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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [7] :
C04B 38/00

A2

(11) International Publication Number: **WO 00/32539**

(43) International Publication Date: 8 June 2000 (08.06.00)

(21) International Application Number: PCT/GB99/03959

(22) International Filing Date: 29 November 1999 (29.11.99)

(30) Priority Data:
9825926.0 27 November 1998 (27.11.98) GB

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(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: REFRACTORY PRODUCTS AND THEIR MANUFACTURE

(57) Abstract

A method of producing a refractory product comprising (a) preparing a foamed particulate ceramic composition from a particulate ceramic composition; (b) shaping the foamed ceramic composition into a shaped pre–fired article; and (c) firing the pre–fired article to produce a refractory product.

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REFRACTORY PRODUCTS AND THEIR MANUFACTURE

The present invention relates to refractory products and their manufacture. In particular, the invention relates to lightweight articles of kiln furniture, and methods of manufacturing the same.

Kiln furniture is the term used to describe the elements of refractory material which together support ceramic articles during the time in which the articles are fired in a kiln. Elements of kiln furniture include saggars, which are circular, elliptical or rectangular vessels with flat bottoms and straight vertical sides. Ceramic articles to be fired in the kiln, known as 'green' articles, are placed in the saggars outside the kiln, and the saggars are then stacked on top of each other in the kiln, or in a kiln car. The green articles are thereby supported in stacks far higher than would be possible if the ceramic articles were to be stacked without the aid of such support. The saggars also serve to protect the green articles from flames, ashes and sulphurous gases. Within the saggars, further support for the ceramic articles may be provided by a combination of small props and rings. If the green articles have been glazed, they are prevented from touching each other, and from contacting the supporting framework at more than a few small points, by means of small refractory pins which are located in vertical refractory columns or pillars.

Alternatively, if the atmosphere inside the kiln is relatively clean, it is possible to dispense with saggars and to stack the green articles on a framework of shelving which is constructed of horizontal platforms or "bats" and vertical posts or "props".

In the case of fine china or porcelain articles, for example fine tableware, it is frequently desirable to support each article on a shaped or profiled refractory base plate to ensure that each article subsides to its desired profile during firing. Such shaped base plates are generally called "setters".

Saggars, bats, props, setters and other articles of kiln furniture, are themselves refractory products, and significant cost is incurred in their production. It is desired that they should be sufficiently robust and durable to have a useful life of at least 100, and preferably at least 200, firings in a kiln.

A known procedure for preparing kiln furniture articles is one which involves firing a compacted precursor composition to produce a mixture of synthetic cordierite and synthetic mullite. Cordierite is a compound which has the chemical formula $2MgO.2Al_2O_3.5SiO_2$. This compound has a very low coefficient of thermal expansion and is therefore a very desirable constituent of a kiln furniture element. However, cordierite suffers from the disadvantage of having a relatively poor flexural strength. It has therefore been found to be

advantageous in the prior art to use as a composition for preparing kiln furniture elements a mixture of compacted particulate precursor materials which, on firing, yields a synthetic mixture of cordierite and mullite. Mullite has the chemical formula $3Al_2O_3.2SiO_2$ and has a flexural strength which is greater than that of cordierite.

Kiln furniture articles produced by this known procedure are heavy and are not easy to handle, eg to facilitate stacking when not in use.

GB-B-2271987 discloses a process of preparing porous ceramic granules comprising preparing a foam from an aqueous mixture of a particulate aluminosiliceous material (eg a clay mineral) and a fluxing material (eg mica or feldspar), dividing the foam into discrete particles to form granules, and calcining the granules at an elevated temperature such that sintering of the aluminosiliceous particules occurs. The porous ceramic granules may be incorporated into a ceramic composition to make ceramic articles such as kiln furniture. The ceramic composition generally comprises ball clay, alumina, talc and a highly aluminous refractory aggregate.

Example 7 of GB-B-2271987 describes foaming an aqueous suspension of an English china clay and extruding the foamed clay mixture. The extruded noodles produced are dried and calcined in a tunnel kiln. The calcined noodles are crushed and then screened. The fraction of crushed material consisting of particles smaller than 0.5 mm are incorporated into a ceramic composition consisting of

ball clay, talc, alumina and a refractory material. The ingredients are mixed together in a dry state and then mixed with water prior to pressing the mixture to form bars. The bars are fired in a kiln to produce a kiln ceramic product.

The disadvantage of this process is that two distinct processing stages are needed to produce the final ceramic product. The first stage includes foaming and extruding a china clay and calcining (or firing) the extrudate to produce porous ceramic granules. The second stage includes mixing the porous ceramic granules with the ceramic composition and firing the mixture to produce the kiln furniture ceramic product. Such a process is time-consuming and uneconomical especially because two firing steps must be carried out.

A purpose of the present invention is to reduce the aforementioned problems and to provide a method of producing refractory products, such as kiln furniture articles, which have an improved combination of properties, including a lighter weight, than those produced as in the prior art.

According to a first aspect of the present invention, there is provided a method of producing a refractory product comprising

(a) preparing a foamed particulate ceramic composition from a particulate ceramic composition;

(b) shaping the foamed ceramic composition into a shaped pre-fired article, and

(c) firing the pre-fired article to produce a refractory product.

According to a second aspect of the present invention, there is provided a refractory product produced by the method according to the first aspect of the invention.

Surprisingly and beneficially, refractory products such as articles of kiln furniture may be manufactured by the method of the invention and may have a low density, eg a bulk fired density of less than 2000kg.m^{-3} (2g.cm^{-3}), eg in the range 150kg.m^{-3} to 1700kg.m^{-3}, but without an unduly large sacrifice in other desirable properties, eg crush strength, flexural strength, thermal shock resistance, low thermal conductivity, low thermal capacity and low coefficient of thermal expansion.

In the method of the invention the ceramic composition is foamed whereas in prior art GB-B-2271987 the china clay alone is foamed. Hence beneficially, only a single firing step is employed to calcine the foamed ceramic composition and produce the ceramic product, advantageously, providing a more economical and efficient process. Additionally, foaming the 'whole' ceramic composition may give rise to a lighter weight product.

Preferably, the ceramic composition may comprise granules of particulate inorganic materials.

The foamed ceramic composition may be compacted by application of a suitable compacting pressure, eg at least 0.1MPa, especially from 0.1MPa to 30MPa, to form the pre-fired article.

Alternatively, or in addition, a binder may be employed to bind together the granules of the foamed

composition during firing. The binder may comprise a moist foamed ceramic forming material.

In step (a) the granules of the ceramic composition may comprise ingredients which react together on firing, eg at a temperature of at least 1000°C, for at least 2 hours, to yield a composition which includes cordierite and mullite. The composition of the pre-fired article may itself contain cordierite and/or mullite, eg as part of the material of the granules of the ceramic composition.

Desirably, the weight ratio of cordierite to mullite in the finished product is in the range of from 5:95 to 95:5, eg from 20:80 to 80:20. A preferred weight ratio range is from 40:60 to 60:40. The total amount of cordierite and mullite may form at least 50%, eg at least 60%, in many cases at least 70%, by weight of the refractory material of the finished product. Silica may form the major constituent (by weight) of any remaining materials comprising the refractory material.

A mixture of precursors suitable for use in the composition of the pre-fired article, for reacting on firing to a temperature of at least 1000°C for at least 2 hours, to form synthetic cordierite, may include a source of alumina, such as bauxite and/or calcined alumina, a source of magnesia, such as talc and/or magnesite, and a source of silica, which may conveniently be an aluminosilicate, such as a kaolin clay or ball clay.

An example of a suitable mullite-rich aluminosilicate material which may be included in the

foamed ceramic composition to be fired is the material which is obtained when a kaolinitic clay mineral is calcined at a temperature of at least 1200°C for at least 2 hours. This material may also include silica. For example, the mullite rich material may contain more than 50% by weight, eg 50% to 70% by weight, mullite. Any remainder may be essentially silica.

It is preferred that the foamed ceramic composition in step (a) may include from about 20% to about 50% by weight of kaolin clay and from about 30% to about 70% by weight of a mullite-rich aluminosilicate material.

The mullite-rich material should preferably be introduced into the composition in a finely divided particulate form.

Examples of other aluminosilicate materials which, on firing to a temperature of at least 1000°C for at least 2 hours, yields a mullite-rich compound which may be used in the composition employed to produce the foamed composition include kaolinitic clays, sillimanite, kyanite, andalusite and dumortierite. In addition to the components mentioned above, the ceramic composition in step (a) may also include a binder material. This binder material may for example comprise a smectite clay, for example a bentonite, or a plastic kaolinitic clay, for example a plastic ball clay. If a plastic ball clay is already present as a source of silica, this will also act as a binder material for the other components of the composition.

Preferred compositions for use to form the pre-fired articles for firing to prepare kiln furniture articles consisting predominantly of a mixture of mullite and cordierite have a composition as defined by Table 1 below:

TABLE 1

Ingredient	**parts by weight**
Mullite-rich aluminosilicate material	40-60
Kaolin clay	25-35
Alumina powder	8-16
Talc	10-20

The kaolin clay may be china clay or ball clay.

The mullite-rich aluminosilicate material preferably comprises particles having a diameter not larger than about 50μm, eg having a mean particle size in the range 1μm to 25μm, especially 1μm to 5μm. The alumina powder advantageously has a particle size distribution such that substantially all of the particles are smaller than 50μm. The talc advantageously has a particle size distribution such that substantially all of the particles are smaller than 20μm and is preferably selected to have a low content of Fe_2O_3 as an impurity.

The ingredients forming the particulate ceramic composition are preferably intimately mixed together in a substantially dry state or accurately controlled into a mixer before being mixed with water and

preferably a surfactant to form a foamed ceramic composition.

Preferably the substantially dry mixture prepared as described above is mixed with sufficient water to form a suspension containing at least 50%, eg from 50% to 75%, by weight of the solid mixture. The percentage by weight of the solid mixture in the suspension may, for example, be in the range from 58% to 65% by weight. The amount of the dispersing agent used is preferably from 0.05% to 1% by weight, based on the dry weight of the solid mixture. The dispersing agent may be one of the agents well known for the dispersion of mineral, eg aluminosilicate, particulate materials, eg a water soluble condensed phosphate salt, a water soluble salt of a polysilicic acid or a water soluble salt of a poly(acrylic acid) or a poly(methacrylic acid).

Preferably, the granules of the foamed ceramic composition may be prepared by producing a foamed wet suspension or paste comprising the particulate ceramic composition and extruding the suspension or paste through one or more dies to produce elongate portions, eg in the form of noodles or strips. The extrudate may be divided or broken, eg by being cut or by the action of being carried by a moving belt, into individual pieces in the form of pellets, prills, etc to serve as the required granules. Preferably, the foamed suspension or paste is formed, eg in the same machine providing the extrusion, by producing a mixture of the particulate inorganic materials and a wet foam.

The pellets or prills may be dried and may preferably be charged into a shaped mould. The shaped mould may have a simple shape, such as, eg a brick-like shape or may have a more complex shape, such as, kiln furniture articles (saggars, setters or the like) as described earlier. The mould may preferably be compacted by application of a suitable compacting pressure.

The foamed paste used may be prepared by a known method but is preferably prepared by introducing a concentrated aqueous suspension, which preferably contains from about 50% to about 75% by weight of inorganic particulate materials, and a dispersing agent for the particulate materials, into the feed end of an extruder machine, whilst a separately generated foam is introduced through an inlet which is preferably situated between the feed end and the outlet of the extruder. The extruder is preferably a compounder extruder of the type which has two co-rotating parallel screws and a casing along the length of which are provided inlets through which liquid additives may be introduced into the material passing through the extruder. The foam may be generated, for example, by forcing a mixture of air, water and a surfactant under pressure through a fine mesh. The foam conveniently consists of bubbles of sizes in the range of from 5μm to 100μm, and most advantageously of bubbles having an average size in the range of from 10μm to 60μm. The foam conveniently has a water content of from 20 to 30 kg,

and most preferably from 22 to 26 kg, per cubic metre of foam.

If the foam is prepared using an anionic or a non-ionic surfactant, it is necessary to introduce through an inlet in the casing of the extruder an acid, for example a mineral acid such as sulphuric or hydrochloric acid, or a flocculant for the aluminosiliceous material (contained in the suspension or paste of the ceramic composition), in order to flocculate the solid material. If, on the other hand, the foam is prepared using a cationic surfactant, for example a higher alkyl trimethyl quaternary ammonium chloride, wherein the higher alkyl group has from 12 to 24 carbon atoms, the suspension of the aluminosiliceous material (within the suspension or paste of ceramic composition) is flocculated on contact with the foam. The suspension introduced into the feed inlet of the extruder may also contain a fluxing material, for example particles of mica and/or feldspar. These may be part of a mineral, eg ball clay, employed in the particulate ceramic composition.

The amount of surfactant employed may be from 0.1% to 5%, eg from 0.1% to 1%, based on the dry weight of the particulate inorganic material to be mixed with the aqueous foam containing the surfactant to form a wet solid foam.

The granules of the foamed ceramic composition when formed following shaping, eg by extrusion, may be dried to a water content of not more than 1% by weight and are preferably dried to a water content of

not more than 0.5% by weight, eg by heating at a temperature in the range 50°C to 200°C.

Generally it is necessary to ensure that the mixture of the inorganic materials and any associated fluxing material (eg as employed in the prior art) in the aqueous foamed suspension is flocculated before the aqueous foamed suspension or foam is extruded. The diameter of the granules formed in this way will be generally not smaller than about 3mm, and will preferably be in the range from about 3mm to about 5mm.

In step (c) the pre-fired article may be fired in a suitable known furnace, at a temperature in the range of from 1000°C to about 1600°C, eg 1200°C to 1500°C for a time of from about 2 hours to about 24 hours.

The refractory product, eg article of kiln furniture, produced by the method of the invention has a low bulk fired density as described earlier (which is greater than the density of the granules used to prepare the pre-fired article because of the degree of compaction which occurs prior to and during firing). The refractory product may have other beneficial properties, for example:

(i) a coefficient of thermal expansion of less than $4x10^{-6}$/°C, eg $3.5x10^{-6}$/°C to $3.9x10^{-6}$°C.

(ii) a fired modulus of rupture at 20°C of at least $15MN.m^{-2}$, eg from $17MN.m^{-2}$ to $27MN.m^{-2}$.

The refractory product may comprise at least 60% by weight, eg at least 70% by weight, eg at least 73%

by weight of a blend of cordierite and mullite. At least 20% by weight may comprise silica.

Embodiments of the present invention will now be described by way of example with reference to the following illustrative Example.

EXAMPLE 1

A composition for preparing a pre-fired article suitable for firing to produce a kiln furniture product comprising predominantly a mixture of mullite and cordierite was prepared. The composition contained the ingredients listed in Table 2 below:

TABLE 2

Ingredient	**% by weight**
Mullite-rich aluminosilicate material	50
Plastic ball clay	25
Alumina powder	10
Talc	15

The mullite-rich aluminosilicate material consisted of particles having a particle size distribution such that substantially all the particles were smaller than 50μm.

The ball clay consisted of particles having a particle size distribution such that 85% by weight consisted of particles having an equivalent spherical diameter smaller than 2μm and the following mineralogical composition:

kaolinite 56% by weight

mica	34% by weight
quartz	10% by weight.

The alumina powder consisted of particles substantially all of which were smaller than 50μm.

The talc was selected to have a low content of Fe_2O_3 and consisted of particles substantially all of which were smaller than 20μm.

The ingredients of the composition comprising the particulate materials described above were intimately mixed together in a mixing device, and the resultant substantially dry mixture was introduced into the feed inlet of a twin screw, co-rotating compounder extruder. At the same time sufficient water to form a suspension containing 60% by weight of the mixture together with 0.7% by weight, based on the dry weight of mixture, of a sodium tripolyphosphate dispersing agent was injected through inlets provided in the casing of the extruder.

An aqueous foam was prepared by forcing a mixture of air, water and a non-ionic surfactant, which was a mixture of higher alkyl dimethylamine oxide compounds, the higher alkyl groups having from 12 to 14 carbon atoms, under pressure through a fine wire mesh. This aqueous foam was introduced into the extruder through an inlet situated approximately midway between the feed inlet and the extruder plate. The mixed foamed composition formed in the extruder was extruded through a plurality of circular apertures of diameter 3mm.

The extruded strings of foamed composition were chopped to form approximately cylindrical pellets or prills of length approximately equal to their diameter. These pellets were then dried in an oven at 180°C for 12 minutes. The dried pellets were charged into a mould of appropriate shape to form the pre-fired article and the pellets were compacted under a pressure of 21MPa. The compacted shaped pre-fired article was removed from the mould and fired at a maximum temperature of 1350°C for a total time of 12 hours.

Fired kiln furniture articles produced following firing in the above method can have a composition such that about 38% by weight consisted of mullite and about 36% by weight consisted of cordierite, about 22% consisted of silica, the remainder being other minor constituents.

CLAIMS

1. A method of producing a refractory product comprising

(a) preparing a foamed particulate ceramic composition from a particulate ceramic composition;

(b) shaping the foamed ceramic composition into a shaped pre-fired article; and

(c) firing the pre-fired article to produce a refractory product.

2. A method according to claim 1, wherein step (a) further comprises preparing the foamed particulate ceramic composition from an aqueous mixture comprising the particulate ceramic composition.

3. A method according to claim 1 or 2, wherein step (b) further comprises extruding the foamed ceramic composition into a shaped configuration.

4. A method according to claim 3, wherein step (b) further comprises breaking or dividing the shaped configuration of extruded ceramic composition into pellets or prills.

5. A method according to claim 4, wherein step (b) further comprises drying the pellets or prills at a temperature of from 50°C to 200°C.

6. A method according to claim 3, 4 or 5, wherein step (b) further comprises charging the foamed

ceramic composition into a shaped mould to produce the shaped pre-fired article.

7. A method according to claim 6, further comprising applying a compacting pressure of at least 0.1 MPa to the foamed ceramic composition in the shaped mould.

8. A method according to claim 5, wherein the pellets or prills in a selected size range are selected to produce the shaped pre-fired article.

9. A method according to any one of the preceding claims, wherein the ceramic composition comprises granules comprising particles of inorganic materials.

10. A method according to claim 9, wherein a binder is employed to bind together the granules of the foamed ceramic composition.

11. A method according to any one of the preceding claims, wherein the firing in step (c) is carried out at a temperature of at least 1000°C for at least 2 hours and the granules of the foamed ceramic composition of the pre-fired article contain ingredients which react together to produce mullite and/or cordierite by such firing.

12. A method according to claim 11, wherein the firing is carried out at a temperature of from 1200°C to 1500°C for at least 2 hours.

13. A method according to any one of the preceding claims, wherein the foamed ceramic composition comprises a source of alumina, a source of magnesia and a source of silica.

14. A method according to claim 13, wherein the source of silica comprises an aluminosiliceous clay.

15. A method according to claim 13 or 14, wherein the foamed ceramic composition also comprises a mullite-containing aluminosiliceous material.

16. A method according to any one of the preceding claims, wherein the foamed ceramic composition comprises from about 20% to about 50% by weight of kaolin clay and from about 30% to about 70% by weight of a mullite-rich aluminosilicate material.

17. A method according to any one of claims 13 to 15, wherein the inorganic materials of the foamed ceramic composition comprises mullite-rich aluminosilicate material at about 40 to about 60 parts by weight, kaolin clay at about 25 to about 35 parts by weight, alumina powder at about 8 to about 16 parts by weight, and talc at about 10 to about 15 parts by weight.

18. A method according to claim 17, wherein the kaolin clay is china clay or ball clay.

19. A method according to claim 15, 16 or 17, wherein the mullite - containing aluminosiliceous material contains at least 50% by weight mullite.

20. A method according to any one of claims 9 to 19, wherein the granules of the foamed ceramic composition have an average size of from 0.1mm to 10mm prior to charging in the mould.

21. A method according to any one of the preceding claims, wherein the foamed granular ceramic composition produced by the method has a bulk density of less than 2000kg.m^{-3}.

22. A refractory product produced by the method according to any one of claims 1 to 21.

23. A product according to claim 22 which is an article of kiln furniture.

24. A product according to claim 22 or 23, which has a density of less than 2000kg.m^{-3}.

25. A product according to claim 22, 23 or 24 which comprises the foamed ceramic composition comprising cordierite and mullite having a weight ratio of cordierite to mullite in the range 5:95 to 95:5.