

DESCRIPTION

Title of Invention

CEMENTITIOUS MATERIAL FOR THREE-DIMENSIONAL
MODELING FOR CONSTRUCTION AND THREE-DIMENSIONAL MODELING
METHOD FOR CONSTRUCTION

Technical Field

[0001]

The present invention relates to a cementitious material for three-dimensional modeling for construction which is mainly used in the fields of civil engineering and construction and the fields of factory products, and a method of three-dimensional modeling for construction using the same.

Background Art

[0002]

In recent years, three-dimensional modeling techniques have been utilized for production of models and parts in the manufacturing and other industries. In a known classification, the techniques are divided into optical modeling (a method of stacking layers of a UV curable resin while curing the layers one by one), an inkjet method (a method of stacking layers of a UV curable resin by irradiating the resin jetted from a printer head with UV rays), powder gypsum modeling (a method of solidifying powder gypsum with a resin or a glue jetted from a printer head), powder sintering modeling (a method of stacking layers of a resin or a metal powder while sintering the resin or metal powder by laser), fused deposition modeling (a method of stacking layers of a thermally fused thermoplastic resin discharged from a thin nozzle). The modeled product mainly contains a resin, gypsum, and a metal. A technique for producing a large modeled product, such as a construction member, using a cementitious material has been more aggressively studied in overseas than in Japan. In Europe, the United States, and China, a large modeled product of a scale of a detached residence has already been produced with an automatic construction machine.

[0003]

For example, as a three-dimensional modeling technique using a cementitious material, PTL 1 discloses a technique in which three-dimensional data created by a computer are cut into a prescribed thickness to create two-

dimensional slice data, mortar having an accelerating agent added and mixed therein is sprayed on a bed (base) while controlling movement of a spray nozzle in the length and width directions based on the two-dimensional slice data, and the sprayed mortar is subjected to self-standing curing to form a solidified layer with a shape based on the two-dimensional slice data, the operation of forming the solidified layer is repeated to sequentially stack the layers in the vertical direction, thus achieving modeling. PTL 2 describes a material for fabricating a mold for producing a casting with a 3D printer and discloses a material containing cement, sand, and a water-soluble silicate as an accelerator. PTLs 3 and 4 disclose a method of producing a prefab member by using a 3D printer and a method of producing an earthquake-resistant concrete wall by using a 3D printer. PTL 5 discloses a technique about a nozzle that discharges a material for 3D printing. PTL 6 discloses a method of producing a cementitious cured product characterized in that a cementitious cured product is molded with a resin mold fabricated by a three-dimensional modeling system.

[0004]

On the other hand, as a cementitious material, a material in which a lignin sulfonic acid-based dispersant and a melamine sulfonic acid-based dispersant are used in combination has already been known as a grout composition or a high strength concrete composition (PTLs 7 and 8). In addition, a PC grout material is known as a material in which a dispersant and a thickener are used together (PTL 9). Furthermore, as a material containing SiO₂-containing calcium aluminate, a cement admixture characterized by containing as essential components 300 parts by weight or less of a gypsum and 0.1 to 20 parts by weight of a setting modifier relative to 100 parts by weight of a calcium aluminosilicate glass and a cement composition in which the cement admixture is blended in a cement (PTL 10), a cement composition containing a calcium aluminosilicate having a CaO/Al₂O₃ molar ratio of 2.0 to 3.5 and having a SiO₂ content of 10 to 25% and one or two or more selected from a latent hydraulic material and a pozzolan material (PTL 11), and the like are known.

[0005]

Furthermore, as a cementitious material for three-dimensional modeling for construction, a cementitious material containing a cement, an aggregate, a dispersant containing a lignin sulfonic acid-based dispersant and a melamine sulfonic acid-based dispersant at a mass ratio R:M of 100:80 to 400, a thickener, a

setting retarder, an amorphous calcium aluminosilicate containing SiO₂ in an amount of 10 to 25% based on oxide, gypsum, and a short fiber is known (PTL 12).

Citation List

Patent Literature

[0006]

PTL 1: JP 10-235623 A

PTL 2: US 8211226

PTL 3: Chinese Patent Application Publication No. 104308988

PTL 4: Chinese Patent Application Publication No. 104153493

PTL 5: US Patent Application Publication No. 2014/0308381

PTL 6: JP 2016-101737 A

PTL 7: JP 2008-247677 A

PTL 8: JP 62-10949 B

PTL 9: JP 2006-290694 A

PTL 10: JP 4-97932 A

PTL 11: JP 2006-232603 A

PTL 12: JP 2018-140906 A

Summary of Invention

Technical Problem

[0007]

Since PTL 1 relates to a technique in which a dry mix mortar obtained by premixing a cement and a fine aggregate and water containing an accelerating agent are jetted while mixing and stirring them with a spray nozzle to subject the mortar to self-standing curing, it is required to further improve the finishing of the modeled product and to further reduce generation of dust. In PTL 2, since a water-soluble silicate is used as an accelerator, there is a problem of a low speed of curing, possibly leading to poor strength developability. PTLs 3 and 4 relate to a technique of producing a member with a 3D printer, and thus, do not have a description about use of a specific material. PTL 5 relates to a shape of a nozzle of a 3D printer, and thus, do not have a description about use of a specific material. PTL 6 relates to a technique of producing a cementitious cured product by molding a resin mold with a 3D printer and filling the resin mold with a cementitious material, and since it is essential to fabricate such a mold, there is a problem in that a cementitious cured product which is a molded product cannot be efficiently produced.

As a cementitious material, various materials as described in PTLs 7 to 11 are known, but no cementitious material that can solve the problems as described above has been known yet. PTL 12 discloses a cementitious material for three-dimensional modeling for construction, but has no description about short-time strength. The present invention is capable of providing a sufficient construction speed.

[0008]

In view of the above problems, the present invention has an object to provide a cementitious material for three-dimensional modeling for construction excellent in self-standing ability and short-time and long-time strength developability, and a method of three-dimensional modeling for construction.

Solution to Problem

[0009]

As a result of various studies for solving the above problems, the present inventor has found that the above problems can be solved by use of a cementitious material that contains an aggregate, a dispersant containing a lignin sulfonic acid-based dispersant and a melamine sulfonic acid-based dispersant at a specific ratio, a diutan gum having a average molecular weight in the range of 2,000,000 to 8,000,000 and having a viscosity of a 0.25 mass% aqueous solution in the range of 2,000 to 10,000 mPa·s, a setting retarder, an amorphous calcium aluminosilicate containing SiO₂ in a specific proportion, a gypsum, and a short fiber all together, thus completing the present invention.

Specifically, the present invention relates to:

- (1) a cementitious material for three-dimensional modeling for construction, containing (A) a cement, (B) an aggregate, (C) a dispersant containing a lignin sulfonic acid-based dispersant (R) and a melamine sulfonic acid-based dispersant (M) at a mass ratio R:M of 100:80 to 400, (D) a diutan gum having an average molecular weight in the range of 2,000,000 to 8,000,000 and having a viscosity of a 0.25 mass% aqueous solution in the range of 2,000 to 10,000 mPa·s, (E) a setting retarder, (F) an amorphous calcium aluminosilicate containing 10 to 25% by mass of SiO₂ based on oxide, (G) a gypsum, and (H) a short fiber,
- (2) the cementitious material for three-dimensional modeling for construction according to the above (1), wherein the dispersant (C) is used in an amount of 0.2 to 3 parts by mass relative to 100 parts by mass of the cement (A),
- (3) the cementitious material for three-dimensional modeling for construction

- according to the above (1) or (2), wherein the diutan gum (D) is used in an amount of 0.03 to 1.0 parts by mass relative to 100 parts by mass of the cement (A),
- (4) the cementitious material for three-dimensional modeling for construction according to any one of the above (1) to (3), wherein the gypsum (G) is used in an amount of 50 to 250 parts by mass relative to 100 parts by mass of the amorphous calcium aluminosilicate (F),
- (5) the cementitious material for three-dimensional modeling for construction according to any one of the above (1) to (4), wherein the amorphous calcium aluminosilicate (F) and the gypsum (G) are used in a total amount of 5 to 30 parts by mass relative to 100 parts by mass of the cement (A),
- (6) the cementitious material for three-dimensional modeling for construction according to any one of the above (1) to (5), wherein the aggregate (B) contains a balloon-type aggregate,
- (7) the cementitious material for three-dimensional modeling for construction according to any one of the above (1) to (6), wherein the setting retarder (E) contains an oxycarboxylic acid,
- (8) the cementitious material for three-dimensional modeling for construction according to any one of the above (1) to (7), wherein the short fiber (H) has an average fiber length of 5 to 15 mm,
- (9) the cementitious material for three-dimensional modeling for construction according to the above (8), wherein the short fiber (H) has an average fiber diameter of 100 to 250 μm and a number of fibers per gram of 5,000/g or more,
- (10) a method of three-dimensional modeling for construction, the method including kneading the cementitious material for three-dimensional modeling for construction according to any one of the above (1) to (9) with water to obtain a wet material, pressure-feeding the wet material with a pump, and stacking layers of the wet material discharged from a nozzle while moving the nozzle to thereby construct a modeled product, and
- (11) the method of three-dimensional modeling for construction according to the above (10), wherein the pump is a rotary positive displacement-type uniaxial eccentric screw pump.

Advantageous Effects of Invention

[0010]

By using the cementitious material for three-dimensional modeling for construction and the method of three-dimensional modeling for construction of the

present invention, it is possible to feed a constant amount of a material and to ensure a constant layering speed. In addition, since excellent self-standing ability and strength developability can be achieved, it is possible to construct a large modeled product in a short period of time.

Brief Description of Drawings

[0011]

Fig. 1 is a schematic diagram showing a three-dimensional modeling experimental system.

Fig. 2 (a) is a schematic diagram of a spray nozzle viewed laterally and Fig 2 (b) is a schematic diagram of the spray nozzle viewed from a discharge opening side.

Fig. 3 is a schematic diagram showing a cross-sectional shape of a three-dimensional modeled product produced in Example 8.

Description of Embodiments

[0012]

In the present invention, “three-dimensional modeling” refers to a technique in which layering modeling of a cross-sectional shape is directly performed based on three-dimensional data without a dedicated tool, such as a mold, to produce a molded product having any shape. It is sometimes referred to as “additive manufacturing” or “rapid prototyping”.

[0013]

[Cementitious material for three-dimensional modeling]

The cementitious material for three-dimensional modeling of the present invention (hereinafter sometimes referred to simply as “cementitious material”) contains (A) a cement, (B) an aggregate, (C) a dispersant containing a lignin sulfonic acid-based dispersant (R) and a melamine sulfonic acid-based dispersant (M) at a mass ratio R:M of 100:80 to 400, (D) a diutan gum having an average molecular weight in the range of 2,000,000 to 8,000,000 and having a viscosity of a 0.25 mass% aqueous solution in the range of 2,000 to 2,0000 mPa·s, (E) a setting retarder, (F) an amorphous calcium aluminosilicate containing 10 to 25% by mass of SiO₂ based on oxide, (G) a gypsum, and (H) a short fiber.

[0014]

<Cement (A)>

As the cement (A) used in the present invention, in general, various portland cements, such as normal, high early strength, ultrahigh early strength,

low heat, and moderate heat cements, various mixed cements in which blast furnace slag, fly ash, or silica is mixed with the portland cements, a filler cement in which a limestone powder, air-cooled blast furnace slag fine powder, or the like having a Blaine's specific surface area of $2,000 \text{ cm}^2/\text{g}$ or more is mixed, an environment harmony cement (eco-cement) produced by using city waste incineration ash or sewage sludge incineration ash as a raw material, an alumina cement which is used in a refractory application, and the like are exemplified. One or two or more of such cements can be used. The Blaine's specific surface area of the cement is preferably $3000 \text{ cm}^2/\text{g}$ or more.

[0015]

<Aggregate (B)>

The aggregate (B) used in the present invention is not particularly limited, and a commercially available natural one, such as an aggregate derived from limestone, an aggregate derived from a siliceous material, or a heavy aggregate having a specific gravity of more than 3.0, can be used. For the purpose of improving self-standing ability, a part of the aggregate used may be a balloon-type aggregate. Balloon-type aggregate is generally referred to as light aggregate, and examples thereof include fly ash balloon, shirasu balloon, and a balloon obtained by sintering and foaming obsidian in a kiln. The light aggregate preferably has a specific gravity of 2.0 or less, more preferably 1.8 or less, and further preferably 0.3 to 1.0.

The aggregate (B) (including balloon-type aggregate) has a maximum particle diameter of 10 mm or less in consideration of the pump pressure feeding ability, and more preferably 5 mm or less.

The amount of the aggregate (B) used is preferably 50 to 300 parts by mass relative to 100 parts by mass of the cement (A), and more preferably 100 to 200 parts by mass. With a too small amount, it tends to be difficult to ensure the self-standing ability, and with a too large amount, it is difficult to ensure appropriate softness to possibly impair the pump pressure feeding ability.

When a balloon-type aggregate is used, the amount of the balloon type aggregate used is preferably 25 parts by mass or less in 100 parts by mass of the aggregate (B), more preferably 1 to 25 parts by mass, and further preferably 3 to 15 parts by mass. With a too large amount, the strength developability decreases or it is difficult to ensure appropriate softness to possibly impair the pump pressure feeding ability. On the other hand, with a too small amount, the self-standing

ability improvement effect is possibly not achieved.

[0016]

<Dispersant (C)>

In the present invention, as the dispersant (C), a dispersant containing a lignin sulfonic acid-based dispersant (R) and a melamine sulfonic acid-based dispersant (M) in which the lignin sulfonic acid-based dispersant (R) and the melamine sulfonic acid-based dispersant (M) are used in combination at a mass ratio R:M of 100:80 to 400 is used. By using the dispersant (C), the flowability of the cementitious material obtained by kneading with water added is ensured and the thixotropy can be improved. The ratio R:M is more preferably 100:100 to 250. When the proportion of the melamine sulfonic acid-based dispersant (M) blended is less than the lower limit, the amount of the dispersant required for achieving desired flowability increases, and the temporal change in the flowability is too large so that the pump pressure feeding may be disrupted. When the proportion of the melamine sulfonic acid-based dispersant (M) blended is more than the upper limit, the setting is retarded to reduce the temporal change in the flowability so that it may be difficult to ensure the self-standing ability after pressure feeding.

The amount of the dispersant (C) used is preferably 0.2 to 3 parts by mass relative to 100 parts by mass of the cement (A), and more preferably 0.5 to 2 parts by mass. With a too small amount, it is possibly difficult to achieve sufficient flowability, and with a too large amount, the setting is retarded to reduce the temporal change in the flowability so that the self-standing ability is possibly lost.

[0017]

<Diutan gum (D)>

In the present invention, a diutan gum (D) having an average molecular weight in the range of 2,000,000 to 8,000,000 and having a viscosity of a 0.25 mass% aqueous solution in the range of 2,000 to 10,000 mPa·s can be used. Here, the viscosity of an aqueous solution having a concentration of 0.25% by mass is a value measured at 25°C with a Brookfield viscometer under a condition of 3 rpm. The diutan gum is, for example, a natural high molecular weight polysaccharide having two glucose units, one glucuronic acid unit, and three rhamnose units as constituting units.

The average molecular weight is preferably the weight average molecular weight (hereinafter, weight average molecular weight is sometimes referred to as molecular weight). The weight average molecular weight is, for example, a value

based on polyethylene oxide standards measured by gel permeation chromatography (GPC) or size exclusion chromatography. Specifically, the weight average molecular weight can be determined by creating a calibration curve with commercially available polyethylene oxide standards using a GPC system (SC-8010 manufactured by TOSOH CORPORATION) with water as a solvent under the following conditions.

Flow rate: 4.0 ml/min

Preset temperature: 40°C

Column configuration: “TSKgel G5000PWXL” manufactured by TOSOH CORPORATION and “TSKgel G3000PWXL” manufactured by TOSOH CORPORATION were connected in series in this order.

Injection of sample: 100 µl (concentration of sample solution: 1 mg/ml)

Detector: RI detector

The amount of the diutan gum (D) used is preferably 0.03 to 1.0 parts by mass relative to 100 parts by mass of the cement (A), and more preferably 0.05 to 0.5 parts by mass. With a too small amount, it is possibly difficult to impart sufficient thixotropy, and with a too large amount, the pump pressure feeding ability and the strength developability are possibly impaired.

[0018]

<Setting retarder (E)>

As the setting retarder (E) used in the present invention, one which is generally commercially available for a cementitious material can be used. Examples thereof include inorganic retarders, such as a phosphate salt, a silicofluoride, copper hydroxide, boric acid or a salt thereof, zinc oxide, zinc chloride, and zinc carbonate. One of them or a mixture of two or more thereof can be used. Examples also include organic retarders, such as oxycarboxylic acids (citric acid, gluconic acid, malic acid, tartaric acid, glucoheptonic acid, oxymalonic acid, lactic acid, and the like) or a salt thereof (hereinafter oxycarboxylic acids and salts of oxycarboxylic acids are sometimes collectively referred to as oxycarboxylic acids) and saccharides typified by sucrose. One of them or a mixture of two or more thereof can be used. Furthermore, a mixture of a combination of a carbonate salt, a bicarbonate salt, a nitrate acid, a hydroxide, or a silicate salt as an inorganic compound and an oxycarboxylic acid or a salt thereof as described above can be used. Among them, one containing an oxycarboxylic acid is preferred, and an oxycarboxylic acid alone or one or more selected from the group consisting of

mixtures of an oxycarboxylic acid and an inorganic compound are more preferred.

The amount of the setting retarder (E) used is preferably 0.05 to 0.7 parts by mass relative to 100 parts by mass of the cement, and more preferably 0.07 to 0.5 parts by mass. With a too small amount, it is possibly difficult to ensure the pot life in consideration of the kneading time and pump pressure feeding, and with a too large amount, the curing time increases so that the self-standing ability is possibly not able to be ensured.

[0019]

<Amorphous calcium aluminosilicate (F)>

The amorphous calcium aluminosilicate (F) containing 10 to 25% by mass of SiO₂ based on oxide used in the present invention (hereinafter described simply as “calcium aluminosilicate”) is an amorphous calcium aluminosilicate having a SiO₂ content of 10 to 25 % by mass obtained by subjecting a mixture of a CaO raw material, an Al₂O₃ raw material, and an SiO₂ raw material to a heat treatment, such as sintering in a kiln or melting in an electric furnace. Since the amorphous calcium aluminosilicate is amorphous, it has a high reactivity.

Here, “amorphous” preferably refers to having a percentage of glass content of 70% or more in point of the reactivity, and more preferably having a percentage of glass content of 90% or more. The percentage of glass content is determined by previously measuring a main peak area S of a crystalline mineral by powder X-ray diffractometry on a sample before heating, heating the sample at 1000°C for 2 hours and then gradually cooling the sample at a rate of 1 to 10°C/minute, measuring a main peak area S₀ of the crystalline mineral after heating by powder X-ray diffractometry, and then calculating the percentage of glass content x using the following equation based on the values of S₀ and S.

$$\text{Percentage of glass content } x (\%) = 100 \times (1 - S/S_0)$$

When the content of SiO₂ is less than 10% by mass, the hydration activity increases and the amount of the setting retarder required for adjusting the curing time increases, which possibly has an influence on the thixotropy and self-standing ability. When the content is more than 25% by mass, the hydration activity decreases and an appropriate curing speed is possibly not able to be achieved.

The calcium aluminosilicate (F) preferably has a molar ratio of CaO and Al₂O₃, CaO/Al₂O₃, based on oxides of 1.5 to 3.5, and more preferably 1.7 to 2.0. In addition, as another component, an alkali metal, such as sodium, potassium, and lithium, can be partially dissolved.

The particle size of the calcium aluminosilicate is preferably 3000 cm²/g or more as the Blaine value. With a too small Blaine value, the strength developability possibly decreases.

[0020]

<Gypsum (G)>

The gypsum (G) used in the present invention is a component that further increases the strength by being used together with the calcium aluminosilicate. As a type of the gypsum (G), anhydrous gypsum, gypsum hemihydrate, and gypsum dihydrate are exemplified, and a gypsum generated as a byproduct in a factory or a naturally produced gypsum can be used. Among them, anhydrous gypsum is preferably used in terms of the strength developability.

The particle size of the gypsum (G) is preferably 3000 cm²/g or more as the Blaine value. With a too small Blaine value, the strength developability enhancing effect is possibly not obtained.

The ratio of the gypsum (G) relative to the calcium aluminosilicate (F) is preferably 50 to 250 parts by mass relative to 100 parts by mass of the calcium aluminosilicate (F), and more preferably 100 to 200 parts by mass. With a too low ratio of the gypsum (G), the strength enhancing effect is possibly not obtained, and with a too high ratio of the gypsum (G), the strength developability possibly plateaus.

[0021]

The total amount of the calcium aluminosilicate (F) and the gypsum (G) used is preferably 5 to 30 parts by mass relative to 100 parts by mass of the cement (A), and more preferably 10 to 20 parts by mass. With a too small amount, the strength enhancing effect is possibly not obtained, and with a too large amount, it is possibly difficult to ensure the pot life or the strength developability possibly decreases.

[0022]

<Short fiber (H)>

As the short fiber (H) used in the present invention, a short fiber generally commercially available as an admixture in a cement can be used. Examples thereof include a vinylon fiber, an acrylic fiber, a nylon fiber, a steel fiber, a glass fiber, a polypropylene fiber, a polyethylene fiber, a polyester fiber, and a basalt fiber. One of these fibers can be used or two or more thereof can be used in combination. Among them, one or more selected from the group consisting of vinylon fibers

having various fiber diameters and fiber lengths or nylon fibers excellent in dispersibility are preferably used.

The average fiber length of the short fiber (H) is preferably in the range of 5 to 15 mm in consideration of previous premixing. The average fiber diameter of the short fiber (H) is preferably 20 to 250 μm in terms of the three-dimensional modeling properties, and more preferably 100 to 250 μm . A fiber with a too small average diameter may be difficult to be available. On the other hand, a fiber with a too large average fiber diameter possibly impairs the pump pressure feeding ability of the wet material, and even if the pump pressure feeding can be performed, increase in the temperature of the wet material with the pressure feeding is too large and the curing time is excessively short, possibly leading to deterioration of the molding ability or reduction in the strength developability of the molded product. By using the short fiber (H) having an average fiber diameter of 20 μm or more, in particular, 100 μm or more, the frictional heat generated in pump pressure feeding of the wet material obtained by adding water to the cementitious material increases to increase the temperature of the wet material discharged from the nozzle tip so that the curing time appropriately decreases, making it possible to achieve continuous higher layering.

As the short fiber (H), a bundled-type fiber in which monofilament fibers are bundled with a binder is more preferred than a monofilament-type fiber since a larger number of fibers can be incorporated in the former type.

The number of fibers per gram of the short fiber (H) is preferably 5,000/g or more. With a too small number per gram, a reinforcing effect and an initial crack suppressing effect by the short fiber (H) are possibly not able to be exhibited. The number of fibers per gram of the short fiber (H) is preferably 500,000/g or less. The number of fibers per gram of the short fiber (H) is determined according to the following equation based on the fineness (dtex, mass (g) per 10,000 m of a monofilament).

Number of fibers (/g) = [1 / (fineness / 10,000 (m))] / average fiber length (m/number)

The amount of the short fiber (H) used is preferably 0.1 to 1.0 parts by mass relative to 100 parts by mass of the total of the cement (A) and the aggregate (B), and more preferably 0.2 to 0.5 parts by mass. With a too small amount, the reinforcing effect is possibly not exhibited, and with a too large amount, the pump pressure feeding is possibly disrupted.

[0023]

<Other components>

In the present invention, various additives, for example, an antifoaming agent, an antirust agent, an antifreezing agent, a shrinkage reducing agent, an inorganic mineral, such as bentonite or sepiolite, and an anion exchanger, such as hydrotalcite; a polymer emulsion; and the like can be added to the extent that the construction and the performance of cured product are not impaired. Besides the materials blended to the cement in advance, an inorganic powder having a hydration activity, such as blast furnace slag, silica fume, or fly ash, can also be used.

[0024]

<Amount of water used>

In the cementitious material of the present invention, a wet material is prepared by kneading with water and is used for three-dimensional modeling. The amount of water used is preferably 13 to 20 parts by mass relative to 100 parts by mass of the cementitious material, and more preferably 15 to 18 parts by mass. With a too small amount, the kneading is possibly difficult, and with a too large amount, the flowability of the wet material increases to possibly deteriorate the self-standing ability.

[0025]

[Method of three-dimensional modeling]

The method of three-dimensional modeling of the present invention will be described with reference to a three-dimensional modeling experimental system 1 shown in Fig. 1 as an example. Note that the three-dimensional modeling experimental system 1 shown in Fig. 1 is not to limit the method of three-dimensional modeling of the present invention. The method of three-dimensional modeling of the present invention is divided into a step of kneading a cementitious material, a step of pressure-feeding with a pump a wet material obtained by kneading, and a step of performing three-dimensional modeling by controlled nozzle movement.

[0026]

A method of kneading a cementitious material adopted in the method of three-dimensional modeling of the present invention is not particularly limited, and the cementitious material can be kneaded with a mixer 10 which is commercially available. Examples thereof include a pan mixer, a forced twin-

screw mixer, and a continuous kneading mixer pump in which kneading and a pressure feeding pump (rotary positive displacement-type uniaxial eccentric screw pump) are integrated.

[0027]

A pump 20 for pressure-feeding the kneaded wet material adopted in the method of three-dimensional modeling of the present invention is not particularly limited as long as it can perform pressure feeding without deteriorating the quality of the wet material. A rotary positive displacement-type uniaxial eccentric screw pump 20 is preferred. The rotary positive displacement-type uniaxial eccentric screw pump 20 is referred to as a mohno pump or a snake pump, and unlike a squeeze pump, no pulsation occurs in pressure feeding, a quantitative pressure feeding can be achieved, and the quantity of discharge can be adjusted by controlling the rotation speed of the motor. The rotary positive displacement-type uniaxial eccentric screw pump 20 is preferred also in that the temperature of the pressure-fed wet material is considered to tend to increase due to the structure, and the curing reaction of the wet material proceeds in a shorter period of time so that the self-standing stability is enhanced, making it possible to increase the continuous layering height. Specifically, the rotary positive displacement-type uniaxial eccentric screw pump 20 is provided with a rotor corresponding to a male screw and a stator corresponding to a female screw, the rotor being disposed in the stator with a sealed space called cavity (for example, a space between a rotor and a stator) formed in a gap, and has a mechanism in which while generating a strong suction force by the rotor rotating in the stator, the cavity moves toward the discharge side to thus continuously deliver a material. In delivery, for example, the rotor undergoes eccentric rotary movement in which the rotor rotates while revolving about the central axis of the stator. Thus, when a material in the first cavity moves to a forward cavity (on the discharge side) by the suction force, the material is heated by the friction resistance against a stator surface. When such a heating phenomenon is utilized, three-dimensional modeling more excellent in the self-standing stability can be achieved while ensuring the pot life. For example, the rotary positive displacement-type uniaxial eccentric screw pump 20 is mentioned in the paragraphs 0063 to 0064 of WO2014/142239.

A pressure feeding pipe 30 can be used in combination with a flexible hose having a withstand pressure of 2 to 4 MPa or partially with a metal pipe. Depending on the discharge amount to be set, the pipe diameter is preferably 20

to 50 mm as the inner diameter. The length of the pressure feeding pipe 30 is not particularly limited, and preferably 20 m or less in consideration of the pressure feeding ability.

[0028]

A wet material discharge part (a tip of the pressure feeding pipe) adopted in the method of three-dimensional modeling of the present invention is preferably provided with a spray nozzle 40. The diameter of a discharge opening 41 (see Fig. 2) is not particularly limited, and may be appropriately set depending on the diameter of the aggregate used and the width to be layered. For example, when the aggregate diameter is 5 mm or less and the layered width is 50 mm or less, the inner diameter of the discharge opening 41 is preferably 5 to 20 mm, and more preferably 8 to 15 mm. The shape of the discharge opening 41 is not particularly limited, and examples thereof include a circular shape, an elliptic shape, a rectangular shape, a cross shape, and a star shape. A flange can be provided around the discharge opening for imparting smoothness to the surface of the wet material discharged. The discharge opening 41 is provided vertically to a bed 50, but the discharge opening 41 may be provided horizontally in some cases.

[0029]

In the method of three-dimensional modeling of the present invention, movement of the nozzle in the horizontal direction and the vertical direction is preferably controlled by a computer, for example, by fixing the spray nozzle 40 onto a robot arm 60 or a portal plotter. For example, the following method is possible. Three-dimensional data created by a computer are cut into a prescribed thickness to create two-dimensional slice data. While controlling movement of the spray nozzle 40 in horizontal directions, such as a length direction, a width direction, and a diagonal direction, based on the two-dimensional slice data, the wet material is discharged from the spray nozzle 40 onto the bed 50, and then the nozzle is moved in the vertical direction. The above operation is repeated to sequentially stack layers of the wet material to achieve modeling of a three-dimensional modeled product (for example, a three-dimensional modeled product having a cross-sectional shape 70 shown in Fig. 3). When the spray nozzle 40 is fixed on the robot arm 60 or the portal plotter, a pulley 80 is preferably used to prevent the pressure feeding pipe 30 from bending and thus clogging.

The rate of movement of the spray nozzle 40 is not particularly limited, and can be varied depending on the layered width of the wet material. When the

amount of the wet material discharged is constant, the width of the wet material layered is larger with a lower speed, and the width of the wet material layered is smaller with a higher speed.

Examples

[0030]

The present invention will be described in detail below based on Examples.
<Example 1>

With 100 parts by mass of a cement, 150 parts by mass of an aggregate, 1.0 parts by mass of a dispersant containing a lignin sulfonic acid-based dispersant (R) and a melamine sulfonic acid-based dispersant (M) at a mass ratio R/M of 100/200, a diutan gum in a type and amount shown in Table 1, 0.25 parts by mass of a setting retarder i, and 20 parts by mass of a mixture of 150 parts by mass of a gypsum with 100 parts by mass of a calcium aluminosilicate shown in Table 1 were blended, and a short fiber a was blended therein in an amount of 0.2 parts by mass relative to 100 parts by mass of the total amount of the cement and the aggregate, thus preparing a cementitious material for three-dimensional modeling (hereinafter sometimes referred to as a cementitious material). To 100 parts by mass of the prepared material, 17 parts by mass of water was added, and the mixture was kneaded with a pan mixer. The mini slump (MS, immediately after kneading and after 20 minutes), the curing time, and the compression strength of the resulting wet material were measured and the MS reduction rate was calculated. The results are shown in Table 1.

[0031]

(Materials used)

<Cement (A)>

Cement: normal portland cement (manufactured by Denka Company Limited, Blaine's specific surface area: 3400 cm²/g)

<Aggregate (B)>

Aggregate: limestone aggregate (manufactured by Denka Company Limited, maximum particle diameter: 1.2 mm, specific gravity: 2.71)

<Dispersant (C)>

Lignin sulfonic acid-based dispersant (R): manufactured by Nippon Paper Industries Co., Ltd., tradename "SAN X P252"

Melamine sulfonic acid-based dispersant (M): manufactured by Sika Ltd., tradename "Sikament FF86/100"

<Diutan gum (D)>

Diutan gum A: synthesized by using glucose as a starting material to perform aerobic fermentation with a microbe of Genus *Alcaligenes*. Molecular weight: 4,100,000, viscosity of 0.25 mass% aqueous solution: 5,600 mPa·s

Diutan gum B: synthesized in the same manner as the diutan gum A except for changing the fermentation time. Molecular weight: 2,200,000, viscosity of 0.25 mass% aqueous solution: 2,300 mPa·s

Diutan gum C: synthesized in the same manner as the diutan gum A except for changing the fermentation time. Molecular weight: 5,300,000, viscosity of 0.25 mass% aqueous solution: 7,500 mPa·s

Diutan gum D: synthesized in the same manner as the diutan gum A except for changing the fermentation time. Molecular weight: 7,800,000, viscosity of 0.25 mass% aqueous solution: 9,600 mPa·s

Diutan gum E: synthesized in the same manner as the diutan gum A except for changing the fermentation time. Molecular weight: 1,800,000, viscosity of 0.25 mass% aqueous solution: 1800 mPa·s

<Thickener other than diutan gum>

Thickener A: cellulose ether-based thickener (manufactured by Shin-Etsu Chemical Co., Ltd., tradename “hi90SH-30000” (viscosity of 2 mass% aqueous solution at 20°C: 30,000 mP·s))

<Setting retarder (E)>

Setting retarder i: citric acid (extra pure reagent)

<Amorphous calcium aluminosilicate (F)>

Calcium aluminosilicate A: prepared by mixing commercially available guaranteed reagents SiO_2 , CaCO_3 , and Al_2O_3 at a prescribed ratio, melting the mixture with heat using a high-frequency furnace at about 2,000°C, rapidly cooling it in water, and pulverizing the resultant (amorphous (hereinafter, in Examples, amorphous means having a percentage of glass content of 90% or more), SiO_2 content: 10.1%, $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio: 1.85, Blaine’s specific surface area: 5,900 cm^2/g)

Calcium aluminosilicate B: prepared in the same manner as calcium silicate A except for changing the ratio of the reagents blended (amorphous, SiO_2 content: 14.9%, $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio: 1.85, Blaine’s specific surface area: 5,800 cm^2/g)

Calcium aluminosilicate C: prepared in the same manner as calcium

silicate A except for changing the ratio of the reagents blended (amorphous, SiO₂ content: 24.6%, CaO/Al₂O₃ molar ratio: 1.85, Blaine's specific surface area: 5,800 cm²/g)

<Gypsum (G)>

Gypsum: pulverized natural anhydrous gypsum (Blaine's specific surface area: 5,200 cm²/g)

<Short fiber (H)>

Short fiber a: vinylon fiber (average fiber length: 12 mm, average fiber diameter: 50 μm, number of fibers: 55,500/g)

[0032]

(Testing method)

Each test was performed in an environment at 20°C.

(1) Blaine's specific surface area

It was measured according to JIS R 5201-1997.

(2) Maximum particle diameter

According to JIS A 1102, the aggregate was screened, and the mesh size of the largest mesh that did not allow the particles to pass through was taken as the maximum particle diameter.

(3) Mini slump (MS)

It was measured according to JIS A 1171. Measurement was performed immediately after kneading and after 20 minutes.

(4) MS Reduction rate

Based on the mini slump values immediately after kneading and after 20 minutes, the MS reduction rate was calculated according to the following equation.

Slump reduction rate (%) = [mini slump (immediately after kneading) - mini slump (after 20 minutes)] / [mini slump (immediately after kneading) × 100]

(5) Curing time

After completing kneading, 2 kg of the wet material was filled in a plastic bag, and the first time when the filled bag was not dented on pushing with a finger was taken as the curing time. Pushing with a finger was performed at intervals of 5 minutes.

(6) Compression strength

A three-part mold of 4 × 4 × 16 cm according to JIS R 5201 was filled with the kneaded material, and the compression strength was measured at material ages of 3 hours, 12 hours, 1 day, and 7 days.

(7) Specific gravity of limestone aggregate

Measurement was performed according to JIS A 1109 and the absolute dry density was taken as the specific gravity.

[0033]

Table 1

Experiment No.	Calcium aluminosilicate	Diutan gum	Amount of diutan gum used (parts by mass)	MS (mm)		MS Reduction rate (%)	Curing time (min)	Compression strength (N/mm ²)				Remarks
				immediately after	after 20 min			3 hours	12 hours	1 day	7 days	
1-1	A	A	0.03	39	26	33.3	49	6.1	10.9	24.8	60.4	Example
1-2			0.05	35	23	34.3	50	6.2	11.0	24.9	61.3	Example
1-3			0.1	32	19	40.6	52	6.5	11.3	25.1	62.5	Example
1-4			0.3	25	15	40.0	53	6.4	11.1	24.3	61.9	Example
1-5			0.5	21	13	38.1	55	6.2	11.1	24.0	61.8	Example
1-6			1.0	20	11	45.0	58	6.0	10.9	24.0	61.0	Example
1-7	B	A	0.03	38	27	28.9	52	6.5	10.9	23.1	60.0	Example
1-8			0.05	34	24	29.4	56	6.7	11.2	24.6	61.2	Example
1-9			0.1	30	19	36.7	58	7.1	11.5	25.6	63.3	Example
1-10			0.3	22	15	31.8	59	6.8	10.9	24.9	63.0	Example
1-11			0.5	20	12	40.0	59	6.7	10.9	24.4	62.5	Example
1-12			1.0	18	11	38.9	60	6.6	10.8	24.0	61.9	Example
1-13	C	A	0.03	40	28	30.0	68	5.8	9.7	22.8	60.0	Example
1-14			0.05	37	25	32.4	69	5.9	9.9	22.9	61.1	Example
1-15			0.1	33	20	39.4	72	6.2	10.2	23.7	61.5	Example
1-16			0.3	26	18	30.8	78	6.1	10.0	23.4	61.2	Example
1-17			0.5	24	15	37.5	85	6.1	10.0	22.9	61.2	Example
1-18			1.0	22	14	36.4	89	5.8	9.6	22.8	60.8	Example
1-19	B	B	0.03	46	33	28.3	53	6.0	10.4	22.9	58.9	Example
1-20			0.05	40	29	27.5	57	6.7	10.6	22.9	59.3	Example
1-21			0.1	34	27	20.6	59	6.8	10.9	23.4	60.5	Example
1-22			0.3	26	20	23.1	60	6.4	10.5	23.3	60.1	Example
1-23			0.5	23	18	21.7	62	6.2	10.3	23.1	59.6	Example
1-24			1.0	21	16	23.8	64	6.1	10.3	22.9	59.2	Example
1-25	B	C	0.03	36	25	30.6	53	5.8	10.5	22.0	58.8	Example
1-26			0.05	31	22	29.0	57	5.9	10.6	22.4	59.4	Example
1-27			0.1	28	20	28.6	61	6.1	10.8	23.1	60.1	Example
1-28			0.3	19	15	21.1	63	5.8	10.7	22.6	59.9	Example
1-29			0.5	17	13	23.5	64	5.7	10.5	22.5	59.8	Example
1-30			1.0	15	11	26.7	68	5.5	10.3	22.5	58.9	Example

Table 1 (continued)

Experiment No.	Calcium aluminosilicate	Diutan gum	Amount of diutan gum used (parts by mass)	MS (mm)		MS Reduction rate (%)	Curing time (min)	Compression strength (N/mm ²)				Remarks
				immediately after	after 20 min			3 hours	12 hours	1 day	7 days	
1-31	B	D	0.03	32	25	21.9	54	5.5	9.5	21.4	58.7	Example
1-32			0.05	29	21	27.6	58	5.6	9.7	21.8	58.9	Example
1-33			0.1	24	19	20.8	62	5.8	10.2	22.4	59.7	Example
1-34			0.3	20	16	20.0	63	5.7	9.9	22.0	58.9	Example
1-35			0.5	17	14	17.6	65	5.7	9.8	21.4	58.4	Example
1-36			1.0	15	10	33.3	66	5.4	9.4	21.3	58.0	Example
1-37	B	E	0.03	52	46	11.5	67	2.0	6.5	15.4	57.0	Comparative Example
1-38			0.05	46	40	13.0	66	1.8	6.7	15.5	57.2	Comparative Example
1-39			0.1	40	36	10.0	64	1.5	6.8	16.2	57.1	Comparative Example
1-40			0.3	35	29	17.1	61	0.9	6.0	15.4	55.6	Comparative Example
1-41			0.5	32	27	15.6	63	-	4.4	13.2	52.1	Comparative Example
1-42			1.0	28	24	14.3	70	-	3.9	12.9	51.4	Comparative Example
1-43	B	Thickener A	0.1	48	34	29.2	65	1.1	5.3		55.6	Comparative Example

-: not measurable or not capable of taking a specimen

Diutan gum: in parts by mass relative to 100 parts by mass of the cement

[0034]

As can be seen from Table 1, in the composition range of the diutan gum of the present invention, the pump pressure feeding ability was not impaired and the self-standing ability was able to be ensured after pressure feeding. Furthermore, since superior values were exhibited as both the initial strength and the long-term strength, an excellent layering rate and an excellent construction speed were able to be achieved. On the other hand, when a diutan gum out of the range of the present invention or another thickener was used, although an MS reduction rate ensuring the self-standing ability was achieved in some cases, the initial strength developability was deteriorated and a sufficient layering rate and a sufficient construction speed were not able to be achieved.

[0035]

<Example 2>

With 100 parts by mass of the cement, 150 parts by mass of the aggregate, a dispersant in a type and amount shown in Table 1, 0.1 parts by mass of the diutan gum A, 0.25 parts by mass of the setting retarder i, and 20 parts by mass of a mixture of 150 parts by mass of the gypsum with 100 parts by mass of the calcium aluminosilicate B were blended, and the short fiber a was blended in an amount of 0.2 parts by mass relative to 100 parts by mass of the total amount of the cement and the aggregate, thus preparing a cementitious material for three-dimensional modeling (hereinafter sometimes referred to as a cementitious material). To 100 parts by mass of the prepared material, 17 parts by mass of water was added, and the mixture was kneaded with a pan mixer. The mini slump (MS, immediately after kneading and after 20 minutes), the curing time, and the compression strength of the resulting wet material were measured and the MS reduction rate was calculated. The results are shown in Table 2.

[0036]

Table 2

Experiment No.	R/M (mass ratio)	R+M total (parts by mass)	MS (mm)		MS Reduction rate (%)	Curing time (min)	Compression strength (N/mm ²)				Remarks
			immediately after	after 20 min			3 hours	12 hours	1 day	7 days	
2-1	-	0	-	-	-	-	-	-	-	-	Comparative Example
2-2	100/80	0.2	27	18	33.3	40	6.2	10.9	24.6	60.1	Example
2-3		0.5	28	18	35.7	44	6.5	11.0	24.8	61.8	Example
2-4		1	31	22	29.0	53	6.6	11.2	24.9	60.8	Example
2-5		2	38	29	23.7	58	6.5	11.1	24.9	60.9	Example
2-6		3	45	33	26.7	67	6.5	11.0	25.0	60.2	Example
2-7	100/100	0.2	26	16	38.5	44	6.7	10.6	25.1	61.1	Example
2-8		0.5	26	16	38.5	50	6.8	10.7	25.0	62.2	Example
2-9		1	29	18	37.9	56	6.8	11.0	25.0	61.8	Example
2-10		2	37	25	32.4	60	6.9	10.9	25.3	61.3	Example
2-11		3	44	28	36.4	69	6.8	10.9	25.1	61.5	Example
2-12	100/200	0.2	25	16	36.0	45	6.9	10.9	24.9	61.1	Example
2-13		0.5	26	16	38.5	52	6.9	11.2	25.3	62.2	Example
2-14		1	30	19	36.7	58	7.1	11.5	25.6	63.3	Example
2-15		2	36	24	33.3	63	6.9	11.3	25.1	63.0	Example
2-16		3	44	27	38.6	70	6.7	11.3	24.9	61.5	Example
2-17	100/400	0.2	28	17	39.3	48	6.3	11.2	24.7	62.0	Example
2-18		0.5	30	19	36.7	55	6.4	11.2	24.8	62.1	Example
2-19		1	32	23	28.1	60	6.6	11.0	25.0	61.9	Example
2-20		2	39	26	33.3	68	6.5	10.8	25.1	62.5	Example
2-21		3	48	30	37.5	75	6.3	10.8	24.9	62.5	Example
2-21	0/100	1	69	20	71.0	32	6.3	10.0	23.6	59.4	Comparative Example
2-22	100/0	1	15	-	-	86	6.3	10.4	23.9	60.0	Comparative Example

-: not measurable or not capable of taking a specimen

R: lignin sulfonic acid-based dispersant

M: melamine sulfonic acid-based dispersant

Total of R and M: in parts by mass relative to 100 parts by mass of the cement

[0037]

As can be seen from Table 2, by using, in combination, the lignin sulfonic acid-based dispersant (R) and the melamine sulfonic acid-based dispersant (M) falling within the range of the present invention, the pump pressure feeding ability was not impaired and an appropriate slump reduction rate was achieved, and thus self-standing ability was able to be ensured after pressure feeding.

[0038]

<Example 3>

With 100 parts by mass of the cement, 150 parts by mass of the aggregate, 1.0 parts by mass of a dispersant containing the lignin sulfonic acid-based dispersant (R) and the melamine sulfonic acid-based dispersant (M) at a mass ratio R/M of 100/200, 0.1 parts by mass of the diutan gum A, 0.25 parts by mass of the setting retarder i, and 20 parts by mass of a mixture having a ratio of the calcium aluminosilicate B to the gypsum shown in Table 3 were blended, and the short fiber a was blended in an amount of 0.2 parts by mass relative to 100 parts by mass of the total amount of the cement and the aggregate, thus preparing a cementitious material for three-dimensional modeling. To 100 parts by mass of the prepared material, 17 parts by mass of water was added, and the mixture was kneaded with a pan mixer. The mini slump (immediately after kneading and after 20 minutes), the curing time, and the compression strength of the resulting wet material were measured in the same manner as in Example 1 and the MS reduction rate was calculated. The results are shown in Table 3.

[0039]

Table 3

Experiment No.	CAS/CS (mass ratio)	MS (mm)		MS Reduction rate (%)	Curing time (min)	Compression strength (N/mm ²)				Remarks
		immediately after	after 20 min			3 hours	12 hours	1 day	7 days	
3-1	100/50	29	18	37.9	39	5.9	10.8	23.9	59.8	Example
3-2	100/100	32	19	36.7	42	6.3	11.1	24.5	61.7	Example
1-9	100/150	30	19	36.7	58	7.1	11.5	25.6	63.3	Example
3-3	100/200	32	21	34.3	60	6.6	11.1	24.9	60.8	Example
3-4	100/250	33	23	30.3	62	6.5	11.0	24.8	60.9	Example

CAS: calcium aluminosilicate B

CS: gypsum

[0040]

It was found that by using 50 to 250 parts by mass of a gypsum relative to 100 parts by mass of a calcium aluminosilicate, an appropriate mini slump reduction rate and an appropriate curing time for ensuring the self-standing ability are achieved.

[0041]

<Example 4>

With 100 parts by mass of the cement, 150 parts by mass of the aggregate, 1.0 parts by mass of a dispersant containing the lignin sulfonic acid-based

dispersant (R) and the melamine sulfonic acid-based dispersant (M) at a mass ratio R/M of 100/200, 0.1 parts by mass of the diutan gum A, 0.25 parts by mass of the setting retarder i, and a mixture of 150 parts by mass of the gypsum with 100 parts by mass of the calcium aluminosilicate B in an amount shown in Table 4 were blended, and the short fiber a was blended in an amount of 0.2 parts by mass relative to 100 parts by mass of the total amount of the cement and the aggregate, thus preparing a cementitious material for three-dimensional modeling. To 100 parts by mass of the prepared material, 17 parts by mass of water was added, and the mixture was kneaded with a pan mixer. The mini slump (immediately after kneading and after 20 minutes), the curing time, and the compression strength of the resulting wet material were measured in the same manner as in Example 1 and the MS reduction rate was calculated. The results are shown in Table 4.

[0042]

Table 4

Experiment No.	CAS+CS total (parts by mass)	MS (mm)		MS Reduction rate (%)	Curing time (min)	Compression strength (N/mm ²)				Remarks
		immediately after	after 20 min			3 hours	12 hours	1 day	7 days	
4-1	5	33	24	27.3	88	3.6	8.9	23.2	62.7	Example
4-2	10	33	23	30.3	75	5.0	9.7	23.9	62.1	Example
4-3	15	32	22	31.3	62	6.5	10.4	24.7	62.9	Example
1-9	20	30	19	36.7	58	7.1	11.5	25.6	63.3	Example
4-4	25	29	18	37.9	47	8.7	12.9	27.6	63.0	Example
4-5	30	27	18	33.3	31	9.9	14.1	28.0	63.0	Example

CAS: calcium aluminosilicate B

CS: gypsum

Total of CAS and CS: in parts by mass relative to 100 parts by mass of the cement

[0043]

It was found that by using a calcium aluminosilicate and a gypsum in a total amount of 5 to 30 parts by mass relative to 100 parts by mass of a cement, an appropriate mini slump reduction rate and an appropriate curing time for ensuring the self-standing ability can be achieved.

[0044]

<Example 5>

With 100 parts by mass of the cement, the aggregate and a balloon-type aggregate in an amounts shown in Table 5, 1.0 parts by mass of a dispersant containing the lignin sulfonic acid-based dispersant (R) and the melamine sulfonic

acid-based dispersant (M) at a mass ratio R/M of 100/200, 0.1 parts by mass of the diutan gum A, 0.25 parts by mass of the setting retarder i, and 20 parts by mass of a mixture of 150 parts by mass of the gypsum with 100 parts by mass of the calcium aluminosilicate B were blended, and the short fiber a was blended in an amount of 0.2 parts by mass relative to 100 parts by mass of the total amount of the cement and the aggregate, thus preparing a cementitious material for three-dimensional modeling. To 100 parts by mass of the prepared material, 17 parts by mass of water was added, and the mixture was kneaded with a pan mixer. The mini slump (immediately after kneading and after 20 minutes), the curing time, and the compression strength of the resulting wet material were measured in the same manner as in Example 1 and the MS reduction rate was calculated. The results are shown in Table 5.

[0045]

(Materials used)

<Aggregate B>

Aggregate: limestone aggregate (manufactured by Denka Company Limited, maximum particle diameter: 1.2 mm, specific gravity: 2.71)

Balloon-type aggregate: manufactured by TOMOE Engineering Co., Ltd., tradename “Cenolite SA” (a particle size-adjusted product of fly ash balloon generated in a thermal power plant, manufactured in China, specific gravity: 0.88, maximum particle diameter: 150 μm or less)

(Material used)

(7) Specific gravity of balloon-type aggregate

Measurement was performed according to JIS A 1134 and the absolute dry density was taken as the specific gravity.

[0046]

Table 5

Experiment No.	Aggregate (parts by mass)	Balloon-type aggregate (parts by mass)	MS (mm)		MS Reduction rate (%)	Curing time (min)	Compression strength (N/mm ²)				Remarks
			immediately after	after 20 min			3 hours	12 hours	1 day	7 days	
5-1	50	0	42	29	31.0	26	8.2	13.6	27.8	67.7	Example
5-2	100	0	36	22	38.9	27	7.9	12.4	0.0	65.5	Example
1-9	150	0	30	19	36.7	58	7.1	11.5	25.6	63.3	Example
5-3	200	0	27	17	37.0	58	6.6	10.8	23.9	62.1	Example
5-4	300	0	22	14	36.4	59	6.0	10.4	23.1	60.1	Example
5-5	149	1	29	15	48.3	59	7.0	11.2	25.4	63.0	Example
5-6	147	3	27	15	44.4	59	6.9	11.0	25.0	62.4	Example
5-7	140	10	26	14	46.2	58	6.0	10.5	24.4	61.3	Example
5-8	135	15	26	14	46.2	60	5.4	9.9	23.8	60.0	Example

Aggregate and balloon-type aggregate: in parts by mass relative to 100 parts by mass of the cement

[0047]

It was found that by using an aggregate in an amount of 50 to 300 parts by mass relative to 100 parts by mass of a cement, an appropriate mini slump reduction rate and an appropriate curing time for ensuring the self-standing ability can be achieved. It was also found that by using a balloon-type aggregate, the MS reduction rate increases and the self-standing ability is enhanced.

[0048]

<Example 6>

With 100 parts by mass of the cement, 150 parts by mass of the aggregate, 1.0 parts by mass of a dispersant containing the lignin sulfonic acid-based dispersant (R) and the melamine sulfonic acid-based dispersant (M) at a mass ratio R/M of 100/200, 0.1 parts by mass of the diutan gum A, a setting retarder in a kind and amount shown in Table 6, and 20 parts by mass of a mixture of 150 parts by mass of the gypsum with 100 parts by mass of the calcium aluminosilicate B were blended, and the short fiber a was blended in an amount of 0.2 parts by mass relative to 100 parts by mass of the total amount of the cement and the aggregate, thus preparing a cementitious material for three-dimensional modeling. To 100 parts by mass of the prepared material, 17 parts by mass of water was added, and the mixture was kneaded with a pan mixer. The mini slump (immediately after kneading and after 20 minutes), the curing time, and the compression strength of the resulting wet material were measured in the same manner as in Example 1 and the MS reduction rate was calculated. The results are shown in Table 6.

[0049]

(Materials used)

<Setting retarder (E)>

Setting retarder i: citric acid (extra pure reagent)

Setting retarder ii: gluconic acid (extra pure reagent)

Setting retarder iii: trisodium citrate (extra pure reagent)

[0050]

Table 6

Experiment No.	Setting retarder (parts by mass)		MS (mm)		MS Reduction rate (%)	Curing time (min)	Compression strength (N/mm ²)				Remarks
			immediately after	after 20 min			3 hours	12 hours	1 day	7 days	
6-1	i	0.05	29	17	41.4	40	8.0	13.0	27.0	63.0	Example
6-2		0.07	29	17	41.4	47	7.5	12.7	26.8	63.1	Example
6-3		0.10	30	18	40.0	50	7.2	12.0	26.1	63.2	Example
1-9		0.25	30	19	36.7	58	7.1	11.5	25.6	63.3	Example
6-4		0.5	31	21	32.3	66	6.7	10.3	24.8	63.2	Example
6-5		0.7	33	23	30.3	78	6.2	9.8	23.7	63.1	Example
6-6	ii	0.05	28	16	42.9	38	8.1	13.1	27.0	61.9	Example
6-7		0.07	29	17	41.4	41	7.7	12.9	26.9	62.8	Example
6-8		0.10	29	18	37.9	54	7.1	12.3	26.4	63.0	Example
6-9		0.25	31	21	32.3	62	7.0	11.1	25.5	62.9	Example
6-10		0.5	33	23	30.3	77	6.3	10.0	24.2	62.1	Example
6-11		0.7	34	24	29.4	89	5.7	9.5	23.5	62.0	Example
6-12	iii	0.05	28	17	39.3	42	7.7	13.0	26.8	61.3	Example
6-13		0.07	30	18	40.0	44	7.3	12.8	26.3	62.4	Example
6-14		0.10	30	20	33.3	52	7.0	12.0	25.7	62.9	Example
6-15		0.25	32	22	31.3	59	7.0	11.3	25.1	63.0	Example
6-16		0.5	34	25	26.5	68	6.5	10.4	24.4	62.4	Example
6-17		0.7	35	26	25.7	80	6.0	10.0	24.2	62.3	Example

Setting retarder: in parts by mass relative to 100 parts by mass of the cement

[0051]

It was found that by using 0.05 to 0.7 parts by mass of a setting retarder containing an oxycarboxylic acid relative to 100 parts by mass of a cement, an appropriate mini slump reduction rate and an appropriate curing time for ensuring the self-standing ability can be achieved.

[0052]

<Example 7>

With 100 parts by mass of the cement, 150 parts by mass of the aggregate, 1.0 parts by mass of a dispersant containing the lignin sulfonic acid-based

dispersant (R) and the melamine sulfonic acid-based dispersant (M) at a mass ratio R/M of 100/200, 0.1 parts by mass of the diutan gum A, 0.25 parts by mass of the setting retarder i, and 20 parts by mass of a mixture of 150 parts by mass of the gypsum with 100 parts by mass of the calcium aluminosilicate B were blended, and a short fiber in a kind and amount shown in Table 7 relative to 100 parts by mass of the total amount of the cement and the aggregate was blended, thus preparing a cementitious material for three-dimensional modeling. To 100 parts by mass of the prepared material, 17 parts by mass of water was added, and the mixture was kneaded with a pan mixer. The mini slump (immediately after kneading and after 20 minutes) and the compression strength of the resulting wet material were measured in the same manner as in Example 1 and the MS reduction rate was calculated. In addition, the initial cracking width was measured according to the following testing method. The results are shown in Table 7.

[0053]

(Materials used)

<Short fiber (H)>

Short fiber a: vinylon fiber (average fiber length: 12 mm, average fiber diameter: 50 μm , number of fibers: 55,500/g)

Short fiber b: nylon fiber (manufactured by Toray Amtecs, Inc., tradename "TOUGH-BINDER" (average fiber length: 10 mm, average fiber diameter: 28 μm , number of fibers: 185,200/g))

Short fiber c: nylon fiber (manufactured by Toray Amtecs, Inc., tradename "TOUGH-BINDER" (average fiber length: 5 mm, average fiber diameter: 28 μm , number of fibers: 370,500/g))

Short fiber d: vinylon fiber (manufactured by Kuraray Co., Ltd., tradename "RECS100L" (average fiber length: 12 mm, average fiber diameter: 130 μm , number of fibers: 8,300/g))

[0054]

(Testing method)

Initial cracking width: a concrete plate (length 30 cm $\times$ width 30 cm $\times$ thickness 6 cm) was placed in a mold, and the wet material of the present invention was provided so as to give a thickness of 2 cm, and the surface was finished with a trowel, thus fabricating a specimen. The specimen was aged in an environment of a humidity of 60% by mass and a temperature of 5°C, and the cracking width after a lapse of 72 hours was measured. The cracking width here means, when

one arbitrary crack generated in the specimen was selected, the width of the crack in the vicinity of the center of the length. When no crack was generated even after a lapse of 72 hours, the initial cracking width was 0.0 mm.

[0055]

Table 7

Experiment No.	Short fiber (parts by mass)		MS (mm)		MS Reduction rate (%)	Initial cracking width (mm)	Compression strength (N/mm ²)				Remarks
			immediately after	after 20 min			3 hours	12 hours	1 day	7 days	
7-1	0		40	28	30.0	0.25	7.0	10.7	25.0	62.0	Comparative Example
7-2	a	0.10	35	24	31.4	0.15	7.0	10.9	25.4	62.1	Example
1-9		0.20	30	19	36.7	0	7.1	10.8	25.6	63.3	Example
7-3		0.30	28	19	32.1	0	7.1	10.8	25.4	61.1	Example
7-4		0.50	24	16	33.3	0	7.1	11.1	25.2	62.2	Example
7-5		1.00	20	14	30.0	0	6.9	10.9	24.9	61.0	Example
7-6	b	0.10	36	25	30.6	0.10	7.0	10.8	25.4	61.8	Example
7-7		0.20	31	18	41.9	0	6.7	10.4	25.6	61.9	Example
7-8		0.30	27	19	29.6	0	6.9	10.5	24.9	62.5	Example
7-9		0.50	22	15	31.8	0	7.0	10.6	25.2	62.4	Example
7-10		1.00	20	14	30.0	0	6.9	10.5	24.2	62.3	Example
7-11	c	0.10	33	23	30.3	0.15	7.0	10.2	25.4	61.4	Example
7-12		0.20	30	20	33.3	0	6.5	10.6	25.6	61.6	Example
7-13		0.30	28	19	32.1	0	6.4	10.3	24.9	62.5	Example
7-14		0.50	25	17	32.0	0	6.9	10.0	25.2	61.4	Example
7-15		1.00	22	14	36.4	0	6.7	10.7	24.9	61.9	Example
7-16	d	0.10	32	24	25.0	0.15	6.8	10.6	25.1	62.2	Example
7-17		0.20	29	19	34.5	0	6.9	10.8	25.2	62.8	Example
7-18		0.30	28	19	32.1	0	6.8	10.6	24.9	63.0	Example
7-19		0.50	26	17	34.6	0	6.5	10.8	25.2	62.4	Example
7-20		1.00	22	14	36.4	0	6.5	10.9	24.7	62.0	Example

Short fiber: in parts by mass relative to 100 parts by mass of the total amount of the cement and the aggregate

[0056]

It was found that by using a short fiber having an average fiber length of 5 to 15 mm in an amount of 0.1 to 1.0 parts by mass relative to 100 parts by mass of the total amount of a cement and an aggregate, an appropriate mini slump reduction rate and an appropriate curing time for ensuring the self-standing ability can be achieved and the initial cracking can be suppressed.

[0057]

<Example 8>

Three-dimensional modeling experiments were actually carried out

according to formulations of Experimental No. 1-22. The environmental temperature was 22°C. The system and conditions used are shown below. The schematic diagram of the three-dimensional modeling experimental system is shown in Fig. 1, and the schematic diagram of the spray nozzle used is shown in Fig. 2. To the mixer 10, 30 kg of a cementitious material for three-dimensional modeling of each of Experiments No. 1-22 and 5.1 kg of water were added and the mixture was kneaded for 3 minutes to prepare a wet material. The resulting wet material was put into the rotary positive displacement-type uniaxial eccentric screw pump 20 equipped with a hopper, and the wet material was pressure-fed via a flexible hose 30 and was discharged from the discharge opening 41 on the nozzle tip of the spray nozzle 40, thus performing modeling of a three-dimensional modeled product having the cross-sectional shape 70 as shown in Fig. 3. Specifically, the wet material was layered vertically relative to the cross-sectional shape 70 to perform modeling of a three-dimensional modeled product. As a result, layers formed of the cementitious material for three-dimensional modeling were able to be sequentially stacked, and a three-dimensional modeled product having a continuous layering height in the vertical direction of 30 cm or more was obtained. That is, a continuous layering of a continuous layering height of 30 cm or more was able to be achieved (see Fig. 3).

[0058]

<Example 9>

Using the three-dimensional modeling experimental system 1, a three-dimensional modeling experiment was performed in the same manner as in Example 8 using the formulation of each of Experiments No.1-9, No.1-39, No.7-17, and No.7-18. The environmental temperature was 24°C. In the experiment, the temperature of the wet material immediately after kneading with a mixer, the temperature of the wet material which was pressure-fed by the rotary positive displacement-type uniaxial eccentric screw pump 20 and was discharged from the discharge opening 41 on the nozzle tip, the curing time, and the continuous layering height were measured. The results are shown in Table 8.

[0059]

(Three-dimensional modeling experimental system)

Mixer 10: pan mixer (manufactured by OKASAN Co.,Ltd., tradename “Damacut Mixer model 2.8”)

Pressure feeding pump 20: rotary positive displacement-type uniaxial

eccentric screw pump (manufactured by knauf PFT, tradename “PFT BOLERO”)

Pressure feeding hose 30: 4 MPa withstanding flexible hose (manufactured by knauf PFT, inner diameter: 1 inch, pressure feeding pipe length: 10 m)

Spray nozzle 40: self-made product (see Fig. 2), nozzle discharge opening diameter: 18 mm (circular)

Robot arm 60: robot arm manufactured by YASKAWA Electric Corporation (tradename “MOTOMAN-MA2010”) was modified and was used with the nozzle fixed on the tip of an arm thereof.

[0060]

(Conditions of modeling)

Hight per layer of cementitious material: 10 mm

Shape of three-dimensional modeled product: truss shape (length: 500 mm, width: 1000 mm, layering width (thickness): about 30 mm) (see Fig. 3)

Discharge amount of wet material: 0.25 m³/hr, nozzle moving speed: 180 mm/second

[0061]

(Testing method)

Temperature of material: measured with a digital thermometer

Curing time: the material discharged from a discharge opening on a nozzle tip was sampled and curing time was measured by the same method as in Example 1.

Continuous layering height: a height when layers of a modeled product were stacked until the resulting molded product was collapsed was measured with a measure.

[0062]

Table 8

Experiment No.	Formulation	Temperature (°C)		Curing time (min)	Continuous layering height (mm)	Remarks
		immediately after	nozzle tip			
9-1	No.1-9	25.5	31.0	28	1000≤	Example
9-2	No.1-39	25.4	30.4	31	430	Comparative Example
9-3	No.7-17	25.8	35.2	26	1000≤	Example
9-4	No.7-18	26.1	40.4	12	1000≤	Example

[0063]

By using a diutan gum falling in the range of the present invention, the

initial strength developability was improved to enhance the continuous layering height. On the other hand, when a diutan gum out of the range of the present invention was used, the initial strength developability was poor, the layered mortar was not able to withstand its own weight, and thus failing to achieve continuous layering.

Industrial Applicability

[0064]

When the cementitious material for three-dimensional modeling for construction and the method of three-dimensional modeling for construction of the present invention are used, it is possible to feed a constant amount of a material, and a constant layering speed can be ensured. In addition, since excellent self-standing ability and strength developability (in particular, initial strength developability) can be achieved, a large modeled product can be constructed in a short period of time. Furthermore, in the present invention, dust is less likely to be generated in molding. Thus, the present invention can be suitably used for production of a civil engineering and construction member and the like.

Reference Signs List

[0065]

- 1: Three-dimensional modeling experimental system
- 10: Mixer
- 20: Pump (rotary positive displacement-type uniaxial eccentric screw pump)
- 30: Pressure feeding pipe (flexible hose)
- 40: Spray nozzle
- 41: Discharge opening
- 50: Bed
- 60: Robot arm
- 70: Cross-sectional shape of three-dimensional modeled product
- 80: Pulley

CLAIMS

[Claim 1]

A cementitious material for three-dimensional modeling for construction, the cementitious material comprising

(A) a cement,

(B) an aggregate,

(C) a dispersant containing a lignin sulfonic acid-based dispersant (R) and a melamine sulfonic acid-based dispersant (M) at a mass ratio R:M of 100:80 to 400,

(D) a diutan gum having an average molecular weight in the range of 2,200,000 to 8,000,000 and having a viscosity of a 0.25 mass% aqueous solution in the range of 2,000 to 10,000 mPa·s,

(E) a setting retarder,

(F) an amorphous calcium aluminosilicate containing 10 to 25% by mass of SiO₂ based on oxide,

(G) a gypsum, and

(H) a short fiber.

[Claim 2]

The cementitious material for three-dimensional modeling for construction according to claim 1, wherein the dispersant (C) is used in an amount of 0.2 to 3 parts by mass relative to 100 parts by mass of the cement (A).

[Claim 3]

The cementitious material for three-dimensional modeling for construction according to claim 1 or 2, wherein the diutan gum (D) is used in an amount of 0.03 to 1.0 parts by mass relative to 100 parts by mass of the cement (A).

[Claim 4]

The cementitious material for three-dimensional modeling for construction according to any one of claims 1 to 3, wherein the gypsum (G) is used in an amount of 50 to 250 parts by mass relative to 100 parts by mass of the amorphous calcium aluminosilicate (F).

[Claim 5]

The cementitious material for three-dimensional modeling for construction according to any one of claims 1 to 4, wherein the amorphous calcium aluminosilicate (F) and the gypsum (G) are used in a total amount of 5 to 30 parts

by mass relative to 100 parts by mass of the cement (A).

[Claim 6]

The cementitious material for three-dimensional modeling for construction according to any one of claims 1 to 5, wherein the aggregate (B) contains a balloon-type aggregate.

[Claim 7]

The cementitious material for three-dimensional modeling for construction according to any one of claims 1 to 6, wherein the setting retarder (E) contains an oxycarboxylic acid.

[Claim 8]

The cementitious material for three-dimensional modeling for construction according to any one of claims 1 to 7, wherein the short fiber (H) has an average fiber length of 5 to 15 mm.

[Claim 9]

The cementitious material for three-dimensional modeling for construction according to claim 8, wherein the short fiber (H) has an average fiber diameter of 20 to 250 μm and having a number of fibers per gram of 5,000/g or more.

[Claim 10]

A method of three-dimensional modeling for construction, the method comprising

kneading the cementitious material for three-dimensional modeling for construction according to any one of claims 1 to 9 with water to obtain a wet material,

pressure-feeding the wet material with a pump, and

stacking layers of the wet material discharged from a nozzle while moving the nozzle to thereby construct a modeled product.

[Claim 11]

The method of three-dimensional modeling for construction according to claim 10, wherein the pump is a rotary positive displacement-type uniaxial eccentric screw pump.