case of a hexahedral structure, all of the 6 faces) can be uniformly restricted such that a moiety where expansion or shrinkage easily occur is not included partially. Accordingly, collapse of the chemical heat storage material structure can be further prevented.

[0015] <3> Embodiments of the chemical heat accumulator according to the first aspect of the invention includes a chemical heat accumulator described in the item <1> or the item <2>, wherein the structure restriction member has a hollow portion that accommodates the chemical heat storage material structure, and each face of the chemical heat storage material structure is at least brought into contact with an inner wall face of the hollow portion and restricted when binding of a heat storing/releasing reaction medium is saturated in the chemical heat storage material structure.

[0016] To be in contact with the inner wall faces of the hollow portion when the binding of the heat storing/releasing reaction medium is saturated (for example, in the case where a metal hydroxide is used as a chemical heat storage material, when the metal hydroxide has been hydrated until maximum hydration) involves the case in which the dimension of the inward form of the hollow portion when the binding has reached the saturated state becomes equal to the dimension of the outward form of the chemical heat storage material structure when the binding of the heat storing/releasing reaction medium is saturated.

When the binding of the heat storing/releasing reaction medium (for example, water in the case of using a metal hydroxide such as Ca(OH)\textsubscript{2} as a chemical heat storage material) is saturated (for example, in the case where a metal hydroxide is used as a chemical heat storage material, when the metal hydroxide has been hydrated until maximum hydration) in the
chemical heat storage material structure, the chemical heat storage material structure is in a state in which the volume is mostly expanded. By obtaining a relationship in which the chemical heat storage material structure contacts with or adheres to the wall faces of the hollow portion when the chemical heat storage material structure reaches this state, excess power application to the structure restriction member at the time of volume expansion can be suppressed. Herewith, as described below, the requirements with respect to the structural strength when the wall (hereinafter, also referred to as the restriction wall) of the structure restriction member is formed with a permeation wall that permits permeation of the heat storing/releasing reaction medium or a heat transfer wall having thermal conductivity can be lowered to a minimum level.

[0017] Further, in the case of forming a state in which the dimension of the inward form of the hollow portion and the dimension of the outward form of the chemical heat storage material structure when the binding of the heat storing/releasing reaction medium is saturated is made equal, it is possible to maintain an almost constant distance between the particles inside the structure that is in the molding stage. As a result, generation of internal cracks accompanying the expansion and shrinkage of the molded body is suppressed, and also it becomes possible to self-repair the generated cracks. Moreover, by suppressing the distortion such as bending or warping in the outward form, the effect of suppressing external defects can be expected, and even when any defects occur at the time of shrinkage, it is possible to self-repair by cooperation with the restriction wall at the time of expansion.

[0018] <4> Embodiments of the chemical heat accumulator according to the first aspect of the invention includes a chemical heat accumulator described in any one of the item <1> to the item <3>, wherein the chemical heat storage material structure that is accommodated in the structure restriction member has a true density ratio of from 45% to 63%.

[0019] When the true density ratio is within the above range, the particles of the chemical heat storage material exhibit binding property to each other, and the distance between the particles is maintained at an appropriate distance. Herewith, the binding reaction of the heat storing/releasing reaction medium (for example, water in the case of using a metal hydroxide such as Ca(OH)$_2$ as a chemical heat storage material) can proceed well, as well as excessive distortion can be suppressed at the time of shrinkage in volume during the dehydration reaction, and it is possible to suppress the interface separation of the chemical heat storage material structure from the inner wall to a low level.

[0020] <5> Embodiments of the chemical heat accumulator according to the first aspect of the invention includes a chemical heat accumulator described in any one of the item <1> to the item <4>, wherein a container that has plural walls corresponding to the polyhedral
structure of the chemical heat storage material structure and a space that is formed with plural
inner wall faces (for example, a hexahedron having an internal hollow formed with 6 walls) is
used as the structure restriction member, at least one of the plural walls is a permeation wall
that permits permeation of a heat storing/releasing reaction medium, and at least one of the
plural walls other than the at least one permeation wall is a heat transfer wall having thermal
cconductivity.

[0021] Since at least one of the walls is a permeation wall that permits permeation of a heat
storing/releasing reaction medium (for example, water in the case of using a metal hydroxide
such as Ca(OH)₂ as a chemical heat storage material), it becomes possible to undergo a
reaction (for example, a hydration reaction) in which the resistance to passage of the heat
storing/releasing reaction medium can be suppressed to a low level and, as a result, higher
efficiency and higher output in chemical heat storage can be achieved. Further, since at least
one of the walls is a heat transfer wall, heat exchange can be conducted well.

[0022] <6> Embodiments of the chemical heat accumulator according to the first aspect of
the invention includes a chemical heat accumulator described in any one of the item <1> to
the item <5>, wherein the chemical heat storage material is a hydration reactive heat storage
material that absorbs heat in conjunction with a dehydration reaction and releases heat in
conjunction with a hydration reaction.

[0023] When the chemical heat storage material is constituted by such a hydration reactive
heat storage material, defects such as cracks or distortion, which may easily occur due to the
change in volume, when the degrees of volume expansion and volume shrinkage that occur at
the time of heat absorption and heat generation are large, and deterioration in reactivity
associated therewith can be effectively prevented.

[0024] <7> Embodiments of the chemical heat accumulator according to the first aspect of
the invention includes a chemical heat accumulator described in any one of the item <1> to
the item <6>, wherein the chemical heat storage material is a hydroxide of an alkaline earth
metal.

[0025] By using a hydroxide of an alkaline earth metal as the chemical heat storage material,
the effects of the present invention are more effectively realized, since the volume change is
large and, and further, the material stability against heat storing/heat releasing reaction
(hydration/dehydration) is high. Therefore, a stable heat storage effect can be obtained over
a long-term.

[0026] Further, the second aspect of the present invention provides a method for producing
the chemical heat accumulator.

Embodiments of the method for producing the chemical heat accumulator according
to the second aspect of the present invention include the followings.

<8> According to the second aspect of the invention, a method for producing a chemical heat accumulator is provided, the method including accommodating a chemical heat storing material structure that includes a granular chemical heat storage material and has a polyhedral structure, after desorbing at least a portion of a heat storing/releasing reaction medium that is bonded to the chemical heat storage material structure, in a structure restriction member that has an internal hollow and restricts each face of the chemical heat storage material structure at least at a portion of the face.

[0027] In the second aspect of the present invention, in the shrinkage state in which the heat storing/releasing reaction medium in the chemical heat storage material structure is desorbed, since the volume of the chemical heat storage material structure is reduced, storage in the structure restriction member can be carried out easily.

Then, after the chemical heat storage material structure having reduced volume is accommodated in the structure restriction member, the heat storing/releasing reaction medium is supplied and is bonded, thereby the volume is expanded. Thus, the chemical heat storage material structure adheres to the wall faces of the interior of the hollow of the structure restriction member, and when the adhesion is enhanced, a restriction state is formed. Even if the structure shrinks thereafter, the adherance to the wall faces is maintained, and therefore the restriction effect can be obtained also at the time of desorption.

[0028] <9> Embodiments of the method for producing the chemical heat accumulator according to the second aspect of the invention includes a method for producing a chemical heat accumulator described in the item <8>, wherein the structure restriction member has a hollow portion having a form which is the same as or homothetic to the form of the polyhedral structure of the chemical heat storage material structure, and, in the accommodating of the chemical heat storage material structure in the structure restriction member, the chemical heat storage material structure is accommodated in a state in which the chemical heat storage material structure from which at least a portion of the heat storing/releasing reaction medium has been desorbed and the hollow portion of the structure restriction member have the same homothetic ratio in each pair of corresponding faces.

[0029] When the form of the hollow portion of the structure restriction member and the form of the polyhedral structure of the chemical heat storage material structure to be accommodated in the hollow portion are the same form or are in a homothetic relationship, and a process is provided of accommodating the chemical heat storage material structure in a state in which the chemical heat storage material structure and the hollow portion that accommodates this structure have the same homothetic ratio in each pair of corresponding
faces (for example, in the case of a hexahedron, a state in which a ratio of two corresponding sides of the chemical heat storage material structure and the hollow portion of the structure restriction member is the same in each of the three axis directions of the three dimensional coordinate axes (X, Y, and Z axes)), restriction of the accommodated chemical heat storage material structure can be conducted with equal weighting.

Advantageous Effects of Invention

[0030] According to the present invention, it is possible to provide a chemical heat accumulator in which a chemical heat storage material is restricted in order to limit the volume change of the chemical heat storage material and also to prevent the chemical heat material structure (molded body) from collapsing in conjunction with the volume change, thereby stably carrying out a reversible reaction that undertakes heat storage and heat release, and a method of producing the chemical heat accumulator.

BRIEF DESCRIPTION OF DRAWINGS

[0031] Fig. 1 is a perspective view showing a chemical heat accumulator according to an embodiment of the present invention.

Fig. 2 is a deal drawing that shows the structure of the chemical heat accumulator shown in Fig. 1 in a decomposed form.

Fig. 3 is a photograph showing the state in which two L shaped jigs that support the molded body are arranged at an interval.

Fig. 4A is a sectional view schematically showing the surface property of a chemical heat storage material structure by means of variation in thickness (irregular state), and Fig. 4B is a graph showing the ratio (thickness error; %) of the thickness variation (maximum thickness - minimum thickness) relative to the target thickness in Fig. 4A by changing the true density ratio.

DESCRIPTION OF EMBODIMENTS

[0032] Hereinbelow, embodiments of the chemical heat accumulator according to the present invention are explained in detail with reference to the drawings, and also, through the explanation, embodiments of the method for producing the chemical heat accumulator according to the present invention are described in detail. It should be noted that, in the following embodiments, the form in which calcium hydroxide \((\text{Ca(OH)}_2)\) which is a hydroxide of an alkaline earth metal is used as the chemical heat storage material is mainly explained. However, the present invention is not limited to the following embodiments.
The embodiments of the chemical heat accumulator and the production method thereof of the present invention are explained in reference to Fig. 1 and Fig. 2. In the present embodiment, a granular substance of Ca(OH)$_2$ is used as the chemical heat storage material, and a chemical heat storage material structure, which is prepared by molding this granular substance into a rectangular cuboid that is a hexahedron, is accommodated in a hexahedral container which has 6 walls, two wide walls among which each being formed with non-woven fabric (permeation wall) that permits permeation of a water (heat storing/releasing reaction medium), and the other four side walls each being formed with a stainless steal board (heat transfer wall) having thermal conductivity, to restrict all the 6 faces of the structure with the 6 walls.

As shown in Fig. 1 and Fig. 2, the chemical heat accumulator 100 according to the present embodiment includes a structure restriction container (structure restriction member) 30, which is configured to have a hexahedral structure having an internal hollow by using two long stainless steel materials 11 with a narrow width, two short stainless steel materials 13 with a narrow width, and two moisture permeation walls 15 that are prepared by fitting up with non-woven fabric in which synthetic fiber is used at a frame material (not shown in the figure) made of stainless steal, and a rectangular cuboid of Ca(OH)$_2$ structure 21, which is accommodated in the structure restriction container and is prepared by molding the Ca(OH)$_2$ powder in accordance with the press molding method.

As shown in Fig. 1 and Fig. 2, the structure restriction container 30 is formed with four heat transfer walls that form a non-end frame structure with the stainless steel materials 11 and the stainless steel materials 13, and two moisture permeation walls (permeation walls) 15 that are prepared by fitting up with non-woven fabric at the frame material (not shown in the figure) made of stainless steel. The four heat transfer walls are provided as side walls having thermal conductivity, in a state of being linked together. The 6 faces of the Ca(OH)$_2$ structure 21 are in a state of being at least in contact with the 6 inner wall faces of the structure restriction container 30. When the Ca(OH)$_2$ structure 21 expands due to the hydration reaction, the outward form of the structure is restricted by the inner walls of the structure restriction container 30, thereby maintaining the form of the structure, and adhesion to the inner walls is increased and thus, the heat can be released to the outside through the heat transfer walls. Further, the volume expansion at the time of hydration reaction is absorbed by the small spaces between the Ca(OH)$_2$ structure and the inner walls, and the spaces for the pore volume in the structure. On the contrary, when the Ca(OH)$_2$ structure 21 shrinks due to the dehydration reaction, by the adhesion of the structure to the inner walls, the shrinkage is limited, whereby the form is maintained.
The moisture permeation walls 15 are made of non-woven fabric prepared by using synthetic fiber and are joined with the stainless steel materials 11 and the stainless steel materials 13 at a portion of the frame material thereof. With the moisture permeation walls 15, migration of water which is generated during the hydration reaction or dehydration reaction at the Ca(OH)₂ structure 21 which is accommodated in the interior of the structure restriction container 30 becomes possible.

For the moisture permeation walls 15, a plate-like material having pores capable of permitting permeation of water can be used without limitation, and the material may be, for example, a mesh material made of stainless steel (for example, SUS316L). In this case, the mesh size is not particularly limited, but is preferably in a range of from 200 mesh to 400 mesh. Further, the material is not limited to a mesh-like material, and a material that is provided with pores having another, arbitrary selected, form can be used. For example, a material that is provided with circular pores at predetermined intervals may be used.

The material of the moisture permeation walls may be any material that can follow or limit the expansion and shrinkage of the chemical heat storage material structure (for example, in the present embodiment, the Ca(OH)₂ structure), and a material which is less likely to cause corrosion, softening or the like, or deterioration such as rusting or the like by the heat storing/releasing reaction medium (for example, in the present embodiment, water) is preferred. Specifically, a metal material such as a stainless steel material or an aluminum material, a resin material, or the like may be used.

As for the stainless steel materials 11 and stainless steel materials 15, a material which is less likely to cause corrosion, softening or the like, or deterioration such as rusting or the like by the heat storing/releasing reaction medium (for example, in the present embodiment, water) and can impart thermal conductivity is preferable. Examples thereof include a metal material such as a stainless steel material or an aluminum material.

The interior of the hollow of the structure restriction container 30 is formed with 6 inner wall faces and has a size of 50 mm x 30 mm x 3 mm, and as described below, the internal dimension of the hollow portion is almost the same size as the size of the Ca(OH)₂ structure 21.

The size of the interior of the hollow can be arbitrary selected according to the purpose, the kind (namely, expansion/ shrinkage ratio) of the chemical heat storage material structure (for example, in the present embodiment, the Ca(OH)₂ structure) to be accommodated, and the volume.

The structure restriction container 30 in the present embodiment accommodates the Ca(OH)₂ structure 21 and restricts the entire 6 faces thereof, such that remarkable volume
expansion or volume shrinkage does not occur at the time of heat absorption accompanying
the dehydration reaction or heat releasing accompanying the hydration reaction.

[0043] The expression "the Ca(OH)$_2$ structure 21 is restricted" means that remarkable
expansion and shrinkage occurring when using the Ca(OH)$_2$ structure 21 or the like is limited.
In the present embodiment, it means that a state, in which the change in volume is limited to a
small amount, is formed by bringing the Ca(OH)$_2$ structure 21 in contact with the structure
restriction container 30, to an extent necessary for suppressing the collapse of the Ca(OH)$_2$
structure 21 which is caused by the difference between the shrinkage of the Ca(OH)$_2$ structure
21 when undergoing a dehydration reaction (desorption of a heat storing/releasing reaction
medium) and the expansion of the Ca(OH)$_2$ structure 21 when undergoing a hydration
reaction (binding of a heat storing/releasing reaction medium).

[0044] Chemical Heat Storage Material -

The Ca(OH)$_2$ structure 21 is a molded body which is obtained by press molding a
granular substance (having an average primary particle diameter of from 6 $\mu$m to 8 $\mu$m) of
Ca(OH)$_2$, that is a chemical heat storage material, and has a true density ratio of 57%.
Chemical heat storage materials are substances which can absorb and release heat by utilizing
chemical reactions. The chemical heat storage material is present in the interior of the
structure in the form of powder. The expression "the chemical heat storage material is in the
form of particles or is granular" means that the chemical heat storage material is in the state of
powder including particles.

[0045] Examples of the chemical heat storage material may include inorganic hydroxides of
alkaline earth metals such as calcium hydroxide (Ca(OH)$_2$), magnesium hydroxide (Mg(OH)$_2$),
barium hydroxide (Ba(OH)$_2$), and hydrates thereof (Ba(OH)$_2$·H$_2$O), inorganic hydroxides of
alkaline metals such as lithium hydroxide monohydrate (LiOH·H$_2$O), and inorganic oxides
such as aluminum oxide trihydrate (Al$_2$O$_3$·3H$_2$O). Among them, a hydration reactive heat
storage material that absorbs heat in conjunction with a dehydration reaction and releases heat
in conjunction with a hydration reaction is preferable, and particularly, calcium hydroxide
(Ca(OH)$_2$) is preferable. Further, a commercially available product in the market may be
used as the chemical heat storage material.

[0046] Here, the storage of heat and release of heat are explained by way of example with
reference to calcium hydroxide (Ca(OH)$_2$).

Ca(OH)$_2$, which is a heat storage material, has a configuration of storing heat
(absorbing heat) in conjunction with dehydration and releasing heat (generating heat) in
conjunction with hydration (restoration to calcium hydroxide). Namely, Ca(OH)$_2$ can
reversibly repeat storage and release of heat according to the following reaction.
Ca(OH)$_2$ $\rightarrow$ CaO + H$_2$O

Further, when the amount $Q$ of heat storage/heat radiation is added to the formula, the following formulae can be obtained.

Ca(OH)$_2$ + $Q$ $\rightarrow$ CaO + H$_2$O
CaO + H$_2$O $\rightarrow$ Ca(OH)$_2$ + $Q$

[0047] The average particle diameter of the granular chemical heat storage material is, by average primary particle diameter, preferably 10 $\mu$m or less, and more preferably 1 $\mu$m or less. The lower limit of the average primary particle diameter is preferably 0.1 $\mu$m. The average primary particle diameter of the chemical heat storage material is measured using a laser diffraction/scattering particle size distribution analyzer, SALD-2000A (trade name, manufactured by Shimadzu Corporation) in accordance with the laser diffraction/scattering method.

[0048] The true density ratio of the Ca(OH)$_2$ structure 21 is 57%. It is preferable that the true density ratio of the chemical heat storage material structure is adjusted to be within the range of from 45% to 63%. The true density ratio indicates how much the substantial ratio of the compositions that constitute the structure excluding the pore is. The fewer the number of pores is, the higher the true density ratio is. When the true density ratio is within the range of from 45% to 63%, the particles of the chemical heat storage material show binding property to each other, and the distance between the particles can be maintained at an appropriate distance. Specifically, when the true density is 45% or higher, the change in volume can be suppressed to an extent such that collapse of the structure or the like does not occur. When the true density is 63% or lower, allowable volume that allows volume expansion may be ensured and good reactivity may be obtained.

Herewith, the hydration reaction (the binding reaction of the heat storing/releasing reaction medium) in the Ca(OH)$_2$ structure 21 can proceed satisfactorily, as well as excessive distortion can be suppressed at the time of volume shrinkage during the dehydration reaction, and interface separation of the Ca(OH)$_2$ structure 21 from the inner wall can be suppressed to a low level.

The true density ratio of the chemical heat storage material structure in the present invention is more preferably in a range of from 51% to 60%, and is particularly preferably in a range of from 55% to 59%.

[0049] The true density ratio is a value determined by measuring the mass [g] and volume [mL] of the chemical heat storage material structure, and calculating based on the measured values according to the following equation.

$$\text{True Density Ratio} [\%] = \frac{\text{Mass}}{\text{Volume}} \times \frac{1}{\text{True Density}} \times 100$$
Further, the Ca(OH)$_2$ structure is formed to have a size of 50 mm x 30 mm x 3 mm, and by being molded to have the same size as the internal dimension of the structure restriction container, a restriction state is formed, and thus, it is possible to maintain an almost constant distance between the particles of the heat storage material powder at the time of molding. As a result, generation of internal cracks accompanying the volume expansion and shrinkage of the Ca(OH)$_2$ structure is suppressed, and also it becomes possible to self-repair the generated internal cracks. Moreover, by suppressing the distortion such as bending or warping of the outward form, the effect of suppressing external defects can be expected, and an effect of self-repairing the defects at the time of expansion, the defects being generated at the time of shrinkage, is obtained.

From this point of view, the case in which the outer dimension of the chemical heat storage material structure that has been subjected to press molding is the same as or within the range that can be recognized as same as the inner dimension of the structure restriction container is preferable. In an embodiment, the outward form of the chemical heat storage material structure that has been subjected to press molding may be in a homothetic relationship with the form of the interior of the hollow of the structure restriction container, may be adopted. In this case, it is preferable that the chemical heat storage material structure from which at least a portion of the heat storing/releasing reaction medium has been desorbed and the hollow portion of the structure restriction container have the same homothetic ratio in each pair of corresponding faces. When the chemical heat storage material structure from which at least a portion of the heat storing/releasing reaction medium has been desorbed and the hollow portion of the structure restriction container have the same homothetic ratio in each pair of corresponding faces (in other words, when the chemical heat storage material structure from which at least a portion of the heat storing/releasing reaction medium has been desorbed and the hollow portion of the structure restriction container are in a homothetic relationship), in the case of accommodating the chemical heat storage material structure and allowing expansion and shrinkage of the chemical heat storage material structure when using, a good adhesion can be obtained against the inner wall faces of the hollow portion of the structure restriction container. The term "homothetic ratio" indicates a ratio of two corresponding sides of the contrasting forms which are in a homothetic relationship, and the ratio (homothetic ratio) is the same in each pair of corresponding sides of the contrasting forms when the contrasting forms are in a homothetic relationship. In the case of, for example, a hexahedron, to have a homothetic relationship means that the ratio of two corresponding sides of the contrasting forms is the same in each of the three axis directions of the three dimensional coordinate axes (X, Y, and Z axes). In this case, when the chemical
heat storage material structure expands or shrinks, the faces are equally restricted in the structure restriction container 30. In addition, from the same reason as that described above, it is preferable that a chemical heat storage material structure of a hydroxide of an alkaline earth metal such as Ca(OH)$_2$ structure is used, and the chemical heat storage material structure is filled to give a true density ratio within the range of from 55% to 59%.

[0052] The content ratio of the chemical heat storage material in the chemical heat storage material structure is, by volume ratio, preferably 50% by volume or higher with respect to the total volume of the structure (50% by mass or higher with respect to the total mass of the structure), and more preferably 90% by volume or higher (90% by mass or higher with respect to the total mass of the structure). When the content of the chemical heat storage material is 50% by volume or higher or 50% by mass or higher, the heat absorption/ radiation amount can be maintained at a high level.

[0053] - Organic Binder -

The chemical heat storage material structure (for example, in the present embodiment, the Ca(OH)$_2$ structure 21) may be molded using an organic binder together with the granular chemical heat storage material (for example, in the present embodiment, Ca(OH)$_2$).

[0054] Generally, particles of granular chemical heat storage materials do not stick each other well, and it is hard to mold the materials. Therefore, in order to impart structure molding property, an organic binder (binding component) may be used in combination with the granular chemical heat storage material. When using an organic binder, crystal control, porosity, and the like can also be enhanced.

[0055] Preferable examples of the organic binder include cellulose resins, examples thereof including modified or unmodified polyvinyl alcohols (PVA) and carboxymethyl cellulose; urethane resins, examples thereof including aqueous urethanes; resin components, examples thereof including starch, and solvent components, examples thereof including diethylene glycol (DEG) and ethanol.

[0056] - Other Components -

The chemical heat storage material structure (for example, in the present embodiment, the Ca(OH)$_2$ structure 21) may include, other than the components described above, one or more other components such as unavoidable impurities or additives, according to the circumstances.

[0057] Next, the method for producing the chemical heat accumulator 100 according to the embodiment of the present invention is described.

In the production of the chemical heat accumulator 100 according to the embodiment of the present invention, Ca(OH)$_2$ is used as the granular chemical heat storage material.
having an average primary particle diameter of $d_{\mu m}$, which is subjected to press molding to produce a rectangular cuboid Ca(OH)$_2$ structure (chemical heat storage material structure) 21 having a size of 50 mm x 30 mm x 3 mm as shown in Fig. 2 (hereinafter, this process is also referred to as a "structure preparation process"). The molding conditions at the time of press molding may be selected as appropriate according to the composition or properties of the chemical heat storage material and the form thereof such as thickness or the like.

[0058] In the structure preparation process in the present embodiment, a Ca(OH)$_2$ powder is subjected to press molding to form a molded body, but it is not always necessary to prepare by conducting press molding, and a commercially available Ca(OH)$_2$ molded body may also be used. The molding processing is not limited to the press molding, and another molding method may be used for conducting molding processing.

[0059] As shown in Fig. 2, a pillar shaped structure restriction container (structure restriction member) 30, which has a size of 50 mm x 30 mm x 3 mm and has a rectangular cross section, is prepared.

Thereafter, a portion of hydrated water is desorbed from the obtained Ca(OH)$_2$ structure 21 to cause volume shrinkage, thereby reducing the volume of the structure to have a size of, for example, 49 mm x 29.4 mm x 2.94 mm, and then the resulting Ca(OH)$_2$ structure is inserted into the structure restriction container 30 from the opening left at one end (23), followed by closing the openings left at the end and another end of the structure restriction container 30 with lid materials 13 (hereinafter, this process is also referred to as a "structure storage process").

[0060] As shown in Fig. 1 and Fig. 2, the structure restriction container 30 is formed with four heat transfer walls that form a non-end form with the stainless steel materials 11 and the stainless steel materials 13, and two moisture permeation walls (permeation walls) 15 that are prepared by fitting up with non-woven fabric made of synthetic fiber at the frame material (not shown in the figure) made of stainless steal. In this process, the 6 faces of the Ca(OH)$_2$ structure 21 do not stick to, but are in contact with the 6 inner wall faces of the structure restriction container 30. When the Ca(OH)$_2$ structure 21 undergoes a hydration reaction and expands, the outward form of the structure is restricted by the inner walls, thereby maintaining the form, and adhesion to the inner walls is increased and thus, the heat can be released to the outside through the heat transfer walls. Further, the volume expansion at the time of hydration reaction is absorbed by the small spaces between the Ca(OH)$_2$ structure and the inner walls, and the spaces for the pore volume in the structure.

[0061] In the present embodiment, in this manner, a chemical heat accumulator, in which 6 faces of the Ca(OH)$_2$ structure 21 that is the chemical heat storage material structure are
restricted by the 6 inner wall faces of the structure restriction container 30, is prepared.

EXAMPLES

[0062] Hereinbelow, the present invention is described more specifically with reference to Examples, but the invention is by no means limited to the following Examples unless they are beyond the spirit of the invention.

[0063] Example 1

As the chemical heat storage material, white powder (JIS R 9001; grade: special grade) of calcium hydroxide (Ca(OH)$_2$) having an average primary particle diameter of 0.8 μm was prepared, and this white powder was mixed with polyvinyl alcohol (PVA) as the organic binder to give an amount of 1% by mass with respect to the total amount including the amount of the white powder, and ion exchanged water. Then, the mixture was subjected to granulation, to prepare a precursor composition for producing the heat storage material structure.

[0064] The average primary particle diameter was measured using a laser diffraction/scattering particle size distribution analyzer, SALD-2000A (trade name, manufactured by Shimadzu Corporation) in accordance with the laser diffraction/scattering method.

[0065] The obtained precursor composition was molded in accordance with the press molding method, to obtain a molded body having a size of 50 mm in length x 30 mm in width x 3 mm in thickness. In this process, the true density ratio was adjusted in the range of from 46.8% to 64.7% (in this case, the density is from 1.05 to 1.45) by controlling the press pressure or the like during molding, thereby preparing plural molded bodies. The details are described in Fig. 4A and Fig. 4B.

[0066] Subsequently, each of the molded bodies was subjected to a heating treatment (baking) at 700°C for 60 minutes, whereby the Ca(OH)$_2$ in the precursor composition was dehydrated and the PVA was removed, and at the same time, the calcium carbonate in the atmosphere was decomposed to perform decarboxylation.

[0067] Then, the molded body which had been subjected to the heating treatment as described above, was set in predetermined jigs capable of supporting the 6 faces of the molded body.

Specifically, non-woven fabric made of synthetic fiber was fixed at one face of a stainless steel board and, on the non-woven fabric, two L shaped jigs made of stainless steel were arranged and placed such that the long sides and the short sides thereof face each other, respectively, as shown in Fig. 3, and then the molded body was set in the place (50 mm x 30 mm x 3 mm) surrounded by the L shaped jigs. Subsequently, another stainless steel board
fitted up with non-woven fabric at one face was prepared, and the stainless steel board with
the non-woven fabric was placed on the molded body such that the non-woven fabric face
contacts with the molded body. In this way, the molded body was set such that the two plane
faces of the molded body was supported by the gas permeable permeation wall made of
non-woven fabric, and the four side faces were supported by the L shaped jigs.

[0068] The molded body in the state in which the 6 faces thereof were covered as described
above was maintained at 200°C for 30 minutes, and was allowed to undergo a hydration
reaction. Thereafter, the molded body was heated again to a temperature of 500°C and
maintained for 15 minutes (dehydration and baking), and then the temperature was lowered
and was maintained at 200°C (hydration). In this manner, the operation of raising and
lowering the temperature to perform baking and hydration was repeated 4 times.

[0069] At last, after performing baking and undergoing the dehydration reaction, the molded
body was peeled off from the non-woven fabric and taken out, thereby obtaining a chemical
heat storage material structure. The obtained chemical heat storage material structure had
been molded to have a size of 50 mm × 30 mm × 3 mm when the chemical heat storage
material has been hydrated until maximum hydration.

[0070] The obtained chemical heat storage material structure was inserted in a pillar body,
which was formed from a stainless steel material (SUS316L) and had a size of 50 mm × 30
mm × 3 mm and a rectangular cross section, as shown in Fig. 2. The bottom portion and the
top portion in the inserting direction were closed with lid materials 13 made of SUS316L. In
this way, a chemical heat accumulator 100 was prepared.

In the chemical heat accumulator thus obtained, the volume of the chemical heat
storage material structure expands after the hydration reaction is caused and heat is generated
when using or the like, thereby forming the state of being stuck to the pillar body and the lid
materials. After the state of being stuck to the pillar body and the lid materials has been
formed, the adhesion state is maintained also at the time of shrinkage, and thus, the volume
change caused by expansion and shrinkage is suppressed.

[0071] With regard to the chemical heat accumulator prepared, the operation of raising and
lowering the temperature to perform baking and hydration was repeated 4 times. Thereafter,
the chemical heat storage material structure was taken out from the pillar body, and the
surface irregularities were measured using a pair of vernier calipers. Results are shown in
Fig. 4A and Fig. 4B. As shown in Fig. 4A, the thickness error (%) is obtained by the
following formula.

\[
\text{Thickness error (\%)} = \frac{(\text{maximum thickness } b - \text{minimum thickness } a)}{\text{target thickness}} \times 100
\]
Comparative Example 1

In the operation in Example 1, the operation of baking and hydration was repeated without setting the molded body in the predetermined jigs that supported the four side faces thereof with L shaped jigs in Example 1.

As a result, the structure had been already destructed, when the molded body was peeled off and taken out. With regard to the portion which had not been destructed, the measurement of surface irregularities was tried in a manner substantially the same as that in Example 1.

As shown in Fig. 4A and 4B, in the chemical heat accumulator of the Example, in which the chemical heat storage material structure was restricted by the jigs and pillar body, destruction due to the repeated use was not seen. Specifically, in the Example, as compared with the Comparative Example in which the preparation was tried without restriction for comparison, variation in thickness related to deflection of the surface, wrinkles, or the like was extremely small, and the form at the time of molding was maintained. This shows that collapse of the form accompanying the expansion and shrinkage when using was prevented.

As described above, with the chemical heat storage material structure being in a state in which all the 6 faces thereof were each in contact with the respective metal wall and were restricted, collapse accompanying expansion or the like during the reaction was prevented.

In the above-described embodiments and examples, Ca(OH)$_2$ and a Ca(OH)$_2$ structure having a hexahedral structure are mainly explained as the chemical heat storage material and the structure thereof. However, the present invention is not limited to the Ca(OH)$_2$ or the hexahedral structure. When a chemical heat storage material other than Ca(OH)$_2$ is used or a polyhedral structure other than the hexahedral structure is made, good results may also be obtained.


All publications, patent applications, and technical standards mentioned in this specification are herein incorporated by reference to the same extent as if each individual publication, patent application, or technical standard was specifically and individually indicated to be incorporated by reference.
1. A chemical heat accumulator comprising:
   a chemical heat storage material structure that includes a granular chemical heat
   storage material and has a polyhedral structure; and
   a structure restriction member that accommodates the chemical heat storage material
   structure and restricts each face of the accommodated chemical heat storage material structure
   at least at a portion of the face.

2. The chemical heat accumulator according to claim 1, wherein the structure
   restriction member has a hollow portion having a form which is the same as or homothetic to
   the form of the polyhedral structure of the chemical heat storage material structure, the
   chemical heat storage material structure is accommodated in the hollow portion, and each face
   of the accommodated chemical heat storage material structure is restricted by an inner wall of
   the hollow portion.

3. The chemical heat accumulator according to claim 1 or claim 2, wherein:
   the structure restriction member has a hollow portion that accommodates the
   chemical heat storage material structure; and
   each face of the chemical heat storage material structure is at least brought into
   contact with an inner wall face of the hollow portion and restricted when binding of a heat
   storing/releasing reaction medium is saturated in the chemical heat storage material structure.

4. The chemical heat accumulator according to any one of claim 1 to claim 3,
   wherein the chemical heat storage material structure has a true density ratio of from 45% to
   63%.

5. The chemical heat accumulator according to any one of claim 1 to claim 4,
   wherein the structure restriction member has a plurality of walls corresponding to the
   polyhedral structure of the chemical heat storage material structure, at least one of the
   plurality of walls is a permeation wall that permits permeation of a heat storing/releasing
   reaction medium, and at least one of the plurality of walls is a heat transfer wall having
   thermal conductivity.

6. The chemical heat accumulator according to any one of claim 1 to claim 5,
wherein the chemical heat storage material is a hydration reactive heat storage material that absorbs heat in conjunction with a dehydration reaction and releases heat in conjunction with a hydration reaction.

7. The chemical heat accumulator according to any one of claim 1 to claim 6, wherein the chemical heat storage material is a hydroxide of an alkaline earth metal.

8. A method for producing a chemical heat accumulator, the method comprising accommodating a chemical heat storing material structure that includes a granular chemical heat storage material and has a polyhedral structure, after desorbing at least a portion of a heat storing/releasing reaction medium that is bonded to the chemical heat storage material structure, in a structure restriction member that has an internal hollow and restricts each face of the chemical heat storage material structure at least at a portion of the face.

9. The method for producing a chemical heat accumulator according to claim 8, wherein:

   the structure restriction member has a hollow portion having a form which is the same as or homothetic to the form of the polyhedral structure of the chemical heat storage material structure; and

   in the accommodating of the chemical heat storage material structure in the structure restriction member, the chemical heat storage material structure is accommodated in a state in which the chemical heat storage material structure, from which at least a portion of the heat storing/releasing reaction medium has been desorbed, and the hollow portion of the structure restriction member have the same homothetic ratio in each pair of corresponding faces.
FIG. 4A

THICKNESS ERROR (\%) = 
(MAXIMUM THICKNESS b - 
MINIMUM THICKNESS a)/ 
TARGET THICKNESS \times 100

FIG. 4B

THICKNESS ERROR 
(\%)

10
5
0
-5
-10
-15

1.05 1.15 1.25 1.35 1.45

1.28 DENSITY g/mL

46.8 51.3 55.8 60.2 64.7

57.1 TRUE DENSITY 
RATIO %
## A. CLASSIFICATION OF SUBJECT MATTER

**INV. F28D20/00 C09K5/16**

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**F28D C09K**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**EPO-Internal**

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>Y</td>
<td>US 2010/252248 Al (SHIMAZU TAKASHI [JP]) ET AL) 7 October 2010 (2010-10-07)</td>
<td>1-9</td>
</tr>
<tr>
<td></td>
<td>paragraphs [0071] - [0086] , [0118] ; fig ures 1-4</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>US 2002/100369 Al (KURI IWA TAKAHI R0 [JP]) ET Al) 1 August 2002 (2002-08-01)</td>
<td>1-9</td>
</tr>
<tr>
<td></td>
<td>abstract; figures 1-10</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>JP 2010 216772 A (TOYOTA CENTRAL RES &amp; DEV) 30 September 2010 (2010-09-30)</td>
<td>1,6-8</td>
</tr>
<tr>
<td></td>
<td>abstract; figure 1</td>
<td></td>
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**[X]** Further documents are listed in the continuation of Box C.  
**[X]** See patent family annex.

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Date of the actual completion of the international search: 4 July 2012

Date of mailing of the international search report: 13/07/2012

Name and mailing address of the ISA:
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Authorized officer: Leclaire, Thomas
<table>
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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>DE 39 32 988 AI (AGENCY IND SCIENCE TECHN [JP] ; IBI DEN CO LTD [JP]) 26 April 1990 (1990-04-26) column 1, line 1 - column 4, line 36 column 7, lines 13-21; figures 1-5</td>
<td>1-5,8,9</td>
</tr>
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</table>

Form PCT/ISA/210 (continuation of second sheet) (April 2005)
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>JP 2009133588 A</td>
<td>18-06-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2010252248 A1</td>
<td>07-10-2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wo 2009069701 A1</td>
<td>04-06-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2002221297 A</td>
<td>09-08-2002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2002100369 A1</td>
<td>01-08-2002</td>
</tr>
<tr>
<td>JP 61265494 A</td>
<td>25-11-1986</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td>JP 2010216772 A</td>
<td>30-09-2010</td>
<td>NONE</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>GB 2224112 A</td>
<td>25-04-1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2097895 A</td>
<td>10-04-1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 4993481 A</td>
<td>19-02-1991</td>
</tr>
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