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(71) Applicants: POLITECNICO DI TORINO [IT/IT]; Corso Duca Degli Abruzzi 24, 1-10129 Torino (IT). UNIVERSITA' DEGLI STUDI DI PADOVA [IT/IT]; Via Villi. Febbraio 2, I- 35122 Padova (IT).

(72) Inventors: BERNARDO, Enrico; c/o Universita' Degli Studi di Padova, Via Villi. Febbraio 2, I- 35122 Padova (IT). CALDIROLA, Marcello; c/o Politecnico di Torino, Corso Duca Degli Abruzzi 24, 1-10129 Torino (IT). FERRARIS, Monica; c/o Politecnico di Torino, Corso Duca Degli Abruzzi 24, 1-10129 Torino (IT).

(74) Agent: GARAVELLI, Paolo; A.BRE.MAR. S.R.L., Via Servais 27, 1-10146 Torino (IT).

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(54) Title: HEAT-INSULATING POROUS GLASS-CERAMIC MATERIAL IN SLABS AND PROCESS FOR PRODUCING SUCH MATERIAL

(57) Abstract: A non-pelletized heat-insulating cellular glass- ceramic material is described, composed of a melting mixture comprising at least one first amount Qiof glass from melting of bottom ash from a burning plant of solid urban wastes, at least one second amount Q_2 of sodium-calcium glass and at least one third amount Q_3 of at least one binding agent. A process is further described for producing such material.

HEAT-INSULATING POROUS GLASS-CERAMIC MATERIAL IN SLABS AND PROCESS FOR PRODUCING SUCH MATERIAL

The present invention refers to a glass-ceramic heat-insulating material and to a process for producing such material.

Various glass materials are known in the art and a base of foamed glass (such as, for example FoamGlas®) and their related production processes: examples of such materials and processes are proposed in US4198224, US5516351, US6478993, JP2012131702 and JP7315953.

In particular:

- US4198224 discloses the process for producing the FoamGlas® material;
- US5516351 discloses a process for producing glass foam from recycled glass;
- US6478993 discloses a process for obtaining the foaming of various materials;
- JP2012131702 discloses porous ceramic and/or glass-ceramic materials with any shape and their related production processes;

- JP7315953 discloses a process for producing porous pellets starting from bottom ashes of various nature with the addition of other elements, such as glass.

In general, therefore, the prior art proposes materials and production processes having one or more of the following features:

- virgin raw materials and materials from recycle are used (as disclosed, for example, in US4198224)
- the sizes of used materials are lower than 60 microns and the addition of one or more foaming agents is provided, among which **Fe_2C>3**, in amounts ranging from 0.05% to 1% in weight (as disclosed, for example, in US6478993) ;
- known materials are made starting from bottom ashes coming from coal-type electric plants, flying ashes with treatment temperatures lower than 1100 °C and treatment times equal to at least 10 minutes obtaining materials with communicating porosities (as disclosed, for example, in JP2012131702);
- in known processes, no binding agents are used (as disclosed, for example, in JP7315953) ;
- continuous ovens are used, which require a pre-heating step, making the production process

relatively long and energetically burdensome;

- known materials are produced as porous pellets or aggregates of porous particles;
- known materials provide a mechanical compression strenght as a maximum equal to 0.6 MPa;
- known processes require extremely long cooking steps (from 12 to 24 hours).

Object of the present invention is solving the above prior art problems, by providing an heat-insulating glass-ceramic material having macro-porous structures, with non-communicating, glass-ceramic porosities and made starting from non-dangerous, vitrified special wastes made inert (such as, for example, bottom ashes coming from burning machines of solid urban wastes) and from recycled glass.

Moreover, an object of the present invention is providing an heat-insulating glass-ceramic material of a continuous and non-pelletized type, therefore having properties which can be reproduced in any point thereof.

Another object of the present invention is providing an heat-insulating glass-ceramic material having a higher mechanical strength with respect to what is proposed by the prior art.

Moreover, an object of the present invention is providing a process for producing an heat-insulating glass-ceramic material with treatment and working steps which are substantially shorter than what is proposed by the prior art, removing the pre-heating step for the in-line oven and allowing a direct inlet of the die, at high temperatures.

Another object of the present invention is providing a process for producing an heat-insulating glass-ceramic material which does not provide for the addition of foaming agents.

The above and other objects and advantages of the invention, as will appear from the following description, are obtained with an heat-insulating glass-ceramic material as claimed in Claim 1.

Moreover, the above and other objects and advantages of the invention are obtained with a process for producing anheat-insulating glass-ceramic material as claimed in claim 5.

Preferred embodiments and non-trivial variations of the present invention are the subject matter of the dependent claims.

It is intended that all enclosed claims are an integral part of the present description.

It will be immediately obvious that numerous variations and modifications could be made to what is described, without departing from the scope of the invention as appears from the enclosed claims.

The present invention will be better described by some preferred embodiments thereof, provided as a non-limiting example.

The present invention therefore refers, as will appear below in more detail, to an heat-insulating glass-ceramic cellular material, preferably manufactured in slabs, non-pelletized, produced starting from bottom ashes from a burning machine of solid urban wastes, mixed with a glass from recycling bell and at least one binding agent, such material being advantageously foamed without the help of external foam-generating agents, but through "self-foaming" reactions, due to oxidation-reduction reactions of the ferric oxide Fe_2O_3 to ferrous oxide FeO, present inside the glass deriving from melting of bottom ashes of the wastes themselves. In particular, the material according to the present invention is made by exploiting the oxidation-reduction reactions of such iron oxide Fe_2O_3 at high temperatures (about 1000-1100 °C) with the production of gas through the reaction

$Fe_2O_3 \rightarrow 2FeO + ½ O_2$ that generates the "bloating" effect, known in the art and, for example, described in:

- C. Riley, "Relation of Chemical Properties to the bloating of clays", Journal of the American Ceramic Society, 1951, vol. 34 [4], pp. 121-128;
- C. Tsai et al., "Effect of SiO_2-Al_2O_3-flux ration change on the bloating characteristics of lightweight aggregate material produced from recycled sewage sludge, Journal of Hazardous materials B134 (2006) pp. 87-93;
- B. Corrochano et al., "Characterization of lightweight aggregates manufactured from washing aggregate sludge and fly ash", Resources, Conservation and Recycling 53 (2009) 571-581.

In particular, the heat-insulating glass-ceramic material according to the present invention is composed of a melting mixture comprising:

- at least one first amount Q_1 of glass from melting of bottom ash;
- at least one second amount Q_2 of sodium-calcium glass ("glass soda-lime") ; and
- at least one third amount Q_3 of at least one binding agent.

Preferably, the first amount Q_1 of glass from melting of bottom ash is included between 30% and 60% in weight, the second amount Q_2 of sodium-calcium glass is included between 60% and 30% in weight and the third amount Q_3 of binding agent is included between 0.01% and 10% in weight, where $Q_1 + Q_2 + Q_3 = 100\%$.

Moreover, preferably, such first amount Q_1 of glass from melting of bottom ash comprises relatively a fourth amount $Q_{1,1}$ substantially equal 15% in weight of calcium oxide, a fifth amount $Q_{1,2}$ substantially equal to 55% in weight of silica, a sixth amount $Q_{1,3}$ included between 3% and 10% in weight of a iron oxide and a remaining seventh amount $Q_{1,4}$ in weight of alumina, where $Q_{1,1} + Q_{1,2} + Q_{1,3} + Q_{1,4} = 100\%$ in weight of Q_1.

Moreover, preferably, such binding agent is kaolin.

Advantageously, glass from melting of bottom ash, sodium-calcium glass and binding agent are inserted into the melting mixture of the material according to the present invention in granular shape, with grain size lower than 100 microns.

The material according to the present invention can therefore be used as heat insulator both for civil and for industrial houses, adapted to be applied also in particular industrial sectors (such as, for example, the petroleum-chemical one).

In particular, the material according to the present invention has the following features:

- more than 90% is composed of recycled material (of which from 44% to 50% is material coming from the treatment of the bottom ashes of solid urban wastes) and is therefore ecologic;
- is completely water-proof since it is composed of closed glass celles;
- since it is glass, it cannot be attacked by rodents and parassites;
- it has a mechanical compression strength included between 1 and 2 MPa (approximately twice the strength offered from comparable prior art materials;
- since it is glass, it is completely uncombustible;
- it is resistant to acids (apart from hydrofluoric acid;
- it can be easily worked;
- it can be manufactured in slabs, also with sizes which can be changed and adjusted upon user specifications;
- it is safer than other classical insulating

materials on the market (such as EPS, insulating materials based on foamed organic foams) because, by resisting at high temperatures, it does not burn nor is in any way liquefied in case of fire, nor generates toxic fumes or gases, since it is not degraded.

The present invention further refers to a process for producing an heat-insulating glass-ceramic material as previously described. In particular, the process according to the present invention comprises the steps of:

a) providing a first amount Q_1 of glass from melting of bottom ash in granular shape;

b) providing a second amount Q_2 of sodium-calcium glass ("glass soda-lime") in granular shape;

c) providing a third amount Q_3 of at least one binding agent in granular shape;

d) mutually mixing such glass from melting of bottom ash, such sodium-calcium glass and such binding agent to obtain a mixture;

e) inserting such mixture into at least one die, preferably having an adequate shape to obtain the material according to the present invention shaped as a slab;

f) introducing, from a temperature next to the ambient one, such die in a oven heated at a temperature included between 1100 and 1200 °C and keeping such die inside such oven for a period of time included between 4 and 25 minutes. It can be noted how such step is fundamental for creating bubbles inside the material according to the present invention: in such step, in fact, the odixation-reduction reactions occur for the iron oxide Fe_20_3 at high temperatures, with the production of gas through the reaction $Fe_20_3 \rightarrow 2FeO + ½ 0_2$, and the trapping inside the half-melted mass of the glass soda-lime, which generates the "bloating" effect;

g) extracting such die from the oven and leaving it cool, with a decreasing temperature ramp, for a period of time included between 55 and 200 minutes.

Preferably, the first amount Q_i of glass from melting of bottom ash is included between 30% and 60% in weight, the second amount Q_2 of sodium-calcium glass is included between 60% and 30% in weight and the third amount Q_3 of binding agent is included between 0.01% and 10% in weight, where $Q_1 + Q_2 + Q_3$ = 100%. Moreover, preferably, such first amount Q_i of glass from melting of bottom ash comprises relatively a fourth amount $Q_{1,1}$

substantially equal to 15% in weight of calcium oxide, a fifth amount $Q_{1,2}$ substantially equal to 55% in weight of silica, a sixth amount $Q_{1,3}$ included between 3% and 10% in weight of a iron oxide and a remaining seventh amount $Q_{1,4}$ in weight of alumina, where $Q_{1,1} + Q_{1,2} + Q_{1,3} + Q_{1,4} = 100\%$ in weight of Q_1. Moreover, preferably, such binding agent is kaolin.

Advantageously, glass from melting of bottom ash, sodium-calcium glass and binding agent in granular shape have a grain size lower than 100 microns .

Preferably, such step a) comprises the substeps of:

a1) providing bottom ash, for example produced by plants for treating solid urban wastes;

a2) melting such bottom ash, for example inside a oven with mobile slab, for a period of time included between 20 and 60 minutes at a temperature included between 1400 and 1500°C;

a3) pouring the melted bottom ash into water: in such step, glass from melting of bottom ash is obtained through a very quick glass-forming process;

a4) milling in granular shape such glass from melting of bottom ash, preferably till a grain size lower than 100 microns is obtained.

Preferably, such step d) comprises the substep dl) of homogenizing the mixture, for example through a dry mixer.

Preferably, the die in step e) is made of a metallic alloy for high temperatures, such as for example an Inconel 601 alloy, covered with alumina powder .

It can be noted how step f) of cooking the material can occur both with a discontinuous oven (of the muffle type), and with a continuous oven. If such cooking step f) occurs with a discontinuous oven (muffle type) , between steps d) and f) the process according to the present invention comprises the substep of heating such oven up to a temperature of 1100-1200°C for a period of time included between 25 and 65 minutes.

If instead the cooking step f) occurs in a continuous oven, such oven must be at the working temperature of 1100-1200 °C.

It can be noted how the heating technique (direct insertion in temperature, or "flash" heating) used in step f) of the process according to the present invention is a known technique, described, for example, in "Micro and macro-cellular sintered glass ceramics from waste", Journal of the European Ceramic Society, vol. 27 [6], 2007 (2415-2422), E. Bernardo.

The present invention as described above, therefore, allows obtaining also the following advantages :

- the disposal of non-dangerous wastes in a dump is avoided, with consequent lowering of the chances of polluting hearth and water tables, due to the release of obnoxious substances (eluates containing heavy metals), reducing the treating and handling costs of ashed;
- an insulating material is produced, with high performances and high added value, with consequent reduction of heat losses by buildings (better energy class) and/or structures and lowering of heating costs both in the civil and in the industrial environments;
- a new use is provided for wastes, transforming them into a "second" raw material;
- easily accessible technologies are used (technologies for high temperature ovens for treating glass) ;
- the use of virgin raw materials 'is strongly

reduced, also reducing emissions due to their extraction, transport and transforming activities, for manufacturing glass, since necessary elements for vitrifying ashes are all present in ashes themselves, while for producing the material according to the present invention glass powder is also used, which does not emit $C0_2$ as instead occurs for manufacturing glass starting from virgin raw materials;

- the reduction of use of virgin raw materials and the reduction of dumps strongly reduces also the environmental impact on the territory, with few soils dedicated to extraction activities and/or polluted by a dump.

CLAIMS

1. Non-pelletized heat-insulating cellular glass-ceramic material characterized in that it is composed of a melting mixture comprising at least one first amount Qi of glass from melting of bottom ash, at least one second amount Q_2 of sodium-calcium glass and at least one third amount Q_3 of at least one binding agent, said first amount Qi of glass from melting of bottom ash comprising relatively a fourth amount $Q_{1,1}$ substantially equal to 15% in weight of calcium oxide, a fifth amount $Q_{1,2}$ substantially equal to 55% in weight of silica, a sixth amount $Q_{1,3}$ included between 3% and 10% in weight of a iron oxide and a remaining seventh amount $Qi_{,4}$ in weight of alumina, where $Q_{1,1} + Q_{1,2} + Qi_{,3} + Q_{1,4} = 100\%$ in weight of Qi, said material being adapted to be foamed through "self-foaming" reactions, due to oxidation-reduction reactions of the ferric oxide Fe_2C_3 to ferrous oxide FeO, present inside the glass deriving from melting of bottom ashes of the wastes themselves.

2. Material according to the previous claim, characterized in that said first amount Q_1 of glass from melting of bottom ash is included between 30% and 60% in weight, said second amount Q_2 of sodium-

calcium glass is included between 60% and 30% in weight and said third amount Q_3 of binding agent is included between 0.01% and 10% in weight, where Qi + Q_2 + Q_3 = 100%.

3. Material according to any one of the previous claims, characterized in that said material is adapted to be made by exploiting the oxidation-reduction reactions of said iron oxide Fe_2O_3 at high temperatures with the production of gas through the reaction $Fe_2O_3 \rightarrow 2FeO + ½ O_2$ that generates a "bloating" effect.

4. Material according to any one of the previous claim, characterized in that said binding agent is kaolin.

5. Process for producing a non-pelletized heat-insulating cellular glass-ceramic material according to any one of claims 1 to 4, characterized in that comprises the steps of:

a) providing a first amount Qi of glass from melting of bottom ash in granular shape;

b) providing a second amount Q_2 of sodium-calcium glass in granular shape;

c) providing a third amount Q_3 of at least one binding agent in granular shape;

d) mutually mixing said glass from melting of bottom ash, said sodium-calcium glass and said binding agent to obtain a mixture;

e) inserting said mixture into at least one die;

f) introducing from a temperature next to the ambient one said die in an oven heated at a temperature included between 1100 and 1200°C and keeping said die inside said oven for a period of time included between 4 and 25 minutes;

g) extracting said die from said oven and leaving it cool, with a decreasing temperature ramp, for a period of time included between 55 and 200 minutes;

wherein said material is foamed through "self-foaming" reactions, due to oxidation-reduction reactions of the ferric oxide Fe_2O_3 to ferrous oxide FeO, present inside the glass deriving from melting of bottom ashes of the wastes themselves.

6. Process according to the previous claim, characterized in that said material is made by exploiting the oxidation-reduction reactions of such iron oxide Fe_2O_3 at high temperatures with the production of gas through the reaction $Fe_2O_3 \rightarrow 2FeO + \frac{1}{2} O_2$ that generates the "bloating" effect.

7. Process according to claim 5 or 6, characterized in that said first amount Q_1 of glass from melting of bottom ash is included between 30%

and 60% in weight, said second amount Q_2 of sodium-calcium glass is included between 60% and 30% in weight and said third amount Q_3 of binding agent is included between 0.01% and 10% in weight, where $Q_1 + Q_2 + Q_3 = 100\%$ and said first amount Q_1 of glass from melting of bottom ash comprises relatively a fourth amount $Q_{1,1}$ substantially equal to 15% in weight of calcium oxide, a fifth amount $Q_{1,2}$ substantially equal to 55% in weight of silica, a sixth amount $Q_{1,3}$ included between 3% and 10% in weight of an iron oxide and a remaining seventh amount $Q_{1,4}$ in weight of alumina, where $Q_{1,1} + Q_{1,2} + Q_{1,3} + Q_{1,4} = 100\%$ in weight of Q_1.

8. Process according to claim 5, characterized in that said binding agent is kaolin.

9. Process according to claim 5, characterized in that said glass from melting of bottom ash, said sodium-calcium glass and said binding agent in granular shape have a grain size lower than 100 microns.

10. Process according to claim 5, characterized in that said step a) comprises the sub-steps of:

a1) providing bottom ash;

a2) melting said bottom ash inside an oven with mobile slab for a period of time included between

20 and 60 minutes at a temperature included between 1400 and 1500°C;

a3) pouring said melted bottom ash into water to obtain said glass from melting of bottom ash;

a4) milling in granular shape said glass from melting of bottom ash.

11. Process according to claim 5, characterized in that said step d) comprises the sub-step dl) of homogenizing said mixture through a dry mixer.

12. Process according to claim 5, characterized in that said die is made of Inconel 601 alloy and covered with alumina powder.

13. Process according to claim 5, characterized in that said step f) occurs in a discontinuous oven and in that it comprises, between said steps d) and f), the sub-step of heating said oven up to said temperature included between 1100 and 1200 °C for a period of time included between 25 and 65 minutes.

14. Process according to claim 5, characterized in that said step f) occurs in a continuous oven, said oven being at said temperature included between 1100 and 1200°C.