

US010385801B2

(12) **United States Patent**
Kobayashi et al.

(10) **Patent No.:** **US 10,385,801 B2**
(45) **Date of Patent:** ***Aug. 20, 2019**

(54) **HEAT-INSULATION FILM, AND HEAT-INSULATION-FILM STRUCTURE**

(71) Applicant: **NGK INSULATORS, LTD.**,
Aichi-prefecture (JP)

(72) Inventors: **Hiroharu Kobayashi**, Nagoya (JP);
Takahiro Tomita, Nagoya (JP);
Akinobu Oribe, Nagoya (JP)

(73) Assignee: **NGK INSULATORS, LTD.**,
Aichi-prefecture (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 88 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **15/157,534**

(22) Filed: **May 18, 2016**

(65) **Prior Publication Data**

US 2016/0258383 A1 Sep. 8, 2016

Related U.S. Application Data

(63) Continuation of application No. PCT/JP2014/079262, filed on Nov. 4, 2014, and a (Continued)

(30) **Foreign Application Priority Data**

Jun. 20, 2012 (JP) 2012-138784
Nov. 19, 2013 (JP) 2013-239274

(51) **Int. Cl.**
C08K 7/24 (2006.01)
B32B 5/16 (2006.01)
(Continued)

(52) **U.S. Cl.**
CPC **F02F 3/12** (2013.01); **B32B 5/16** (2013.01); **B32B 5/30** (2013.01); **B32B 9/005** (2013.01);
(Continued)

(58) **Field of Classification Search**
CPC B32B 3/10; B32B 3/14; B32B 3/18; B32B 3/22; B32B 5/16; B32B 5/22; B32B 5/30;
(Continued)

(56) **References Cited**

U.S. PATENT DOCUMENTS

2,704,105 A * 3/1955 Robinson H01B 3/002
423/328.2
3,225,131 A * 12/1965 Conklin H01B 7/02
162/138

(Continued)

FOREIGN PATENT DOCUMENTS

DE 19625492 C1 1/1998
JP 60-159496 A 8/1985

(Continued)

OTHER PUBLICATIONS

English translation of the Written Opinion for PCT Patent App. No. PCT/JP2014/079262 (dated Feb. 3, 2015).

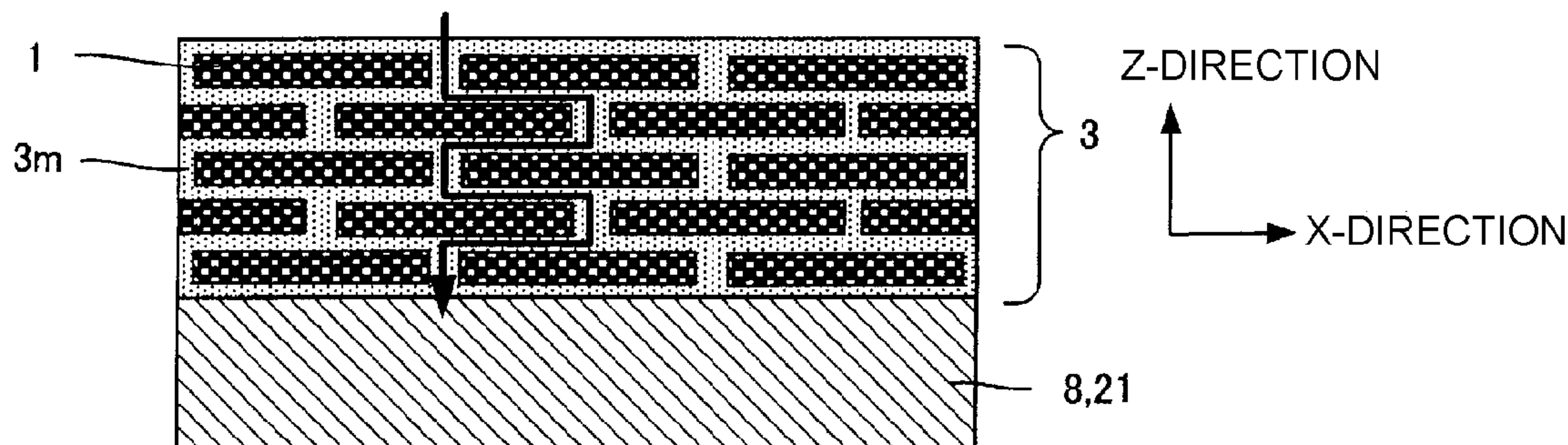
(Continued)

Primary Examiner — Z. Jim Yang
(74) *Attorney, Agent, or Firm* — Cermak Nakajima & McGowan LLP; Tomoko Nakajima

(57) **ABSTRACT**

In a heat-insulation film, porous plate fillers are dispersed in a matrix to bond the porous plate fillers. The porous plate filler includes plates having an aspect ratio of 3 or more, a minimum length of 0.1 to 50 μm and a porosity of 20 to 90%. In the heat-insulation film, a volume ratio between the porous plate fillers and the matrix is from 50:50 to 95:5. In the heat-insulation film in which the porous plate fillers are used, a length of a heat transfer path increases and a thermal conductivity can be decreased, as compared with a case where spherical or cubic fillers are used.

11 Claims, 4 Drawing Sheets



Related U.S. Application Data

continuation-in-part of application No. 14/574,564, filed on Dec. 18, 2014, which is a continuation of application No. PCT/JP2013/067006, filed on Jun. 20, 2013.

(51) **Int. Cl.**

F02F 3/12 (2006.01)
B32B 5/30 (2006.01)
C04B 38/00 (2006.01)
F02F 1/00 (2006.01)
F02F 1/24 (2006.01)
F02F 1/42 (2006.01)
B32B 9/00 (2006.01)
B32B 27/20 (2006.01)
C04B 35/48 (2006.01)

(52) **U.S. Cl.**

CPC **B32B 27/20** (2013.01); **C04B 35/48** (2013.01); **C04B 38/00** (2013.01); **C08K 7/24** (2013.01); **F02F 1/00** (2013.01); **F02F 1/24** (2013.01); **F02F 1/42** (2013.01); **B32B 2264/102** (2013.01); **B32B 2307/304** (2013.01); **B32B 2307/3065** (2013.01); **B32B 2307/554** (2013.01); **C01P 2004/20** (2013.01); **C01P 2004/22** (2013.01); **C04B 2201/30** (2013.01); **C04B 2201/32** (2013.01); **C04B 2235/3246** (2013.01); **C04B 2235/6025** (2013.01); **F02F 2001/249** (2013.01)

(58) **Field of Classification Search**

CPC Y10T 428/2982; Y10T 428/2991–2998; Y10T 428/16; Y10T 428/161; Y10T 428/162; Y10T 428/163–168; Y10T 428/17; Y10T 428/18–187

See application file for complete search history.

(56)

References Cited

U.S. PATENT DOCUMENTS

4,660,861 A * 4/1987 Argy F16L 59/029
 138/149
 4,919,995 A 4/1990 Joly
 5,072,886 A * 12/1991 Morrison B01J 23/04
 241/1
 5,167,988 A * 12/1992 Yano C23D 3/00
 428/324
 5,665,810 A * 9/1997 Patchett B29C 49/00
 524/449
 5,932,309 A * 8/1999 Smith B32B 27/20
 428/373
 6,165,594 A * 12/2000 Moh G09F 3/02
 428/207
 7,514,145 B2 * 4/2009 Akioka C08J 3/122
 425/6
 2003/0038278 A1 * 2/2003 Ishihara H01L 23/15
 252/500
 2004/0052976 A1 * 3/2004 Buczek B05D 1/40
 427/598
 2005/0208338 A1 * 9/2005 Fernie C23C 30/00
 428/701
 2005/0287348 A1 * 12/2005 Faler B32B 5/18
 428/315.5
 2006/0153769 A1 * 7/2006 Robinson C01F 7/02
 423/625
 2006/0231201 A1 * 10/2006 Smith B32B 5/16
 156/307.3
 2006/0257662 A1 * 11/2006 Bujard C09C 1/0015
 428/404
 2007/0098803 A1 * 5/2007 Dobbs A61K 9/14
 424/489

2007/0259185 A1 * 11/2007 Hingst B32B 18/00
 428/408
 2008/0058459 A1 * 3/2008 Brand C08K 9/04
 524/493
 2008/0107856 A1 * 5/2008 Argoitia C09C 1/0015
 428/43
 2008/0171811 A1 * 7/2008 Guiselin B01J 21/04
 523/216
 2008/0280140 A1 * 11/2008 Ferrari C25F 3/12
 428/402
 2009/0238982 A1 * 9/2009 Florent C03C 17/007
 427/387
 2010/0159329 A1 * 6/2010 Sugiura H01M 4/131
 429/231.4
 2010/0266847 A1 * 10/2010 Wickert B01J 20/28016
 428/402
 2010/0277872 A1 * 11/2010 Ito H01L 23/3737
 361/715
 2011/0027549 A1 * 2/2011 Boutaghou B24D 18/0054
 428/206
 2011/0040013 A1 * 2/2011 Tsapatsis B01D 69/148
 524/430
 2011/0076480 A1 * 3/2011 Skoog C04B 26/30
 428/312.6
 2011/0114870 A1 * 5/2011 Yang C04B 26/10
 252/62
 2012/0028018 A1 * 2/2012 Cho C03C 14/004
 428/220
 2012/0171438 A1 * 7/2012 Roberts, III B82Y 30/00
 428/206
 2012/0189871 A1 * 7/2012 Hecht F01D 5/288
 428/697
 2013/0203328 A1 * 8/2013 Givot B24D 5/02
 451/548
 2013/0260139 A1 * 10/2013 Kamada C03C 17/007
 428/328
 2013/0288055 A1 * 10/2013 Doshita C01B 33/12
 428/402
 2013/0289133 A1 * 10/2013 Doshita C01B 33/12
 514/769
 2014/0050925 A1 * 2/2014 Sueda C01G 9/02
 428/402
 2014/0212655 A1 * 7/2014 Matsuno G02B 5/208
 428/323
 2014/0348559 A1 * 11/2014 Miyahara G03G 15/2057
 399/333
 2015/0010721 A1 * 1/2015 Tanida H05K 5/0086
 428/34.5
 2015/0104626 A1 * 4/2015 Tomita C09D 1/00
 428/402
 2015/0118482 A1 * 4/2015 Kagawa C04B 35/111
 428/188
 2015/0329431 A1 * 11/2015 Deville C04B 35/111
 428/188
 2016/0025035 A1 * 1/2016 Kadoshima F16J 1/01
 252/62
 2016/0185074 A1 * 6/2016 Kagawa H01L 23/3737
 428/341

FOREIGN PATENT DOCUMENTS

JP 62-57869 A2 12/1987
 JP 63-215497 A 9/1988
 JP 08-156173 A 6/1996
 JP 11-270778 A 10/1999
 JP 2008-200922 A 9/2008
 JP 2011-052630 A 3/2011
 JP 2011-220419 11/2011
 JP WO 2012096171 A1 * 7/2012 C01B 33/12
 JP WO 2013191263 A1 * 12/2013 C09D 1/00
 WO WO2011/027214 A2 3/2011

(56)

References Cited

FOREIGN PATENT DOCUMENTS

OTHER PUBLICATIONS

Extended European Search Report for European Patent App. No. 14863720.0 (dated Aug. 28, 2017).

International Search Report and Written Opinion for PCT Patent App. No. PCT/JP2014/079262 (dated Feb. 3, 2015), with English translation of the ISR.

U.S. Appl. No. 14/574,564, Tomita et al., filed Dec. 18, 2014.

* cited by examiner

FIG.1

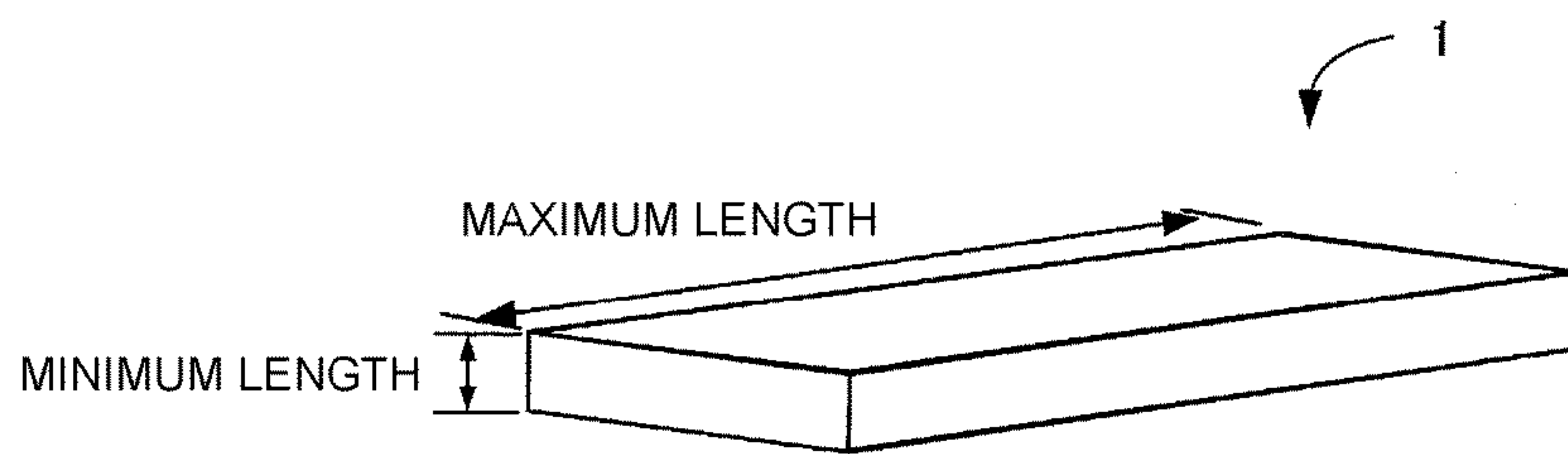


FIG.2

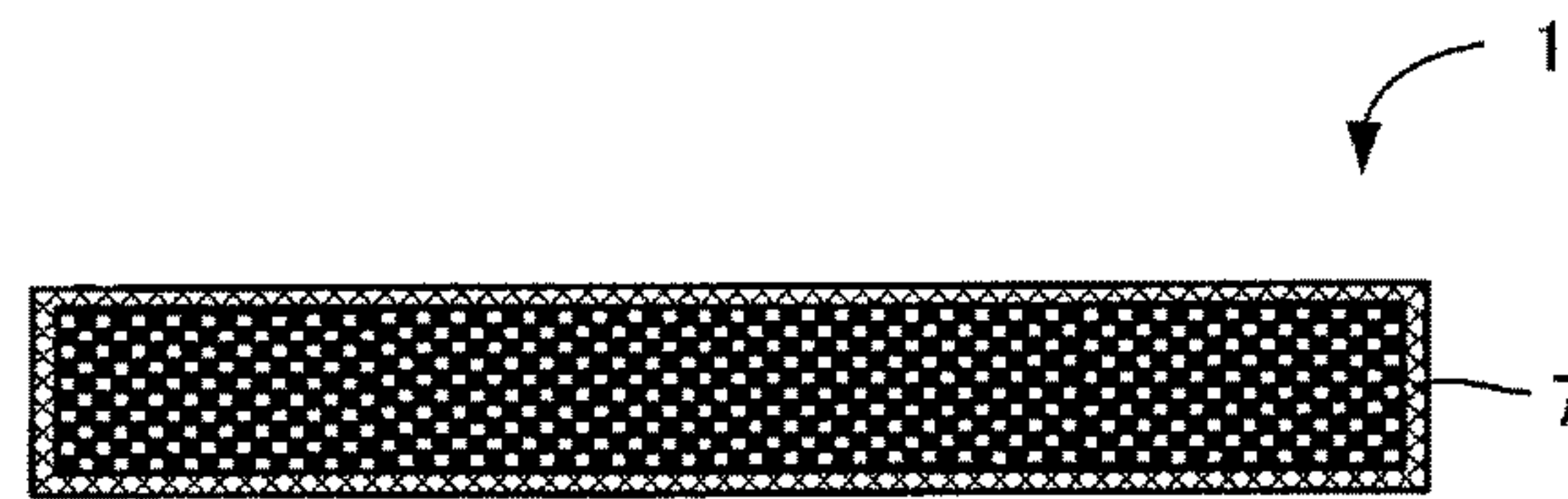


FIG.3A

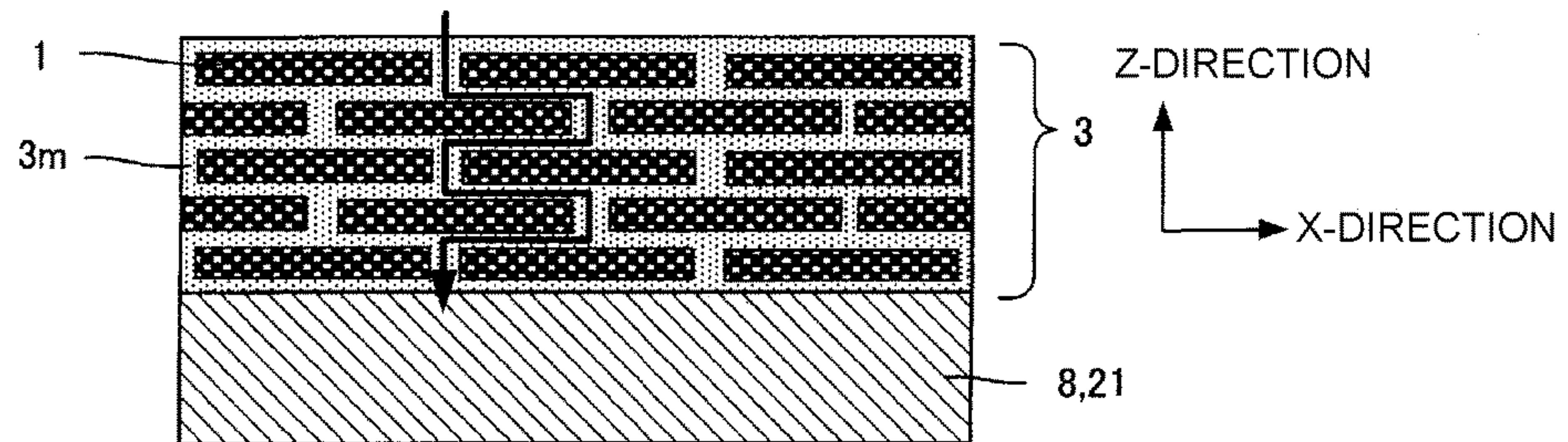


FIG.3B

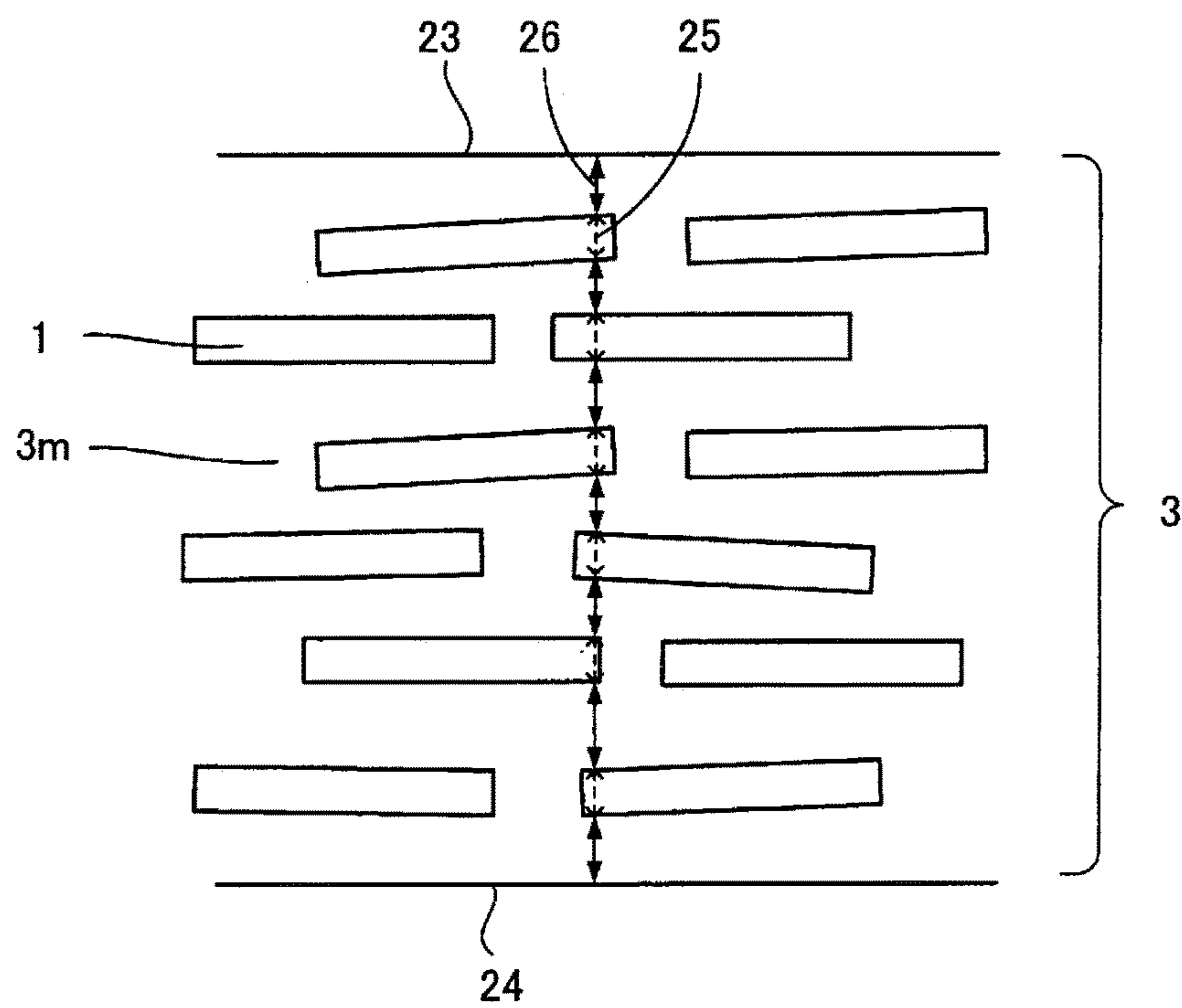


FIG.4

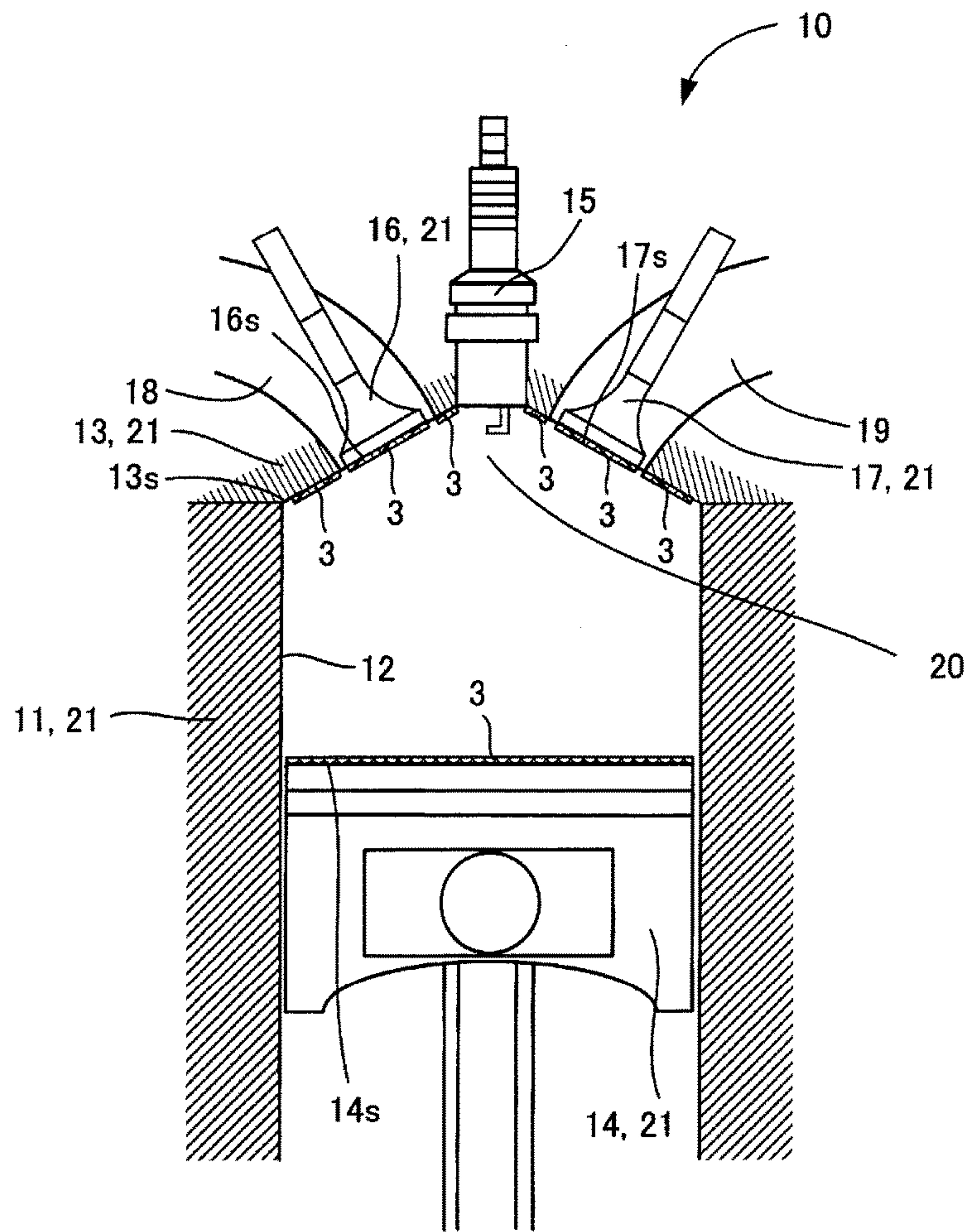


FIG.5A

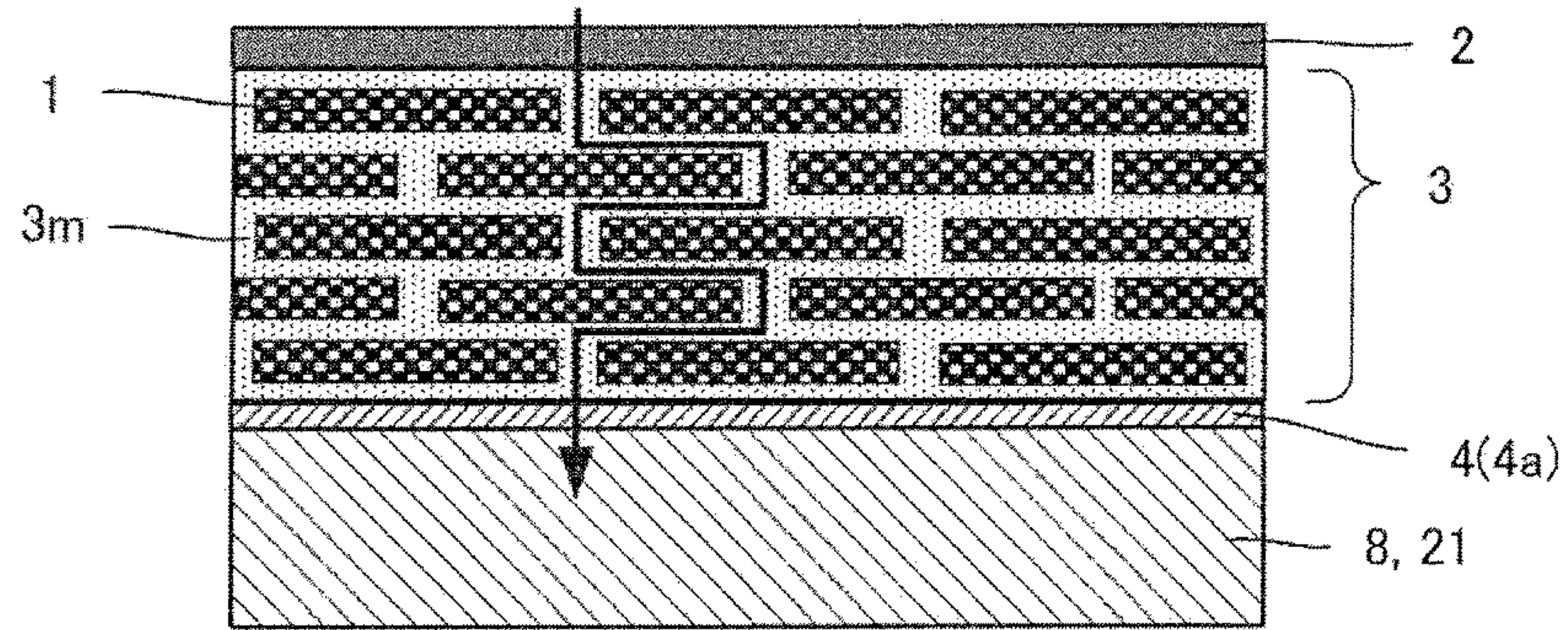


FIG.5B

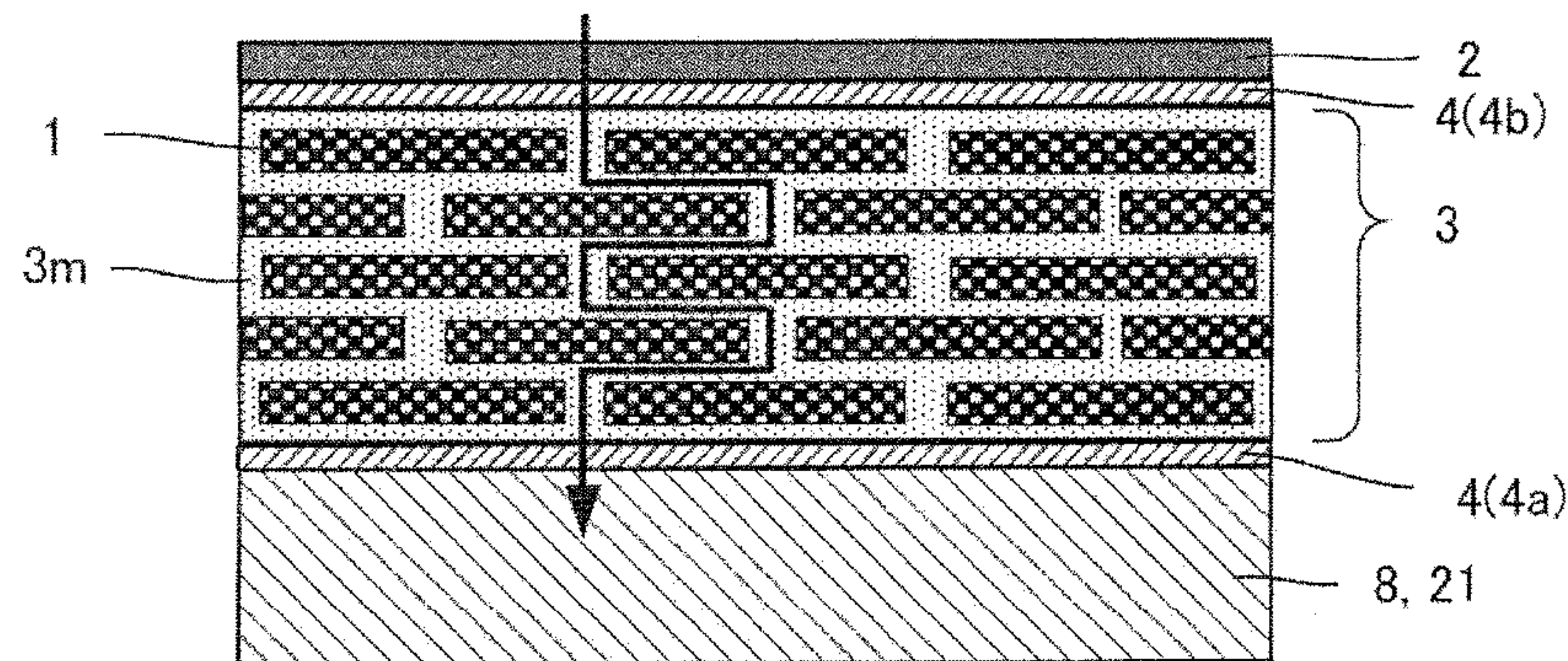
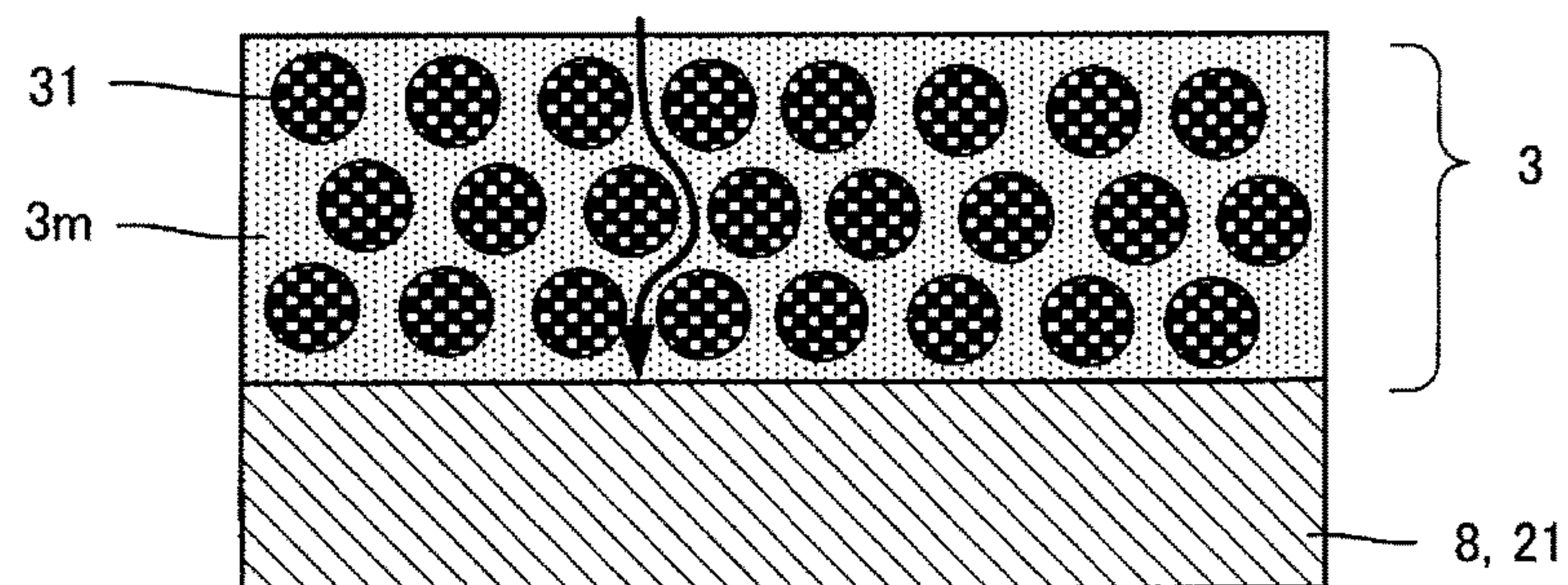


FIG.6



1

**HEAT-INSULATION FILM, AND
HEAT-INSULATION-FILM STRUCTURE****CROSS-REFERENCE TO RELATED
APPLICATIONS**

This application is a continuation of international application PCT/JP2014/079262, filed Nov. 4, 2014, which claims priority from Japanese application JP2013-239274, filed Nov. 19, 2013. This application is also a continuation-in-part of pending U.S. application Ser. No. 14/574,564, filed Dec. 12, 2014, which is a continuation of international application PCT/JP2013/067006, filed Jun. 20, 2013, which claims priority from Japanese priority application JP2012-138784, filed Jun. 20, 2012. The contents of these applications are incorporated herein in their entirety.

TECHNICAL FIELD

The present invention relates to a heat-insulation film in which a heat insulation effect improves, and a heat-insulation-film structure.

BACKGROUND ART

There is required a heat-insulation film which is formed on a surface to improve a heat insulation efficiency and flame retardance. In Patent Document 1, a coating film is disclosed which has a high surface hardness and can prevent the surface from being damaged. The coating film is formed by dispersing hollow particles made of silica shells in a binder. By a wear resistance and high hardness of the hollow particles made of the silica shells, the wear resistance of a substrate on which the coating film is formed can improve. Additionally, the flame retardance can improve due to heat insulation properties of the hollow particles made of the silica shells.

In Patent Document 2, there is disclosed an internal combustion engine including a structural member in which a heat insulation performance improves. In the internal combustion engine of Patent Document 2, a heat-insulation material is disposed adjacent to an inner wall of an exhaust passage, and a high-temperature operative gas (an exhaust gas) flows along through channels made of the heat-insulation material. In the heat-insulation material, MSS (mesoporous silica sphere) particles having an average particle diameter of 0.1 to 3 μm are laminated in a state where the respective particles are densely bonded to one another via a bonding material. In the MSS particles, an infinite number of mesopores having an average pore diameter of 1 to 10 nm are formed.

CITATION LIST

Patent Documents

[Patent Document 1] JP-A-2008-200922
[Patent Document 2] JP-A-2011-52630

SUMMARY OF THE INVENTION

Problem to be Solved by the Invention

in Patent Document 1, hollow particles made of silica shells having outer diameters of about 30 to 300 nm are substantially uniformly dispersed in an organic resin binder, an inorganic polymer binder or an organic/inorganic com-

2

posite binder, and hence heat insulation properties of a coating film can be obtained. Additionally, in Patent Document 2, there are densely laminated MSS (mesoporous silica sphere) particles having mesopores in which an average particle diameter is from 0.1 to 3 μm and an average pore diameter is from 1 to 10 nm, and hence a heat insulation performance is high.

The hollow particles or porous particles for use in Patent Document 1 or 2 have a low thermal conductivity, and hence it is presumed that a matrix portion except the particles (a phase which bonds the particles to each other) becomes a main heat transfer path. These particles are cubic or spherical, and hence a path of heat comparatively shortens as shown in FIG. 6, and the thermal conductivity does not sufficiently decrease.

Objects of the present invention are to provide a heat-insulation film in which a heat insulation effect improves, and to provide a heat-insulation-film structure.

Means for Solving the Problem

The present inventors have found that the above problems can be solved by providing a heat-insulation film in which porous plate fillers are dispersed in a matrix to bond the porous plate fillers and a volume ratio between the porous plate fillers and the matrix is in a predetermined range. That is, according to the present invention, there are provided a heat-insulation film and a heat-insulation-film structure as follows.

[1] A heat-insulation film in which porous plate fillers including plates having an aspect ratio of 3 or more, a minimum length of 0.1 to 50 μm and a porosity of 20 to 90% are dispersed in a matrix to bond the porous plate fillers, and a volume ratio between the porous plate fillers and the matrix is from 50:50 to 95:5.

[2] The heat-insulation film according to the above [1], wherein when a line is drawn from a first surface to a second surface on an opposite side to the first surface in a thickness direction in a cross section parallel to the thickness direction, a ratio between a sum of lengths of line segments present on the porous plate fillers and a sum of lengths of line segments present on the matrix is from 50:50 to 95:5.

[3] The heat-insulation film according to the above [1] or [2], wherein a thermal conductivity of the porous plate filler is 1 W/(m·K) or less.

[4] The heat-insulation film according to any one of the above [1] to [3], wherein a heat capacity of the porous plate filler is from 10 to 3000 kJ/(m³·K).

[5] The heat-insulation film according to any one of the above [1] to [4], wherein the porous plate filler includes pores of a nanoorder.

[6] The heat-insulation film according to any one of the above [1] to [5], wherein the porous plate filler includes a metal oxide.

[7] The heat-insulation film according to any one of the above [1] to [6], wherein the porous plate filler includes particles having particle diameters of 1 nm to 10 μm .

[8] The heat-insulation film according to any one of the above [1] to [7], wherein a heat capacity is 1500 kJ/(m³·K) or less.

[9] The heat-insulation film according to any one of the above [1] to [8], wherein a thermal conductivity is 1.5 W/(m·K) or less.

[10] A heat-insulation-film structure in which the heat-insulation film according to any one of the above [1] to [9] is formed on a substrate.

[11] The heat-insulation-film structure according to the above [10], which has, on the surface of the heat-insulation film, a surface dense layer including ceramics and/or glass and having a porosity of 5% or less.

[12] The heat-insulation-film structure according to the above [11], which includes a buffer bonding layer having a thickness smaller than the heat-insulation film, between the substrate and the heat-insulation film and/or between the heat-insulation film and the surface dense layer.

Effect of the Invention

In a heat-insulation film which includes porous plate fillers including plates having an aspect ratio of 3 or more, a minimum length of 0.1 to 50 μm and a porosity of 20 to 90% and in which a volume ratio between the porous plate fillers and the matrix is from 50:50 to 95:5, a length of a heat transfer path increases and a thermal conductivity can be decreased as compared with a case where spherical or cubic fillers are used. Consequently, even a thin heat-insulation film has a heat insulation effect higher than before. Additionally, a bonding area between the porous plate fillers via the matrix is larger as compared with a case where the spherical fillers or the like are used, and hence a strength can increase. Furthermore, the porous plate fillers are the plates, and hence concavity and convexity are hard to be formed on the outermost surface of the heat-insulation film, and particle drop of the porous plate fillers, i.e., deficiency of the heat-insulation film can be prevented.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view showing one embodiment of a porous plate filler;

FIG. 2 is a schematic view showing another embodiment of the porous plate filler;

FIG. 3A is a schematic view showing one embodiment of a heat-insulation film and a heat-insulation-film structure of the present invention;

FIG. 3B is a schematic view to explain directing of a ratio by a line;

FIG. 4 is a schematic view showing one embodiment of an engine;

FIG. 5A is a schematic view showing another embodiment of the heat-insulation film and the heat-insulation-film structure of the present invention;

FIG. 5B is a schematic view showing still another embodiment of the heat-insulation film and the heat-insulation-film structure of the present invention; and

FIG. 6 is a schematic view showing a heat-insulation film and a heat-insulation-film structure of a comparative example.

MODE FOR CARRYING OUT THE INVENTION

Hereinafter, embodiments of the present invention will be described with reference to the drawings. The present invention is not limited to the following embodiments, and change, modification and improvement can be added without departing from the gist of the present invention.

1. Porous Plate Filler

FIG. 1 shows one embodiment of a porous plate filler 1. The porous plate filler 1 is a plate having an aspect ratio of 3 or more, its minimum length is from 0.1 to 50 μm , and a porosity is from 20 to 90%. The porosity is more preferably from 40 to 85% and further preferably from 50 to 80%. A thermal conductivity of the porous plate filler 1 can be

decreased by setting the porosity to 20% or more, and a strength thereof can be acquired by setting the porosity to 90% or less. In the present description, the porosity is obtained by the following equation.

$$\text{Porosity (\%)} = (1 - (\text{apparent particle density} / \text{true density})) \times 100$$

In the above equation, the apparent particle density is measured by a liquid immersion method in which mercury is used. Additionally, the true density is measured by pycnometry after sufficiently grinding the porous plate filler.

Additionally, in the present description, the aspect ratio is defined by a maximum length/a minimum length of the porous plate filler 1. Here, the maximum length is a length maximized when particles (the porous plate filler 1) are sandwiched between a pair of parallel surfaces. Additionally, the minimum length is a length minimized when the particles are similarly sandwiched between the pair of parallel surfaces, and corresponds to a so-called thickness in a case where the filler is a flat plate. The porous plate filler 1 which is the plate includes not only a flat plate (the plate which is flat and is not bent) but also a bent flat plate and a plate having a thickness (the minimum length) which is not constant, as long as the aspect ratio is 3 or more and the minimum length is from 0.1 to 50 μm . Additionally, the filler may have a shape such as a fibrous shape, a needle shape or a billet shape. Among these shapes, the porous plate filler 1 is preferably the flat plate. Additionally, a surface shape of the plate may be any shape such as a square, a quadrangular shape, a triangular shape, a hexagonal shape or a round shape. That is, the porous plate filler 1 may have any shape as long as the filler is the flat plate.

It is preferable that the aspect ratio of the porous plate filler 1 is 3 or more. The larger the aspect ratio is, the longer a heat transfer path becomes and the lower the thermal conductivity of the heat-insulation film 3 becomes, because the heat transfer path is deflected when the heat-insulation film 3 is formed. However, when the aspect ratio is excessively large, it becomes difficult to handle the filler during manufacturing, and yield might be deteriorated. For example, when the minimum length is decreased to increase the aspect ratio, the strength might not sufficiently be obtained. On the other hand, when the maximum length is increased, the porous plate filler 1 might become large and be damaged. Consequently, the aspect ratio is more preferably 3 or more and 50 or less, further preferably 3.5 or more and 40 or less, and most preferably 4 or more and 30 or less.

When the porous plate filler 1 is included in the heat-insulation film 3 as described later, a heat insulation effect can improve.

It is preferable that the porous plate filler 1 includes pores of a nanoorder. Here, the nanoorder indicates a size of 1 nm or more and less than 1000 nm. When the pores of such a range are included, the heat insulation effect can improve.

It is preferable that the porous plate filler 1 includes pores having pore diameters of 10 to 500 nm. One filler may have one pore (a hollow particle) or a large number of pores (porous particles). The hollow particle is a particle in which one closed pore is present. The porous particles are particles having porous inner portions, i.e., the particles including the pores except the hollow particles. The porous plate filler 1 includes not only the porous particles but also the hollow particles. That is, the number of the pores to be included in the porous plate filler 1 may be one or large, and the pore may be the closed pore or an open pore. When the porous

plate filler **1** having such pores is included in the heat-insulation film **3**, the heat insulation effect can improve due to the pores.

Examples of a material of the porous plate filler **1** include hollow plate-shaped glass and hollow plate-shaped ceramic. Additionally, the examples of the material include mesoporous silica, mesoporous titania, mesoporous zirconia, and Shirasu balloons. Alternatively, an example of the filler is also a porous plate filler obtained by an after-mentioned manufacturing method.

It is preferable that the porous plate filler **1** includes a metal oxide, and it is further preferable that the porous plate filler is constituted only of the metal oxide. This is because, when the metal oxide is included, ion bonding properties between a metal and oxygen are strong and hence the thermal conductivity is easy to decrease as compared with a non-oxide (e.g., a carbide or a nitride) of the metal.

In the porous plate filler **1**, it is preferable that the metal oxide is an oxide of one selected from the group consisting of elements such as Zr, Y, Al, Si, Ti, Nb, Sr, La, Hf, Ce, Gd, Sm, Mn, Yb, Er and Ta or a complex oxide of two or more selected from the group. When the metal oxide is the oxide or the complex oxide of these elements, heat conduction is hard to be caused by lattice vibration (phonons) which is a main factor of the heat conduction. An example of the material of the porous plate filler **1** is specifically a material obtained by adding Gd_2O_3 , Yb_2O_3 , Er_2O_3 or the like to $ZrO_2-Y_2O_3$. Further specifically, the examples of the material include $ZrO_2-HfO_2-Y_2O_3$, $ZrO_2-Y_2O_3-La_2O_3$, $ZrO_2-HfO_2-Y_2O_3-La_2O_3$, $HfO_2-Y_2O_3$, $CeO_2-Y_2O_3$, $Gd_2Zr_2O_7$, $Sm_2Zr_2O_7$, $LaMnAl_{11}O_{19}$, YTa_3O_9 , $Y_{0.7}La_{0.3}Ta_3O_9$, $Y_{1.08}Ta_{2.76}Zr_{0.24}O_9$, $Y_2Ti_2O_7$, and $LaTa_3O_9$.

The porous plate filler **1** may be an inorganic material, an organic material, or a composite material of the inorganic material and the organic material. Above all, it is preferable that the material is an inorganic material such as zirconia, partially stabilized zirconia (e.g., yttria partially stabilized zirconia), completely stabilized zirconia (e.g., yttria completely stabilized zirconia), yttrium oxide, alumina, silica, titania, niobium oxide, strontium oxide, lanthanum oxide, zirconium, yttria, aluminum, silicon, titanium, niobium, strontium, lanthanum, rare earth zirconate (e.g., lanthanum zirconate), rare earth silicate (e.g., yttrium silicate), niobate (e.g., strontium niobate), mullite, mica, spinel, zircon, magnesia, ceria, silicon carbide, silicon nitride, aluminum nitride or strontium carbonate. The material is more preferably a metal oxide such as zirconia, partially stabilized zirconia (e.g., yttria partially stabilized zirconia), completely stabilized zirconia (e.g., yttria completely stabilized zirconia), yttrium oxide, alumina, silica, titania, niobium oxide, strontium oxide or lanthanum oxide. One of them may be used alone, or any combination of two or more of them may be used.

It is preferable that the porous plate filler **1** includes particles having particle diameters of 1 nm to 10 μm . The particle may be a particle constituted of one crystal grain (a single crystalline particle) or a particle constituted of a large number of crystal grains (a polycrystalline particle). That is, it is preferable that the porous plate filler **1** is an assembly of particles having particle diameters of this range. For the particle diameter, a size of one particle of a particle group constituting a framework of the porous plate filler **1** (in the case of a spherical particle, the size is a diameter, and in another case, the size is a maximum diameter) is measured from an image of electron microscope observation. The particle diameter is more preferably from 1 nm to 5 μm and

further preferably from 50 nm to 1 μm . When the porous plate filler **1** having the particle diameters of such a range is included in the heat-insulation film **3**, the heat insulation effect can improve.

The minimum length of the porous plate filler **1** is from 0.1 to 50 μm , more preferably from 0.5 to 20 μm , further preferably from 2 to 15 μm , and most preferably from 2 to 10 μm . When the minimum length of the porous plate filler **1** is shorter than 0.1 μm , it might be difficult to keep the shape of the porous plate filler **1** in manufacturing steps. In a case where the minimum length of the porous plate filler **1** is longer than 50 μm , there decreases the number of layers in the porous plate filler **1** when included in the heat-insulation film **3**, so that the heat transfer path becomes close to a straight line and accordingly shortens, and the thermal conductivity of the heat-insulation film **3** might be high. Additionally, when the minimum length of the porous plate filler **1** is short, the heat-insulation film **3** can be thinned. That is, even in the thin heat-insulation film **3**, the heat insulation effect can improve.

The thermal conductivity of the porous plate filler **1** is preferably 1 W/(m·K) or less. The thermal conductivity is more preferably 0.7 W/(m·K) or less, further preferably 0.5 W/(m·K) or less, and most preferably 0.3 W/(m·K) or less. When the porous plate filler **1** having such a thermal conductivity is included in the heat-insulation film **3**, the heat insulation effect can improve.

A heat capacity of the porous plate filler **1** is preferably from 10 to 3000 kJ/(m³·K). The heat capacity is more preferably from 10 to 2500 kJ/(m³·K), further preferably from 300 to 2000 kJ/(m³·K), and most preferably from 400 to 1500 kJ/(m³·K). When the porous plate filler **1** having the heat capacity of such a range is included in the heat-insulation film **3**, the heat insulation effect can improve. It is to be noted that in the present description, the heat capacity is generally argued per unit volume called volumetric specific heat, and hence a unit is kJ/m³·K.

It is preferable that, as shown in FIG. 2, the porous plate filler **1** has a coating layer **7** having a thickness of 1 nm to 1 μm in at least a part of its surface. Furthermore, the coating layer **7** is preferably a thermal resistance film in which heat conduction is inhibited and/or radiant heat is reflected and/or the lattice vibration (the phonons) is scattered. When the thermal resistance film having a thickness of several tens nm is formed on the surface of the porous plate filler **1**, the thermal conductivity of the heat-insulation film **3** can preferably further be decreased. The thermal resistance film may be any film as long as a material thereof is not the same as in the porous plate filler to be coated, and the porous plate filler **1** is preferably coated with a dissimilar material (e.g., alumina or zinc oxide). Even when the thermal resistance film is dense or porous, there is not any problem, but it is preferable that the film is dense. When the thermal resistance film is formed in a part of the surface of the porous plate filler **1**, an effect of decreasing the thermal conductivity can be obtained, but when the whole surface of the porous plate filler **1** is coated with the thermal resistance film, the effect of decreasing the thermal conductivity can further be obtained.

Next, a manufacturing method of the porous plate filler **1** will be described. Examples of the manufacturing method of the porous plate filler **1** include press molding, casting, extrusion, injection molding, tape forming, and a doctor blade method. Any method may be used, but hereinafter, the doctor blade method will be described as an example.

First, a pore former, a binder, a plasticizer, a solvent and the like are added to ceramics powder to be mixed by a ball mill or the like, thereby preparing a green sheet forming slurry.

As the ceramics powder, there may be used zirconia powder, partially stabilized zirconia powder (e.g., yttria partially stabilized zirconia powder), completely stabilized zirconia powder (e.g., yttria completely stabilized zirconia powder), alumina powder, silica powder, titania powder, lanthanum oxide powder, yttria powder, rare earth zirconate powder (e.g., lanthanum zirconate powder), rare earth silicate powder (e.g., yttrium silicate powder), niobate powder (e.g., strontium niobate powder), mullite powder, spinel powder, zircon particles, magnesia powder, yttria powder, ceria powder, silicon carbide powder, silicon nitride powder, aluminum nitride powder or the like. One of them may be used, or any combination of two or more of them may be used. Additionally, the powder is not limited to dried powder, and the powder may be used in a colloidal state (a sol state) in which the powder is dispersed in water or an organic liquid medium. As the pore former, there may be used latex particles, melamine resin particles, PMMA particles, polyethylene particles, polystyrene particles, carbon black particles, foamable resin, water absorbable resin or the like. As the binder, there is usable polyvinyl butyral resin (PVB), polyvinyl alcohol resin, polyvinyl acetate resin, polyacrylic resin or the like. As the plasticizer, DBP (dibutyl phthalate), DOP (dioctyl phthalate) or the like is usable. As the solvent, xylene, 1-butanol or the like is usable.

The above green sheet forming slurry is subjected to a vacuum defoaming treatment, thereby adjusting a viscosity into 100 to 10000 cps. Afterward, a green sheet is formed by a doctor blade device so that a thickness of the green sheet after fired is from 0.1 to 100 μm , and an outer shape of the green sheet is cut into a dimension of (0.5 to 200) mm \times (0.5 to 200) mm. A cut formed body is fired at 800 to 2300° C. for 0.5 to 20 hours and this fired body is suitably ground, whereby a porous thin plate-shaped filler (the porous plate filler **1**) can be obtained. It is to be noted that the green sheet before fired may be processed into a predetermined surface shape (a square, a quadrangular shape, a hexagonal shape or a round shape) or the like by cutting or punching, and then fired, whereby the porous thin plate-shaped filler can be obtained without performing grinding after the firing.

2. Coating Composition

A coating composition includes the porous plate filler **1** mentioned above, and one or more selected from the group consisting of an inorganic binder, an inorganic polymer, an organic/inorganic hybrid material, oxide sol and water glass. Furthermore, the coating composition may include a dense filler, a viscosity modifier, a liquid medium, a dispersing agent and the like. The heat-insulation film **3** can be formed by applying the coating composition and performing drying and/or a heat treatment. Specific substances to be included in the coating composition are cement, bentonite, aluminum phosphate, silica sol, alumina sol, boehmite sol, zirconia sol, titania sol, tetramethyl orthosilicate, tetraethyl orthosilicate, polysilazane, polycarbosilane, polyvinyl silane, polymethyl silane, polysiloxane, polysilsesquioxane, silicone, geopolymer, sodium silicate and the like. Additionally, in the case of the organic/inorganic hybrid material, there are desirable an acryl-silica based hybrid material, an epoxy-silica based hybrid material, a phenol-silica based hybrid material, a polycarbonate-silica based hybrid material, a nylon-silica based hybrid material, a nylon-clay based hybrid material, an acryl-alumina based hybrid material, an acryl-calcium silicate hydrate based hybrid material and the like.

A viscosity of the coating composition is preferably from 0.1 to 5000 mPa·s and further preferably from 0.5 to 1000 mPa·s. When the viscosity is smaller than 0.1 mPa·s, the coating composition flows after applied, and a thickness of the coating film might be non-uniform. When the viscosity is larger than 5000 mPa·s, the coating composition does not have any fluidity and might not uniformly be applied.

The heat-insulation film **3** in which the porous plate fillers **1** are uniformly dispersed in a matrix **3m** can be obtained by adjusting the viscosity. For example, when the viscosity is excessively high, the porous plate fillers **1** are hard to be uniformly dispersed, and a portion where there are less porous plate fillers **1** is easily generated in the heat-insulation film **3**. Dispersing properties of the porous plate fillers **1** in the coating composition (the slurry) can be increased by adding the dispersing agent, thereby making it possible to form the heat-insulation film **3** which is homogeneous. That is, by increasing the dispersing properties of the porous plate fillers **1**, the homogeneous heat-insulation film **3** can be obtained and the thermal conductivity can be decreased.

3. Heat-Insulation Film

The heat-insulation film **3** will be described with reference to FIG. 3A. In the heat-insulation film **3** of the present invention, the porous plate fillers **1** mentioned above are dispersed in the matrix **3m** to bond the porous plate fillers **1**. The matrix **3m** is a component which is present around the porous plate fillers **1** and between the particles of the fillers and bonds these particles to each other.

In the heat-insulation film **3** of the present invention, it is preferable that the porous plate fillers **1** are arranged in the form of layers (laminated). The arrangement in the form of the layers mentioned herein indicates that a large number of porous plate fillers **1** are present in the matrix **3m** in a state where the porous plate fillers **1** are oriented in a direction in which a direction of the minimum length of the porous plate filler **1** is parallel to a thickness direction of the heat-insulation film **3**. It is to be noted that at this time, positions of the porous plate fillers **1** (a position of the center of gravity) do not have to be orderly periodically arranged in X, Y and Z-directions of the heat-insulation film **3** (provided that the Z-direction is defined as the thickness (film thickness) direction), and there is not any problem even when the fillers are present at random. There is not any problem when the number of the layers is 1 or more, but the larger number of the layers is more preferable and the number of the layers is desirably 5 or more. When the porous plate fillers **1** are laminated in the form of the layers in the heat-insulation film **3**, the heat transfer path is deflected to lengthen, and the heat insulation effect can improve. In particular, for the positions of the porous plate fillers **1**, as shown in FIG. 3A, the fillers preferably are not orderly arranged in the Z-direction (the fillers preferably shift alternately), because the heat transfer path is more deflected to lengthen.

As shown in FIG. 3A, a matrix **3m** portion in which the thermal conductivity is high becomes a main heat transfer path, but the heat-insulation film **3** of the present invention includes the porous plate fillers **1**, and the heat transfer path makes more detours to a direction in which heat is not to be transferred (the film thickness direction). That is, a length of the heat transfer path increases, and hence the thermal conductivity can be decreased. Additionally, a bonding area between the porous plate fillers **1** via the matrix **3m** is larger than that between spherical fillers **31** (see FIG. 6), and hence a strength of the whole heat-insulation film increases, and erosion, peeling or the like is hard to occur.

In the heat-insulation film **3**, the porous plate fillers **1** are dispersed in the matrix **3m** to bond the porous plate fillers **1**,

and a volume ratio between the porous plate fillers and the matrix is preferably from 50:50 to 95:5. The volume ratio is more preferably from 60:40 to 90:10 and further preferably from 70:30 to 85:15. When the volume ratio between the porous plate fillers **1** and the matrix **3m** is in this range, the thermal conductivity can further be decreased. Consequently, a thickness of the heat-insulation film **3** can be decreased. In consequence, there is required less space in which the heat-insulation films **3** are disposed, and cost can be decreased. Additionally, the matrix **3m** having a function of bonding the porous plate fillers **1** is easy to exert a sufficient bonding force, and the porous plate fillers **1** can be prevented from peeling. That is, the strength of the film can increase. Furthermore, thermal stress can be decreased at a time of bonding to the dissimilar material. As described above, when the space for the porous plate fillers **1** increases, the heat insulation effect can improve, and when a space for the matrix **3m** increases, the strength of the film can increase. When the volume ratio between the porous plate fillers **1** and the matrix **3m** is in the above range, heat insulation properties is compatible with the strength of the film.

Directing of the ratio between the porous plate fillers **1** and the matrix **3m** by a line will be described with reference to FIG. 3B. It is to be noted that FIG. 3A is an ideal schematic view, and FIG. 3B is a schematic view to explain measurement of a dispersed state of the porous plate fillers **1** dispersed in the matrix **3m**. FIG. 3B shows a line segment **25** present on the porous plate fillers **1** and a line segment **26** present on the matrix **3m**.

Additionally, in the heat-insulation film **3**, when a line is drawn from a first surface **23** to a second surface **24** on an opposite side to the first surface in a thickness direction in a cross section parallel to the thickness (film thickness) direction, a ratio between a sum of lengths of the line segments **25** present on the porous plate fillers **1** and a sum of lengths of the line segments **26** present on the matrix **3m** is preferably from 50:50 to 95:5. The ratio is more preferably from 60:40 to 90:10 and further preferably from 70:30 to 85:15. Specifically, 10 lines are randomly drawn in the cross section parallel to the thickness (film thickness) direction, a ratio between the line segments is obtained, and an average of the ratios is calculated. Additionally, deviations of the porous plate fillers **1** in the matrix **3m** can be judged by the ratio between the sums of the lengths of the line segments. For example, as to each of the 10 randomly drawn lines, there is obtained the ratio between the sum of the lengths of the line segments **25** present on the porous plate fillers **1** and the sum of the lengths of the line segments **26** present on the matrix **3m**. When the average of these ratios is obtained and there is the ratio which is as much as $\pm 10\%$ or more away from the average of the ratios, it can be judged that the positions where the porous plate fillers **1** are present noticeably deviate. In the heat-insulation film **3** of the present invention, there is not any ratio that is as much as $\pm 10\%$ or more away from the average of the ratios, and the porous plate fillers **1** are uniformly present in the matrix **3m**. Thus, it can be considered that when the line is drawn from the first surface **23** to the second surface **24** in the thickness direction in the cross section parallel to the thickness direction and when the sum of the lengths of the line segments **25** present on the porous plate fillers **1** and the sum of the lengths of the line segments **26** present on the matrix **3m** are in the above range, the porous plate fillers **1** are arranged in an amount in which the heat insulation effect can be exerted, in the thickness direction. Additionally, it can be considered that a sufficient amount of the matrix **3m** is also disposed to maintain the strength of the film. That is, when the sum of the

lengths of the line segments **25** present on the porous plate fillers **1** and the sum of the lengths of the line segments **26** present on the matrix **3m** are in this range, the thermal conductivity can further be decreased, and the strength of the film can sufficiently be obtained.

In the heat-insulation film **3**, the porous plate fillers **1** are the plates, and hence concavity and convexity are hard to be formed on the outermost surface of the heat-insulation film **3** as compared with the case of the spherical fillers. Therefore, even in a case where shock is given to a heat-insulation film portion, particle drop of the porous plate fillers **1**, i.e., deficiency of the heat-insulation film **3** can be prevented.

It is preferable that the heat-insulation film **3** of the present invention includes at least one of ceramics, glass and resin as the matrix **3m**. From the viewpoint of a thermal resistance, ceramics or glass is more preferable. More specifically, examples of a material forming the matrix **3m** include silica, alumina, mullite, zirconia, titania, silicon nitride, acid silicon nitride, silicon carbide, acid silicon carbide, calcium silicate, calcium aluminate, calcium aluminosilicate, aluminum phosphate, aluminosilicate, potassium aluminosilicate, and glass. These materials are preferably amorphous from the viewpoint of the thermal conductivity. Alternatively, in a case where the material of the matrix **3m** is ceramics, the matrix is preferably an assembly of particulates having particle diameters of 500 nm or less. When the assembly of the particulates having the particle diameters of 500 nm or less is used as the matrix, the thermal conductivity can further be decreased. Additionally, in a case where the material forming the matrix **3m** is a resin, examples of the material include a silicone resin, a polyimide resin, a polyamide resin, an acrylic resin, and an epoxy resin.

In the heat-insulation film **3**, it is preferable that a porosity of the whole heat-insulation film **3** is from 10 to 90%, a porosity of the porous plate filler **1** is from 20 to 90%, and a porosity of the matrix **3m** is from 0 to 70%.

In the heat-insulation film **3** of the present invention, a thickness is preferably from 1 μm to 5 mm. According to such a thickness, the heat insulation effect can be obtained without adversely affecting characteristics of a substrate **8** coated with the heat-insulation film **3**. It is to be noted that the thickness of the heat-insulation film **3** can suitably be selected in the above range in accordance with its use application.

In the heat-insulation film **3** of the present invention, a heat capacity is preferably 1500 kJ/($\text{m}^3 \cdot \text{K}$) or less, more preferably 1300 kJ/($\text{m}^3 \cdot \text{K}$) or less, further preferably 1000 kJ/($\text{m}^3 \cdot \text{K}$) or less, and most preferably 500 kJ/($\text{m}^3 \cdot \text{K}$) or less. When the heat-insulation film has a low heat capacity, for example, a temperature of the heat-insulation film **3** is easy to drop after exhaust of fuel in a case where the heat-insulation film **3** is formed in an engine combustion chamber **20** (see FIG. 4). Consequently, a problem such as abnormal combustion of an engine **10** can be inhibited.

In the heat-insulation film **3** of the present invention, the thermal conductivity is preferably 1.5 W/($\text{m} \cdot \text{K}$) or less. The thermal conductivity of the heat-insulation film **3** is further preferably 1 W/($\text{m} \cdot \text{K}$) or less and most preferably 0.5 W/($\text{m} \cdot \text{K}$) or less. The heat-insulation film has a low thermal conductivity, whereby the heat transfer can be inhibited.

The heat-insulation film **3** can be formed by applying the abovementioned coating composition onto the substrate **8** and drying the coating composition. Additionally, the film can be formed by performing a heat treatment after the drying. At this time, the thick heat-insulation film **3** can be formed by repeatedly performing the applying and the

drying or the heat treatment. Alternatively, the heat-insulation film 3 is formed on a virtual substrate, and then the virtual substrate is removed, thereby separately preparing the heat-insulation film 3 singly formed into a thin plate, and the heat-insulation film 3 may be adhesively bonded to or bonded to the substrate 8. As the substrate 8, a metal, ceramics, glass, plastic, wood, cloth, paper or the like is usable. Especially, examples of the substrate 8 made of the metal include iron, an iron alloy, stainless steel, aluminum, an aluminum alloy, a nickel alloy, a cobalt alloy, a tungsten alloy, and a copper alloy.

4. Heat-Insulation-Film Structure

A heat-insulation-film structure of the present invention will be described with reference to FIG. 3A and FIG. 4. As shown in FIG. 3A, the heat-insulation-film structure of the present invention is a heat-insulation-film structure in which the heat-insulation film 3 mentioned above is formed on the substrate 8. Furthermore, FIG. 4 shows an engine combustion chamber structure of one embodiment of the heat-insulation-film structure.

As shown in FIG. 4, the engine combustion chamber structure of the one embodiment of the heat-insulation-film structure of the present invention includes heat-insulation films 3 formed on surfaces of the engine constitutional members 21 (a substrate 8) constituting an engine combustion chamber 20. The heat-insulation films 3 of the present invention are included, whereby a heat insulation performance of the engine combustion chamber 20 can improve.

The heat-insulation films 3 are disposed on the surfaces (inner walls) of the engine constitutional members 21 constituting the engine combustion chamber 20. Specifically, examples of the surfaces include an upper surface 14s of a piston 14, valve heads 16s and 17s of a suction valve 16 and an exhaust valve 17, and a bottom surface 13s of a cylinder head 13.

The engine 10 has a cylinder block 11 in which a cylinder 12 is formed, and the cylinder head 13 attached to cover the upper surface of the cylinder block 11. In the cylinder 12 of the cylinder block 11, the piston 14 is slidably disposed in an upward-downward direction.

An ignition plug 15 is attached to the cylinder head 13. Additionally, the suction valve 16 and the exhaust valve 17 are attached, the suction valve 16 is constituted to open and close a suction passage 18 formed in the cylinder head 13, and the exhaust valve 17 is constituted to open and close an exhaust passage 19.

As shown in FIG. 4, the heat-insulation film 3 is disposed on the upper surface 14s of the piston 14. Furthermore, the heat-insulation films 3 are similarly disposed on the valve heads 16s and 17s of the suction valve 16 and the exhaust valve 17 and the bottom surface 13s of the cylinder head 13. These surfaces are surfaces which form the engine combustion chamber 20, and these surfaces include the heat-insulation films 3, whereby the heat insulation performance can improve.

The suction valve 16 is opened to supply the fuel to the engine combustion chamber 20 surrounded by the cylinder 12, the cylinder head 13 and the piston 14, and the fuel is ignited by the ignition plug 15 and then combusted. By this combustion, the piston 14 is pressed downward. An exhaust gas generated by the combustion is exhausted by opening the exhaust valve 17.

In the engine 10 (see FIG. 4), it is necessary to acquire heat insulation properties of the engine combustion chamber 20 at a time of combustion in a cycle of suction, combustion, expansion and exhaust, and hence in a case where the heat-insulation films 3 are disposed in the engine combus-

tion chamber 20, it is necessary to adjust a thickness of each film to such an extent that the heat insulation effect can be obtained. However, when air newly sucked inside at a time of suction takes heat accumulated in the heat-insulation film 3 to heighten a gas temperature, a problem such as abnormal combustion might occur. To eliminate this problem, it is preferable that the heat-insulation film 3 has a small heat capacity while having the thickness with which the heat insulation effect can be obtained. Therefore, the thickness of the heat-insulation film 3 is more preferably in a range of 1 μ m to 5 mm and further preferably in a range of 10 μ m to 1 mm. When the thickness of the heat-insulation film 3 is adjusted in this range, the heat insulation effect can sufficiently be obtained and the occurrence of the problem of the abnormal combustion or the like can be inhibited.

FIG. 5A shows another embodiment of the heat-insulation-film structure. The embodiment of FIG. 5A is the embodiment of the heat-insulation-film structure in which a buffer bonding layer 4 (a first buffer bonding layer 4a), a heat-insulation film 3 and a surface dense layer 2 are formed on a substrate 8.

As shown in FIG. 5A, it is preferable that the heat-insulation-film structure of the present invention includes, on the surface of the heat-insulation film 3, the surface dense layer 2 including ceramics and/or glass and having a porosity of 5% or less. In a case where the heat-insulation film 3 is formed on an inner surface of a combustion chamber or a pipe of an engine of a car or the like, absorption of fuel or adhesion of cinders can be prevented when the surface dense layer 2 is formed on the outermost surface of the heat-insulation film 3.

Furthermore, when the structure has the surface dense layer 2 on the surface of the heat-insulation film 3, radiation can be reflected by the surface dense layer 2 at a time of combustion of the fuel in an engine combustion chamber 20 and heat can be radiated from the surface dense layer 2 at a time of exhaust, in a case where the engine combustion chamber 20 includes the heat-insulation films 3. Additionally, the heat-insulation film 3 can inhibit heat transfer from the surface dense layer 2 to engine constitutional members 21. Therefore, at the time of the combustion of the fuel, a temperature of an inner wall of the engine constitutional member 21 (a wall surface constituting the engine combustion chamber 20) is easy to rise following a gas temperature of the engine combustion chamber 20.

It is preferable that the heat-insulation-film structure of the present invention includes the buffer bonding layer 4 having a thickness smaller than the heat-insulation film 3, between the substrate 8 and the heat-insulation film 3 (FIG. 5A) and/or between the heat-insulation film 3 and the surface dense layer 2 (see FIG. 5B: a second buffer bonding layer 4b). When the heat-insulation film 3 is formed on the substrate 8 and the buffer bonding layer 4 is disposed, peeling due to reaction between the substrate 8 and the heat-insulation film 3 or mismatch of thermal expansion can be inhibited in a case where the heat-insulation-film structure is used at high temperatures or used under an environment which receives a heat cycle.

Hereinafter, the surface dense layer 2 and the buffer bonding layer 4 will be described in detail.

(Surface Dense Layer)

The surface dense layer 2 is a layer including ceramics denser than the heat-insulation film 3 formed on the surface of the heat-insulation-film 3 of a porous structure. In the surface dense layer 2, a porosity is 5% or less, preferably from 0.01 to 4%, and more preferably from 0.01 to 3%. According to such a dense layer, it is possible to prevent heat

conduction due to convection of the gas (fuel) at the time of the combustion of the fuel. Additionally, the layer is dense, and hence the absorption of the fuel or adhesion of soot or cinders is hard to occur.

It is preferable that a material of the surface dense layer **2** is similar to the heat-insulation film **3**, and it is further preferable that the material has the same composition as in the heat-insulation film and a porosity of 5% or less. The surface dense layer **2** can be made of ceramics, and examples of the material include alumina, silica, mullite, silicon nitride, acid silicon nitride, silicon carbide, acid silicon carbide, titania, zirconia, zinc oxide, and glass.

The surface dense layer **2** is made of a material which inhibits radiation heat transfer from combustion flame of a heat source at the time of the combustion of the fuel. Additionally, it is preferable that the surface dense layer **2** is easy to radiate its own heat at the time of the exhaust of the fuel. For this purpose, it is preferable to control a reflectance and a radiation rate in a wavelength region predicted from Wien's displacement law ($\lambda_m T = 2898$ [$\mu\text{m}\cdot\text{K}$] in which λ_m is a wavelength indicating a maximum radiation strength and T indicates a temperature). That is, the reflectance is preferably large in a wavelength smaller than $2\ \mu\text{m}$ and the radiation rate is preferably large in a wavelength larger than $2\ \mu\text{m}$.

According to the surface dense layer **2** having the porosity of 5% or less, the radiation heat transfer to an inner wall constituting the engine combustion chamber **20** can be inhibited immediately after start of the combustion and in a first half of the combustion. Additionally, in a second half of the combustion and an exhaust step, when the temperature lowers, heat is radiated from the surface dense layer **2** to the exhaust gas, thereby making it possible to prevent a suction gas to be next introduced from reaching a high temperature.

In the surface dense layer **2**, the reflectance in the wavelength of $2\ \mu\text{m}$ is preferably larger than 0.5. The surface dense layer has such a reflectance, and hence the heat conduction to the heat-insulation film **3** can be inhibited.

In the surface dense layer **2**, the radiation rate in the wavelength of $2.5\ \mu\text{m}$ is preferably larger than 0.5. Additionally, the surface dense layer has such a radiation rate, and hence the heated surface dense layer **2** can be easy to cool down.

The surface dense layer **2** is preferably thinner, but its thickness is appropriately in a range of 10 nm to $100\ \mu\text{m}$. Additionally, a heat capacity of the surface dense layer **2** is preferably $3000\ \text{kJ}/(\text{m}^3\cdot\text{K})$ or less and more preferably $1000\ \text{kJ}/(\text{m}^3\cdot\text{K})$ or less. The thickness is in the above range and the heat capacity is small (a thin film and a small volume), so that in the case where the engine combustion chamber **20** includes the heat-insulation film **3** and the surface dense layer **2**, a temperature of the inner wall of the engine constitutional member **21** is easy to follow the gas temperature in the engine combustion chamber **20**. A difference between the gas temperature and the temperature of the surface dense layer **2** decreases, and a cooling loss can be decreased.

In the surface dense layer **2**, a thermal conductivity is preferably $3\ \text{W}/(\text{m}\cdot\text{K})$ or less. When the thermal conductivity is in this range, the heat conduction to the heat-insulation film **3** can be inhibited.

(Buffer Bonding Layer)

The buffer bonding layer **4** is present between the substrate **8** (the engine constitutional member **21**) and the heat-insulation film **3** and/or between the heat-insulation film **3** and the surface dense layer **2**, and a thickness of the buffer bonding layer is smaller than that of the heat-insula-

tion film **3**. According to the buffer bonding layer **4**, it is possible to eliminate mismatch of thermal expansion or Young's modulus between both layers which come in contact with this buffer bonding layer, and it is possible to inhibit peeling due to the thermal stress.

The buffer bonding layer **4** is preferably made of a material having an adhesively bonding function or a material which can be formed as a thin film. An example of the buffer bonding layer **4** is a layer made of an inorganic binder, an inorganic polymer, oxide sol, water glass, a brazing material, or a plating film. Alternatively, the buffer bonding layer **4** may be a layer made of these materials combined with a substance similar to the heat-insulation film **3**. Additionally, the buffer bonding layer can be obtained by bonding the heat-insulation film **3** singly formed into the thin plate to the substrate **8** (the engine constitutional member **21**) by the above material.

It is preferable that a thermal expansion coefficient of the buffer bonding layer **4** is larger than that of one of two adjacent layers and smaller than that of the other layer. Additionally, it is preferable that the Young's modulus of the buffer bonding layer **4** is smaller than those of the other two adjacent layers. According to such a constitution, a mismatch between the layers can be eliminated, and the peeling due to the thermal stress can be inhibited.

In the buffer bonding layer **4**, a thermal resistance is preferably large, and specifically, the thermal resistance is preferably $10^{-6}\ \text{m}^2\text{K}/\text{W}$ or more. Furthermore, the thermal resistance is preferably from 10^{-6} to $10\ \text{m}^2\text{K}/\text{W}$, more preferably from 10^{-5} to $10\ \text{m}^2\text{K}/\text{W}$, and further preferably from 10^{-4} to $10\ \text{m}^2\text{K}/\text{W}$. By forming the buffer bonding layer **4**, the heat insulation effect can further sufficiently be obtained. Additionally, by forming the buffer bonding layer **4**, the mismatch of thermal expansion of bodies to be bonded can be buffered, and a thermal shock resistance and a thermal stress resistance can improve.

Furthermore, the buffer bonding layer **4** preferably has a material composition to inhibit mutual reaction of the respective layers which come in contact with the buffer bonding layer, and consequently, an oxidation resistance and a reaction resistance improve and a durability of the heat-insulation film **3** improves.

The heat-insulation film of the present invention can be disposed in the engine combustion chamber **20**, and additionally, the heat-insulation film is utilizable in a pipe, a cooling device, a building material or the like.

(Manufacturing Method)

Next, a manufacturing method of the heat-insulation-film structure will be described in an example of an engine combustion chamber structure.

In a case where the structure is constituted to have the first buffer bonding layer **4a** between the inner wall constituting the engine combustion chamber **20** (the engine constitutional member **21**) and the heat-insulation film **3**, materials which form the first buffer bonding layer **4a** are applied (e.g., the inorganic binder or the inorganic polymer, the oxide sol, the water glass and the brazing material) or formed into the plating film on the engine constitutional member **21**, and the heat-insulation film **3** is formed thereon.

The heat-insulation film **3** can be formed by applying, onto the predetermined substrate **8**, the coating composition in which the porous plate filler **1** is dispersed in the inorganic binder or the inorganic polymer, the oxide sol, the water glass or the like, followed by drying, and further performing the heat treatment. A preparing composition of the coating composition is determined in consideration of volumes of the matrix **3m** and the porous plate filler **1** which are present

after dried and heated. Specifically, a weight ratio is obtained from a ratio volume to be prepared, via a density, and weights of the porous plate filler **1** and the matrix **3m** are measured, whereby a desirable volume ratio can be obtained.

Alternatively, porous thin plates may separately be prepared and attached to the engine constitutional member **21** by use of the material which forms the first buffer bonding layer **4a** as a bonding material.

In a case where the structure is constituted to have the second buffer bonding layer **4b** between the heat-insulation film **3** and the surface dense layer **2**, the second buffer bonding layer **4b** is formed on the heat-insulation film **3** in the same manner as in the first buffer bonding layer **4a**, and the surface dense layer **2** is formed thereon.

The surface dense layer **2** can be formed by forming the heat-insulation film **3** (or forming the second buffer bonding layer **4b**) and additionally performing a sputtering method, a PVD method, an EB-PVD method, a CVD method, an AD method, flame spraying, a plasma spray method, a cold spray method, plating, a heat treatment after wet type coating, or the like. Alternatively, a dense thin plate may separately be prepared as the surface dense layer **2** and bonded to a substrate material (the first buffer bonding layer **4a** or the engine constitutional member **21**) by use of a bonding material made of a material which forms the heat-insulation film **3**. Alternatively, a dense thin plate may separately be prepared as the surface dense layer **2** and bonded to the heat-insulation film **3** by the second buffer bonding layer **4b**.

EXAMPLES

Hereinafter, the present invention will be described in more detail on the basis of examples, but the present invention is not limited to these examples.

Examples 1 to 7 and Comparative Examples 1 and 2

First, a pore former (latex particles or melamine resin particles), polyvinyl butyral resin (PVB) as a binder, DOP as a plasticizer and xylene and 1-butanol as solvents were added to yttria partially stabilized zirconia powder, and mixed in a ball mill for 30 hours, to prepare a green sheet forming slurry. This slurry was subjected to a vacuum defoaming treatment to adjust a viscosity into 4000 cps, and then a green sheet having a thickness of 10 μm after fired was formed by a doctor blade device and cut into a dimension of an outer shape of 50 mm \times 50 mm. This formed body was fired at 1100 $^{\circ}$ C. for one hour, and ground after fired, to obtain a porous thin plate filler (a porous plate filler **1**).

The porous plate filler **1** included pores having pore diameters of 50 nm and had a thickness (a minimum length) of 10 μm . Additionally, when an aspect ratio of each of 20 optional porous plate fillers was measured, its value was 4. Additionally, in the porous plate filler **1**, a thermal conductivity was 0.30 W/(m \cdot K), a heat capacity was 1000 kJ/(m 3 \cdot K), a porosity was 60%, and a particle diameter was 0.13 μm .

Additionally, the same material as in the porous plate filler **1**, which was separately formed into about 0.5 mm \times 5 mm \times 30 mm, was fired, its thermal diffusivity was measured by a light AC method, specific heat of the same material was measured by a DSC method, and a product of the thermal diffusivity, the specific heat and a density (an apparent

particle density) was obtained as the thermal conductivity. Additionally, the porosity was obtained by the following equation.

$$\text{Porosity (\%)} = (1 - (\text{the apparent particle density} / \text{a true density})) \times 100$$

In the above equation, the apparent particle density was measured by a liquid immersion method in which mercury was used. Additionally, the true density was measured by pycnometry after sufficiently grinding the porous plate filler **1**.

The heat capacity of the porous plate filler **1** was calculated as follows. The specific heat was measured by the DSC method, and a product of the specific heat and the density (the apparent particle density) was obtained as the heat capacity of the porous plate filler **1**. The apparent particle density was measured by the liquid immersion method in which mercury was used.

Additionally, for the particle diameter, a fine structure (FE-SEM) of the porous plate filler **1** was observed, a size of one particle was measured by image processing, and an average value of 10 particles was obtained.

Next, polysiloxane which became a matrix **3m**, the porous plate filler **1** and a coating composition including water were prepared, applied onto a SUS substrate (a diameter of 10 mm and a thickness of 1 mm) which was a substrate **8** and dried, followed by a heat treatment at 200 $^{\circ}$ C. to form a heat-insulation film **3**. At this time, in the heat-insulation film **3**, five or more porous plate fillers **1** were laminated in a thickness direction, and its thickness was about 100 μm in all the films.

(Directing of Volume Ratio by Area)

A cross section of the heat-insulation film **3** which was parallel to the thickness direction was observed with an SEM. From areas of the porous plate fillers **1** and the matrix **3m** in the cross section, a volume ratio between the porous plate fillers **1** and the matrix **3m** was calculated.

(Ratio Directing by Line)

The cross section of the heat-insulation film which was parallel to the thickness direction was observed with the SEM. In the cross section in the thickness direction, a line was drawn from a first surface to a second surface on an opposite side to the first surface in the thickness direction. A sum of lengths of line segments of the line present on the porous plate filler and a sum of lengths of line segments of the line present on a matrix were obtained, and a filler ratio and a matrix ratio were calculated.

Specifically, 10 lines were randomly drawn in the cross section parallel to the thickness (film thickness) direction, and in each line, there was obtained a ratio between a sum of lengths of line segments **25** present on the porous plate filler **1** and a sum of lengths of line segments **26** present on the matrix **3m**. Further, an average of these ratios was obtained (directing by the line (an average value)). Additionally, by judging whether or not there was a ratio which was as much as $\pm 10\%$ or more away from the average of the ratios, it was judged whether or not positions where the porous plate fillers **1** were present noticeably deviated (directing by the line (deviation evaluation)). For example, in a case where the filler ratio was 80% in the average of the ratios, when the ratios of all the 10 lines were from 70 to 90%, the evaluation was G (good), but on the other hand, when there was even one ratio which was out of 10%, e.g., 65%, the evaluation was N (no good).

(Thermal Conductivity)

A thermal conductivity in the cross section of the heat-insulation film **3** which was parallel to the thickness direction was measured in a laser flash two-layer model.

(Heat Capacity)

A heat capacity of the heat-insulation film **3** was calculated from a product of specific heat \times a density (an apparent particle density) obtained by grinding the heat-insulation film **3** and then measuring the specific heat by a DSC method.

(Peeling Properties)

A cold cycle at 200° C. to room temperature was carried out as much as 10 times, and it was observed whether or not the heat-insulation film **3** peeled from the SUS substrate. As to the results of peeling properties, no peeling (excellent) is indicated by E, no peeling (good) is indicated by G, and peeling (no good) is indicated by N.

Table 2 shows results of the directing of the volume ratio by the area, the ratio directing by the line, the thermal conductivity, the heat capacity and the peeling properties concerned with the heat-insulation film of each of Examples 1 to 7 and Comparative Examples 1 and 2.

Examples 8 to 17

Porous plate fillers **1** were obtained in steps similar to those of Examples 1 to 7 and Comparative Examples 1 and 2. Afterward, an aspect ratio, a porosity, a particle diameter, a thermal conductivity and a heat capacity of each porous plate filler were obtained by methods similar to those of Examples 1 to 7 and Comparative Examples 1 and 2, and Table 1 shows the results.

Next, polysiloxane, the porous plate filler **1** and a coating composition including water were prepared so that volume ratios of the porous plate filler **1** and a matrix **3m** were 80% of the porous plate filler **1** and 20% of the matrix **3m**, and they were applied onto a SUS substrate (a diameter of 10 mm and a thickness of 1 mm) which was a substrate **8**, and dried, followed by a heat treatment at 200° C. to obtain a heat-insulation film **3**. Afterward, by methods similar to those of each of Examples 1 to 7 and Comparative Examples 1 and 2, directing by the line on the heat-insulation film **3** (deviation evaluation) was carried out, and a thermal conductivity, a heat capacity and peeling properties were obtained. Table 2 shows the results.

TABLE 1

	Filler					Heat capacity (kJ/(m ³ · K))
	Aspect ratio	Minimum length (μ m)	Porosity	Particle dia. (μ m)	Thermal conductivity (W/(m · K))	
Comparative Example 1	4	10	60%	0.13	0.30	1000
Example 1	4	10	60%	0.13	0.30	1000
Example 2	4	10	60%	0.13	0.30	1000
Example 3	4	10	60%	0.13	0.30	1000
Example 4	4	10	60%	0.13	0.30	1000
Example 5	4	10	60%	0.13	0.30	1000
Example 6	4	10	60%	0.13	0.30	1000
Comparative Example 2	4	10	60%	0.13	0.30	1000
Example 7	4	10	60%	0.13	0.30	1000
Example 8	8	10	60%	0.13	0.30	1000
Example 9	20	2	60%	0.13	0.30	1000
Example 10	4	3	60%	0.13	0.30	1000
Example 11	4	7	60%	0.13	0.30	1000
Example 12	4	15	60%	0.13	0.30	1000
Example 13	4	10	52%	0.13	0.50	1250
Example 14	4	10	70%	0.13	0.15	750
Example 15	4	10	78%	0.13	0.10	560
Example 16	4	10	60%	0.07	0.28	1000
Example 17	4	10	60%	0.90	0.50	1000

TABLE 2

	Directing by line				Heat-insulation film			
	Directing by volume		(average value)		Directing by line (deviation evaluation) Within 10%	Thermal conductivity (W/(m · K))	Heat capacity (kJ/(m ³ · K))	Peeling properties
	Filler ratio	Matrix ratio	Filler ratio	Matrix ratio				
Comparative Example 1	98%	2%	98%	2%	G	0.32	1012	N
Example 1	95%	5%	94%	6%	G	0.36	1030	G
Example 2	90%	10%	88%	12%	G	0.37	1060	E
Example 3	85%	15%	82%	18%	G	0.38	1090	E
Example 4	80%	20%	81%	19%	G	0.4	1120	E
Example 5	70%	30%	72%	28%	G	0.8	1180	E
Example 6	50%	50%	53%	47%	G	1.5	1300	E
Comparative Example 2	40%	60%	42%	58%	G	2.7	1360	E

TABLE 2-continued

	Directing by line					Heat-insulation film		
	Directing by volume		(average value)		Directing by line (deviation evaluation) Within 10%	Thermal conductivity (W/(m · K))	Heat capacity (kJ/(m ³ · K))	Peeling properties
	Filler ratio	Matrix ratio	Filler ratio	Matrix ratio				
Example 7	85%	15%	82%	18%	N	0.43	1090	G
Example 8	80%	20%	80%	20%	G	0.32	1120	E
Example 9	80%	20%	80%	20%	G	0.31	1120	E
Example 10	80%	20%	80%	20%	G	0.33	1120	E
Example 11	80%	20%	80%	20%	G	0.34	1120	E
Example 12	80%	20%	84%	16%	G	0.43	1120	E
Example 13	80%	20%	81%	19%	G	0.70	1320	E
Example 14	80%	20%	81%	19%	G	0.30	920	E
Example 15	80%	20%	81%	19%	G	0.25	768	E
Example 16	80%	20%	81%	19%	G	0.38	1120	E
Example 17	80%	20%	81%	19%	G	0.70	1120	E

In the heat-insulation film **3** of each of Examples 1 to 17, the volume ratio between the porous plate fillers and the matrix was from 50:50 to 95:5, the thermal conductivity was 1.5 W/(m·K) or less, and the heat capacity was 1500 kJ/(m³·K) or less. It is to be noted that when the thermal conductivity or the heat capacity is in this range, it can be considered that the heat-insulation film is excellent in heat insulation effect and flame retardance. Additionally, the heat-insulation films **3** of the Examples 1 to 17 were also excellent in peeling properties because peeling did not occur. In the heat-insulation film **3** of Example 7, as compared with Example 3, a ratio obtained from a volume was equal, but it was judged in the ratio directing by the line that positions where the porous plate fillers **1** were present noticeably deviated. Consequently, in Example 7, the thermal conductivity was higher than in Example 3.

In Example 8, the aspect ratio of the porous plate filler **1** was large as compared with Example 4. Consequently, in the heat-insulation film **3** of Example 8, a heat transfer path lengthened and the thermal conductivity was low, as compared with Example 4. In Example 9, a minimum length of the porous plate filler **1** was short and the aspect ratio was large, as compared with Example 4. Consequently, in the heat-insulation film **3** of Example 9, the number of layers of the porous plate filler **1** increased and the thermal conductivity of the film was low, as compared with Example 4.

In Example 10, the minimum length of the porous plate filler **1** was short as compared with Example 4. In Example 11, the minimum length of the porous plate filler **1** was longer than in Example 10 but shorter than in Example 4. Consequently, in Example 10 and Example 11, the thermal conductivity of the heat-insulation film **3** was low as compared with Example 4, and in Example 10, the thermal conductivity of the heat-insulation film **3** was further lower than in Example 11. In Example 12, the minimum length of the porous plate filler **1** was long as compared with Example 4. Consequently, the number of the layers of the porous plate filler **1** of Example 12 decreased and the thermal conductivity of the heat-insulation film **3** was high.

In Example 13, the porosity of the porous plate filler **1** was low as compared with Example 4. Consequently, the thermal conductivity and heat capacity of the heat-insulation film **3** were high. In Example 14, the porosity of the porous plate filler **1** was high and the thermal conductivity was low, as compared with Example 4. Consequently, the thermal conductivity and heat capacity of the heat-insulation film **3** were low. In Example 15, the porosity of the porous plate filler **1** is further higher than in Example 14. Consequently, the

thermal conductivity and heat capacity of the heat-insulation film **3** were further low. In Example 16, particle diameters of particles included in the porous plate filler **1** were small and the thermal conductivity was low, as compared with Example 4. Consequently, the thermal conductivity of the heat-insulation film **3** was low. In Example 17, the particle diameters of the particles included in the porous plate filler **1** were large and the thermal conductivity was high, as compared with Example 4. Consequently, the thermal conductivity of the heat-insulation film **3** was high.

INDUSTRIAL APPLICABILITY

A heat-insulation film of the present invention and a heat-insulation-film structure are applicable to an engine of a car or the like, a pipe, a building material, a cooking device or the like.

DESCRIPTION OF REFERENCE NUMERALS

1: porous plate filler, **2**: surface dense layer, **3**: heat-insulation film, **3m**: matrix, **4**: buffer bonding layer, **4a**: first buffer bonding layer, **4b**: second buffer bonding layer, **7**: coating layer, **8**: substrate, **10**: engine, **11**: cylinder block, **12**: cylinder, **13**: cylinder head, **13s**: bottom surface (of the cylinder head), **14**: piston, **14s**: upper surface (of the piston), **15**: ignition plug, **16**: suction valve, **16s**: valve head, **17**: exhaust valve, **17s**: valve head, **18**: suction passage, **19**: exhaust passage, **20**: engine combustion chamber, **21**: engine constitutional member, **23**: first surface, **24**: second surface, **25**: line segment present on the porous plate filler, **26**: line segment present on the matrix, and **31**: spherical filler.

The invention claimed is:

1. A heat-insulation film in which porous plate fillers comprising plates having an aspect ratio of 3 or more, a thickness of 0.1 to 50 μm and a porosity of 20 to 90% are dispersed in a matrix to bond the porous plate fillers, and a volume ratio between the porous plate fillers and the matrix is from 60:40 to 90:10,

wherein when a line is drawn from a first surface to a second surface on an opposite side to the first surface in a thickness direction in a cross section parallel to the thickness direction, a ratio between a sum of lengths of line segments present on the porous plate fillers and sum of lengths of line segments present on the matrix is from 50:50 to 95:5.

2. The heat-insulation film according to claim 1, wherein a thermal conductivity of the porous plate filler is 1 W/(m·K) or less.

3. The heat-insulation film according to claim 1, wherein a heat capacity of the porous plate filler is from 10 to 3000 kJ/(m³·K). 5

4. The heat-insulation film according to claim 1, wherein the porous plate filler comprises pores of a nanoorder.

5. The heat-insulation film according to claim 1, wherein the porous plate filler includes a metal oxide. 10

6. The heat-insulation film according to claim 1, wherein the porous plate filler comprises particles having particle diameters of 1 nm to 10 μm.

7. The heat-insulation film according to claim 1, wherein a heat capacity of the film is 1500 kJ/(m³·K) or less. 15

8. The heat-insulation film according to claim 1, wherein a thermal conductivity of the film is 1.5 W/(m·K) or less.

9. A heat-insulation-film structure in which the heat-insulation film according to claim 1 is formed on a substrate.

10. The heat-insulation-film structure according to claim 9, which has, on the surface of the heat-insulation film, a surface dense layer including ceramics and/or glass and having a porosity of 5% or less. 20

11. The heat-insulation-film structure according to claim 10, which comprises a buffer bonding layer having a thickness smaller than the heat-insulation film, between the substrate and the heat-insulation film and/or between the heat-insulation film and the surface dense layer. 25

* * * * *