

TITLE OF THE INVENTION

CALCIUM SILICATE BOARD AND METHOD OF MANUFACTURING SAME

BACKGROUND OF THE INVENTION5 Field of the Invention

The present invention relates to a calcium silicate board excelling in fire resistance and non-combustibility, which is used as an interior/exterior building material, and a method of manufacturing the same.

10 Description of Background Art

A calcium silicate board is a plate-shaped product manufactured by forming a mixture of calcium silicate raw materials, fillers, reinforcing fibers, and the like using a paper-milling technique (calendering), dehydration press-
15 forming, extrusion-forming, or the like. These calcium silicate boards exhibit high specific strength, are lightweight, and have stability with respect to heat. Therefore, calcium silicate boards have been widely used as building materials such as wall materials, ceiling materials, and
20 flooring materials.

However, calcium silicate boards generally contain about 10% of water due to high hygroscopicity. Because of this, steam bursts, destruction, cracks, partial delamination, and the like tend to occur during a fire due to sudden vaporization of water
25 contained in the calcium silicate boards. Therefore, calcium silicate boards excelling in fire resistance and non-combustibility have been demanded. The fire resistance of the

calcium silicate board is such that physical destruction such as steam bursts, destruction, cracks, and partial delamination does not occur, or occurs only to a small extent. For example, fire resistance is measured according to the evaluation methods prescribed in JIS A1304 and BS (British standard) 476 Parts 20 and 22. The non-combustibility of the calcium silicate board relates to heat conductivity through the calcium silicate board. For example, non-combustibility is measured according to the evaluation methods prescribed in JIS A1321 and BS 476 Part 4. As the heat conductivity is lower, non-combustibility is evaluated as superior.

As an invention relating to a method for improving the fire resistance of the calcium silicate board, the applicant of the present invention has proposed a method of manufacturing a calcium silicate formed article in Japanese Patent Application Laid-open No. 6-305807. This method uses calcium sulfate dihydrate as a raw material for forming a calcium silicate formed article. Calcium sulfate dihydrate shrinks when converted to anhydrous calcium sulfate (II) during autoclave-curing, thereby forming minute pores in the calcium silicate formed article. This increases the aeration rate to 1.5×10^{-5} ml·cm/sec·cm²·cm H₂O or more, whereby a calcium silicate formed article excelling in explosion resistance (fire resistance) is obtained.

However, since a sufficient amount of oxygen is supplied to the inside of the calcium silicate formed article through the minute pores during a fire, organic fibers included in the

formed article as reinforcing fibers are burnt not only near the surface of the formed article, but also inside the formed article, thereby exhibiting inferior non-combustibility. For example, in the case where a test specimen formed by laminating
5 calcium silicate formed articles with an aeration rate of 1.5×10^{-5} ml·cm/sec·cm²·cm H₂O or more as the above application to a thickness of 50 mm is placed in an electric furnace at 750°C, the period of time required for the temperature at the center of the test specimen to reach 800°C from room temperature is
10 only 20 minutes or less. This clearly shows that the above calcium silicate formed article exhibits insufficient non-combustibility.

Accordingly, an object of the present invention is to provide a calcium silicate board excelling in fire resistance
15 with an aeration rate of 1.5×10^{-5} ml·cm/sec·cm²·cm H₂O or more and excelling in non-combustibility, and a method of manufacturing the same.

SUMMARY OF THE INVENTION

20 The present inventors have conducted extensive studies in view of the above situation. As a result, the present inventors have found that a calcium silicate board containing a specific amount of a carbonate substance which decomposes at 700 to 850°C can prevent the temperature inside the calcium
25 silicate board from rising. This is because the endothermic reaction of the carbonate substance occurs during a fire due to decarboxylation, whereby a calcium silicate board excelling

in non-combustibility can be obtained. This finding has led to the accomplishment of the present invention.

Specifically, the present invention provides a calcium silicate board comprising a calcium silicate hydrate crystal matrix, anhydrous calcium sulfate (II), reinforcing fibers, and a carbonate substance which decomposes at 700 to 850°C, wherein the content of the carbonate substance is 5 to 30 wt%.

The present invention also provides a method of manufacturing a calcium silicate board, comprising the steps of mixing water and a mixture containing calcium silicate raw materials, calcium sulfate dihydrate, reinforcing fibers, and a carbonate substance which decomposes at 700 to 850°C, forming the mixture into a formed product by calendering, autoclave-curing the formed product, and drying the cured product, wherein the content of the calcium sulfate dihydrate and the carbonate substance in the mixture is 12 to 45 wt% and 5 to 30 wt%, respectively.

The present invention also provides a method of manufacturing a calcium silicate board, comprising the steps of mixing water and a mixture containing calcium silicate raw materials, calcium sulfate dihydrate, reinforcing fibers, a carbonate substance which decomposes at 700 to 850°C, and wollastonite, forming the mixture into a formed product by calendering, autoclave-curing the formed product, and drying the cured product, wherein the content of calcium sulfate dihydrate, the carbonate substance, and wollastonite in the mixture is 12 to 45 wt%, 5 to 30 wt%, and 5 to 30 wt%,

respectively.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows an example of DTA results for dolomite and
5 calcium carbonate.

DETAILED DESCRIPTION OF THE INVENTION

AND PREFERRED EMBODIMENTS

The calcium silicate board according to the present
10 invention comprises a calcium silicate hydrate crystal matrix,
anhydrous calcium sulfate (II), reinforcing fibers, and a
carbonate substance which decomposes at 700 to 850°C. The
carbonate substance content is 5 to 30 wt%. The calcium
silicate board is manufactured by a method of forming a mixture
15 of calcium silicate raw materials, calcium sulfate dihydrate,
reinforcing fibers, and a carbonate substance which decomposes
at 700 to 850°C into a formed product by calendering or the like,
and autoclave-curing the formed product, for example. The
calcium silicate board according to the present invention will
20 be described below in accordance with an example of the
manufacturing method thereof.

The calcium silicate raw materials used in the present
invention form a calcium silicate hydrate crystal matrix by
autoclave-curing and mainly consist of silicic acid raw
25 materials and lime raw materials. The silicic acid raw
materials supply SiO_2 components. As examples of the silicic
acid raw materials, silica rock, diatomaceous earth, iron-

blast-furnace slag, fly ash, and the like can be given. Of these, the use of silica rock is preferable. Use of silica rock ensures that calcium sulfate dihydrate is easily dehydrated and converted to anhydrous calcium sulfate (II). Individual use
5 of diatomaceous earth tends to inhibit formation of anhydrous calcium sulfate (II). It is preferable to use diatomaceous earth in combination with silica rock in order to prevent such a disadvantage. The lime raw materials supply CaO components. As examples of the lime raw materials, calcium hydroxide,
10 calcium oxide, portland cement, and the like can be given.

Calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is dehydrated during autoclave-curing to form anhydrous calcium sulfate (II) (CaSO_4) through calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and anhydrous calcium sulfate (III). As calcium sulfate dihydrate,
15 calcium sulfate dihydrate in the form of either needle-shaped crystals or amorphous powder may be used. Of these, it is preferable to use calcium sulfate dihydrate in the form of needle-shaped crystals. Needle-shaped crystal calcium sulfate dihydrate shrinks during autoclave-curing to form
20 needle-shaped crystal anhydrous calcium sulfate (II), thereby forming slender pores by linking one another. This increases the aeration rate of the calcium silicate board. Moreover, heat shrinkage of the calcium silicate matrix can be reduced due to the needle-shaped crystal form.

25 Reinforcing fibers provide mechanical strength to the calcium silicate board. There are no specific limitations to the type of reinforcing fibers. For examples, pulp,

alkali-resistant glass fibers, carbon fibers, and organic synthetic fibers such as polypropylene fibers and aramid fibers can be given. Of these, use of pulp is preferable because pulp is economical.

5 The carbonate substance which decomposes at 700 to 850°C absorbs heat by decarboxylation at 700 to 850°C, and preferably 750 to 850°C, thereby providing non-combustibility to the calcium silicate board during a fire. As examples of the carbonate substance, dolomite, calcium carbonate, and the like
10 can be given. Dolomite is generally represented by $\text{CaCO}_3 \cdot \text{MgCO}_3$, although the composition varies depending on the production area. Use of dolomite is preferable. Dolomite exhibits superior endothermic effects owing to two endothermic reaction peaks, including a peak at about 790°C resulting from
15 decarboxylation of MgCO_3 , and a peak at about 870°C resulting from decarboxylation of CaCO_3 . The endothermic reaction peaks are measured by DTA (Differential Thermal Analysis). Figure 1 shows an example of DTA results for dolomite. In Figure 1, dolomite exhibits two endothermic reaction peaks at about 790°C
20 and at about 870°C. The entire endothermic reaction caused by decomposition with a peak at about 790°C occurs within the temperature range of 700 to 850°C. The starting point of the endothermic reaction caused by decomposition with a peak at about 870°C is within the temperature range of 700 to 850°C.
25 Specifically, dolomite decomposes at 700 to 850°C, thereby causing a sufficient endothermic reaction to occur.

It is preferable to use dolomite containing a sufficient

amount of MgCO_3 components in order to ensure that a sufficient endothermic reaction occurs at 700 to 850°C. It is particularly preferable to use dolomite having an MgO analysis value (reduced value of MgCO_3) of 13 wt% or more, and preferably 17 wt% or more.

5 Such dolomite causes a sufficient endothermic reaction to occur, thereby increasing non-combustibility of the calcium silicate board.

The average particle diameter of the carbonate substance is preferably 10 to 100 μm , and still more preferably 10 to 60
10 μm . The average particle diameter used herein refers to a median diameter (particle diameter at 50% in accumulated volume distribution). If the average particle diameter is less than 10 μm , the carbonate substance may not be sufficiently collected using a calendering machine at the time of calendering, whereby
15 non-combustibility of the resulting calcium silicate board may decrease. Moreover, this may decrease yield of the product per raw materials. If the average particle diameter exceeds 100 μm , formation of the calcium silicate hydrate crystal matrix from the calcium silicate raw materials may be hindered during
20 autoclave-curing. This causes defects to occur in the matrix, whereby the bending strength of the calcium silicate board may decrease. Calcium carbonate is known as a carbonate substance which decomposes at a high temperature. However, calcium carbonate decomposes at a relatively high temperature (about
25 900°C) as shown in Figure 1, thereby providing insufficient non-combustibility.

In addition to the above raw materials, fillers such as

wollastonite (CaSiO_3), talc, mica, pearlite, and vermiculite can be used as the raw material for the calcium silicate board of the present invention, as required. Of these, use of wollastonite, talc, and pearlite is preferable for the following reasons. Specifically, wollastonite decreases the firing shrinkage rate. Talc improves the surface properties and construction capability (nailing characteristics) of the calcium silicate board. Use of pearlite leads to reduction of weight.

When manufacturing the calcium silicate board of the present invention using the above raw materials, a mixture containing the calcium silicate raw materials, calcium sulfate dihydrate, reinforcing fibers, and the carbonate substance which decomposes at 700 to 850°C, is prepared. The proportion of calcium sulfate dihydrate in the mixture is adjusted so that the proportion of anhydrous calcium sulfate (II) in the resulting calcium silicate board is 10 to 35 wt%, and preferably 20 to 30 wt%. Specifically, the proportion of calcium sulfate dihydrate is 12 to 45 wt%, and preferably 25 to 38 wt%. If the proportion is less than 12 wt%, the aeration rate of the resulting calcium silicate board becomes less than 1.5×10^{-5} ml·cm/sec·cm²·cm H₂O, whereby fire resistance may decrease. If the proportion exceeds 45 wt%, bending strength of the resulting calcium silicate board may decrease.

The proportion of the carbonate substance which decomposes at 700 to 850°C in the mixture is 5 to 30 wt%, and preferably 10 to 20 wt%. If the proportion is less than 5 wt%,

non-combustibility of the resulting calcium silicate board may decrease. If the proportion exceeds 30 wt%, bending strength of the resulting calcium silicate board may decrease. The proportion of raw materials other than calcium sulfate
5 dihydrate and the carbonate substance which decomposes at 700 to 850°C may be appropriately determined.

The proportion of fillers optionally added to the mixture is 5 to 30 wt%, and preferably 10 to 25 wt%. If the proportion is less than 5 wt%, the effect of the addition may be insufficient.
10 If the proportion exceeds 30 wt%, the strength of the resulting calcium silicate board may decrease. In particular, the addition of wollastonite as a filler in the above range reduces the firing shrinkage rate.

After the addition of water and the like, the mixture is
15 formed into a green sheet (raw board) by calendering or the like. As the calendering method, a method using a cylinder calendering machine and the like can be given. The green sheet is then autoclave-cured while applying pressure to form a calcium silicate hydrate crystal matrix from the calcium silicate raw
20 materials. At the same time, anhydrous calcium sulfate (II) is formed by dehydration of calcium sulfate dihydrate. Autoclave-curing is carried out at a temperature of 164 to 200°C, and preferably 179 to 183°C, and a pressure of 6 to 15 kgf/cm², and preferably 9 to 10 kgf/cm², for a retention time of 3 to
25 20 hours, and preferably 8 to 12 hours. After autoclave-curing, the cured product is appropriately dried to obtain a calcium silicate board.

The calcium silicate board of the present invention obtained using the above method or the like comprises a calcium silicate hydrate crystal matrix, anhydrous calcium sulfate (II), reinforcing fibers, and a carbonate substance which decomposes
5 at 700 to 850°C. The content of the carbonate substance is 5 to 30 wt%. The calcium silicate hydrate crystal matrix is a substrate containing calcium silicate crystals as a major component, which is formed from the calcium silicate raw materials by autoclave-curing as described above.

10 Anhydrous calcium sulfate (II) is formed by the dehydration of calcium sulfate dihydrate. The content of anhydrous calcium sulfate (II) in the calcium silicate board is 10 to 35 wt%, and preferably 20 to 30 wt%. If the content of anhydrous calcium sulfate (II) is less than 10 wt%, the
15 aeration rate may decrease. If the content exceeds 35 wt%, the bending strength of the resulting calcium silicate board may decrease.

Reinforcing fibers and the carbonate substance which decomposes at 700 to 850°C do not substantially react with the
20 calcium silicate raw materials, which are allowed to remain in the calcium silicate board. The content of the carbonate substance which decomposes at 700 to 850°C in the calcium silicate board is 5 to 30 wt%, and preferably 10 to 20 wt%. If the content of the carbonate substance is less than 5 wt%,
25 non-combustibility of the calcium silicate board may decrease. If the content exceeds 30 wt%, bending strength of the calcium silicate board may decrease.

Fillers optionally included in the calcium silicate board of the present invention do not substantially react with the calcium silicate raw materials, which are allowed to remain in the calcium silicate board. The content of fillers in the calcium silicate board is 5 to 30 wt%, and preferably 10 to 25 wt%. If the content is less than 5 wt%, the effect of addition may be insufficient. If the content exceeds 30 wt%, the strength of the resulting calcium silicate board may decrease. In particular, the addition of wollastonite as a filler in the above range reduces the firing shrinkage rate.

Bending strength of the calcium silicate board of the present invention is 100 kgf/cm² or more, preferably 120 kgf/cm² or more, and still more preferably 120 to 200 kgf/cm². The aeration rate of the calcium silicate board measured according to BS 1902 Part 1A is 1.5×10^{-5} ml·cm/sec·cm²·cm H₂O or more, and preferably 2.0×10^{-5} ml·cm/sec·cm²·cm H₂O or more. The heat linear shrinkage rate of the calcium silicate board is within the range of $\pm 2.0\%$, and preferably $\pm 1.8\%$. The calcium silicate board does not cause steam bursts or cracks to occur in the fire resistance test according to BS 476 Part 22. In the non-combustibility test according to BS 476 Part 4, rise in temperature at the center of the test specimen and inside the furnace is respectively less than 50°C. The calcium silicate boards according to the present invention can be used as building materials such as wall materials, ceiling materials, and flooring materials, and the like.

EXAMPLES

The present invention will be described in more detail by examples, which should not be construed as limiting the present invention.

5 Example 1

36 parts by weight of calcium silicate matrix raw materials (silica rock: 8 parts by weight, diatomaceous earth: 7 parts by weight, calcium hydroxide: 18 parts by weight, portland cement: 3 parts by weight), 24 parts by weight of
10 wollastonite, 32 parts by weight of calcium sulfate dihydrate, 5 parts by weight of pulp, and 10 parts by weight of dolomite were mixed according to the composition of the raw materials shown in Table 1. The mixture was calendered using a cylinder calendering machine according to a conventional method to
15 obtain a green sheet (raw board) with a thickness of 9 mm having the above composition. The green sheet was autoclave-cured at a temperature of 179°C and a pressure of 9 kgf/cm² for a retention time of 11 hours, and then dried using a hot blast at 120 to 140°C to obtain a calcium silicate board. The composition of
20 the resulting calcium silicate board is shown in Table 2.

Bulk density, bending strength, aeration rate, and heat linear shrinkage rate of the resulting calcium silicate board were measured. Fire resistance and non-combustibility were evaluated. The aeration rate was measured according to BS 1902
25 Part 1A. Fire resistance and non-combustibility were evaluated according to BS 476 Part 22 and BS 476 Part 4, respectively. Bending strength and heat shrinkage rate were

measured as follows.

Bending strength:

Load was applied to the calcium silicate board vertically to the orientation direction of the reinforcing fiber (pulp).

- 5 The bending strength was determined by dividing the stress at a point where the calcium silicate board broke by the cross section of the calcium silicate board.

Heat linear shrinkage rate:

- 10 The calcium silicate board was heated at 1000°C for 3 hours, and then cooled to room temperature. The dimensional change during the heating was measured.

The evaluation results are shown in Table 3.

TABLE 1

15

Composition of raw materials	Example			Comparative Example		Reference Example
	1	2	3	1	2	1
Calcium silicate raw materials						
Silica rock	8	8	8	16	20	8
Diatomaceous earth	7	6	6	7	8	6
Calcium hydroxide	18	17	17	26	26	17
Portland cement	3	3	3	3	4	3
Wollastonite	24	23	23	13	19	23
Calcium sulphate dihydrate	32	25	25	38	0	25
Pulp ^{*1}	5	5	5	5	5	5
Dolomite ^{*2}	10	18	-	-	-	-
Dolomite ^{*3}	-	-	18	-	-	-
Calcium carbonate ^{*4}	-	-	-	-	18	18
Total	107	105	105	108	100	105

* The unit used in Table 1 is "part(s) by weight".

^{*1} Pulp which was beaten until the amount of water drained was 300 ml according to JIS P8121 "Canadian standard freeness

test" was used.

*² Average particle diameter (median diameter): 50 μm , MgO
content: 18 wt%

*³ Average particle diameter (median diameter): 15 μm , MgO
5 content: 14 wt%

*⁴ Average particle diameter (median diameter): 15 μm

TABLE 2

Composition of calcium silicate board	Example			Comparative Example		Reference Example
	1	2	3	1	2	1
Calcium silicate hydrate crystal matrix	36	34	34	52	58	34
Wollastonite	24	23	23	13	19	23
Anhydrous calcium sulphate (II)	25	20	20	30	0	20
Pulp	5	5	5	5	5	5
Dolomite	10	18	18	-	-	-
Calcium carbonate	-	-	-	-	18	18
Total	100	100	100	100	100	100

* The unit used in Table 2 is "part(s) by weight".

TABLE 3

Properties of calcium silicate board	Example			Comparative Example		Reference Example
	1	2	3	1	2	1
Bulk density (g/cm ³)	0.91	0.91	0.90	0.84	0.90	0.91
Bending strength (kgf/cm ²)	172	180	175	191	185	178
Aeration rate ($\times 10^{-5}$ ml·cm/sec·cm ² ·cm H ₂ O)	2.4	2.6	2.5	1.6	0.2	1.8
Heat linear shrinkage rate (%)	1.6	1.7	1.7	1.6	5.0	1.7
Fire resistance test						
Steam bursts	None	None	None	None	Occurred	None
Cracks	None	None	None	None	Occurred	None
Non-combustibility test						
Temperature rise at center of specimen (°C)	39	3	0	122	35	72
Non-combustibility evaluation ^{*1}	Good	Good	Good	Bad	Good	Bad
Temperature rise inside furnace (°C)	47	40	45	48	48	47
Non-combustibility evaluation ^{*1}	Good	Good	Good	Good	Good	Good

*1 Evaluation standard: Good = less than 50°C, Bad = 50°C or more

Examples 2 and 3, Comparative Examples 1 and 2, and Reference Example 1

A calcium silicate board was obtained in the same manner as in Example 1 except for changing the composition of the raw materials as shown in Table 1. The composition of the resulting calcium silicate board is shown in Table 2. The calcium silicate board was evaluated in the same manner as in Example 1. The evaluation results are shown in Table 3.

According to the present invention, a calcium silicate board excelling in fire resistance with an aeration rate of 1.5×10^{-5} ml·cm/sec·cm²·cm H₂O or more and excelling in non-combustibility can be obtained.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

WHAT IS CLAIMED IS:

1. A calcium silicate board comprising a calcium silicate hydrate crystal matrix, anhydrous calcium sulfate (II),
5 reinforcing fibers, and a carbonate substance which decomposes at 700 to 850°C, wherein the content of the carbonate substance is 5 to 30 wt%.
2. The calcium silicate board according to claim 1, wherein the carbonate substance is dolomite.
- 10 3. The calcium silicate board according to claim 2, wherein the dolomite contains 13 wt% or more of MgO.
4. The calcium silicate board according to claim 1 or 2, wherein the carbonate substance has an average particle diameter of 10 to 100 μm .
- 15 5. The calcium silicate board according to claim 1 or 2, having an aeration rate of $1.5 \times 10^{-5} \text{ ml} \cdot \text{cm} / \text{sec} \cdot \text{cm}^2 \cdot \text{cm H}_2\text{O}$ or more, bending strength of 100 kgf/cm² or more, and a heat linear shrinkage rate within the range of $\pm 2.0\%$.
- 20 6. A method of manufacturing a calcium silicate board, comprising the steps of: mixing water and a mixture containing calcium silicate raw materials, calcium sulfate dihydrate, reinforcing fibers, and a carbonate substance which decomposes at 700 to 850°C; forming the mixture into a formed product by calendering; autoclave-curing the formed product; and drying
25 the cured product; wherein the content of calcium sulfate dihydrate and the carbonate substance in the mixture is 12 to 45 wt% and 5 to 30 wt%, respectively.



7. A method of manufacturing a calcium silicate board,
comprising the steps of: mixing water and a mixture containing
calcium silicate raw materials, calcium sulfate dihydrate,
reinforcing fibers, a carbonate substance which decomposes at
5 700 to 850°C, and wollastonite; forming the mixture into a formed
product by calendering; autoclave-curing the formed product;
and drying the cured product; wherein the content of calcium
sulfate dihydrate, the carbonate substance, and wollastonite
in the mixture is 12 to 45 wt%, 5 to 30 wt%, and 5 to 30 wt%,
10 respectively.

