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CERAMIC SUBSTANCE AND METHOD OF MAKING IT

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The following statement is a full description of this invention, including the best method of performing it known to us:

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The present invention relates to ceramic materials and is concerned with a method of producing ceramic materials including dispersed fibres.

Certain techniques using fluids at very high temperatures depend to a certain extent on the availability of materials having a low heat conductivity combined with a high resistance to thermal shock. It is known that these two properties are very difficult to make compatible in that, whilst ceramic materials generally have low heat conductivity, the resistance of such materials to thermal shock is generally relatively slight.

It is also known that the thermal shock which a ceramic element having a determined shape can bear is proportional to the breaking strain (S) and is inversely proportional to the product of the coefficient of expansion (α) and Young's modulus E. To reduce Young's modulus and thereby to increase the resistance to thermal shock, it has been proposed to produce ceramic substances retaining a plastic state. However, experience shows that the breaking strain (S) of such materials is simultaneously reduced, thus making such materials unfit for numerous uses whilst not making a marked improvement in their resistance to thermal shock.

It is also known to make a mat of, for example, alumina fibre or zirconia fibre, with the majority of the fibres having an orientation perpendicular to the surface of the mat, on which a ceramic material has been cast. Thus, surfaces having very good resistance to thermal shock, combined with excellent mechanical properties in
one particular direction may be provided. However, this method does not enable parts to be produced which have high isotropic mechanical resistance, that is, high mechanical strength in different directions, nor does it enable the casting of elements having complex shapes and yet having at the same time good resistance to thermal shock and an improved mechanical strength in all directions. There are many problems where it is desirable to be able to protect or shield sensitive elements intended to be placed in a chemically aggressive medium at high temperature by surrounding them with a material which protects against heat and simultaneously against chemical action and at the same time has improved mechanical qualities.

The experiments carried out by the inventors have shown that it was possible to produce isotropic substances having a relatively low Young's modulus (E) and thereby being capable of withstanding a higher thermal shock, by incorporating various ceramic fibres dispersed in a cement substance. The improvement in the resistance to thermal shock becomes particularly evident when the percentage of ceramic fibres incorporated exceeds 20% of the total weight.

Ceramic materials have been produced by present method using ceramic fibres comprising, for example, alumina, zirconia or boron. A ceramic fibre having an alumina content of more than 85%, for example 88%, the remainder being formed by silica SiO₂ has also been used in the method according to the present invention. Such fibres are incorporated in a hydraulic binding agent.
basically consisting of calcium aluminate after a preparation according to the description given hereinbelow. An isotropic ceramic substance for which Young's modulus \( E \) is at least 20 times lower than in known ceramic substances is thus obtained. The coefficient of expansion \( \alpha \) decreases substantially whereas the breaking strain \( S \) remains constant, so that the resistance to thermal shock is improved to a marked extent.

Moreover, it should be noted that the resistance to corrosion of such a product remains, generally, very close to that of the hydraulic binding agent used. In the present case, where the incorporated fibre consists basically of alumina and where the hydraulic binding agent used is calcium aluminate, the same resistance to corrosion when hot as in ceramic substances basically consisting of alumina and calcium aluminate is found.

It is essential for the fibres to be homogeneously distributed and randomly oriented in the admixture in order to obtain a product having isotropic mechanical strength. In a preferred embodiment this is achieved by rapidly stirring an admixture comprising excess water, the weight of water present being not less than the weight of binding agent, and removing the excess water at a later stage.

In accordance with one aspect of the present invention there is provided compound isotropic ceramic substance having very great resistance to thermal shocks, said substance comprising randomly oriented ceramic fibres homogeneously dispersed in a proportion greater than 20% of the total weight of the final product in a hydraulic binding agent constituted by calcium aluminate.
In accordance with a further aspect of the present invention there is provided a method of producing a ceramic isotropic material comprising (i) forming an admixture comprising homogeneously distributed and randomly oriented ceramic fibres, a hydraulic binding agent comprising calcium aluminate, and water, in which admixture the weight of fibres is more than 20% of the combined weight of fibres and binding agent, and (ii) subjecting the admixture to elevated temperature to calcine the same and form the desired ceramic material.

This method of producing a ceramic material can be achieved by mixing the ingredients with a weight of water substantially in the order of the weight of the solid ingredients, and by rapidly stirring said admixture comprising excess water. This characteristic is easily justified by the fact that the fibres must be distributed evenly in the mass without forming heterogeneous nuclei and without assuming a particular direction.

The following Example illustrates the invention.

EXAMPLE

A ceramic fibre comprising 88% alumina and 12% silica marketed under the name FIBRAL, a Trade Mark of Societe Generale des Produits Refractaires (S.G.P.R.) was incorporated in a proportion greater than 20% of the total weight of solids present in a high alumina cement. The mixture was made by rapidly stirring the solid components in a mixer and adding a weight of water at least equal to the weight of cement. Under these conditions, it was possible to incorporate fibres up to 80% of the total weight, progressively adding the required water.
The mixture obtained was moulded and then vibrated after which excess water rose to the surface of the mixture. This water was completely removed by mopping. (When several successive operations are carried out, it is necessary to mop the product after each vibrating operation before adding a further quantity of freshly obtained mixture.) The vibrating operations were stopped when the assembly assumed the consistency of a raw ceramic substance. The mixture was then allowed to set for a few hours.

Drying was then effected using known techniques with temperature stages adapted to the shape and dimensions of the part being made.

In general, for parts having small dimensions, the drying is carried out by raising the temperature by, for example, 20 degrees C per hour and holding the temperature at, say, 100°C and 300°C for a period of a few hours.

For parts having large dimensions, the temperature is generally increased more slowly, for example by 10 degrees C per hour.

The part was then calcined at temperatures of from 1000°C to 1300°C, with the temperature being increased at the rate described above.

The product obtained was a composite ceramic material having a dispersed structure which was part fibrous and part cement. It had a Young's modulus in the order of 20,000 kg/sq. cm. (compared with the more normal values in the range from 500,000 to 800,000 kg/sq. cm. for conventional ceramic materials) and a tensile strength
in the order of 11 kg/sq. cm. The compressive strength was approximately 100 kg/sq. cm. and the coefficient of expansion decreased by about 25% for a given temperature. In the other hand, it was observed that the coefficient of heat conductivity was very slight, being from 0.2 to 0.4 w/m°C.

Remarkably, the product had a negligible shrinkage when setting as well as when stoving.

Thus, the product of the embodiment of the method according to the invention described above is an isotropic ceramic material having a Young's modulus (E) at least 10 times less than in conventional ceramic substances. The coefficient of expansion is decreased substantially, whereas the breaking strain (S) remains constant, so that the resistance to thermal shock is considerably improved.

Moreover, the resistance to corrosion of the product remains generally very similar to that of the high alumina cement used. In the Example described, where the incorporated fibre comprises alumina and where the cement is a high alumina cement, the same resistance to corrosion when hot is found as in conventional ceramic substances consisting of alumina and calcium aluminate.

A ceramic material having similarly improved properties has been obtained by the same method but incorporating a fibre comprising stabilised zirconia, for example, at least 98% zirconia stabilised with yttrium oxide, in the hydraulic binding agent.

In the embodiment of the method according to the invention described above the dispersion of the ceramic fibres in the hydraulic binding agent is promoted by...
incorporating excess water in the admixture. However, dispersion of the ceramic fibres has also been obtained in the dry state by admixing the hydraulic binding agent with the ceramic fibre, both completely dry, in, for example, a Y-shaped mixer. Water required for the hydraulic setting process is then incorporated in a subsequent stage.

Ceramic materials produced by the method according to this invention may be used to protect the magnetic circuits of an electromagnetic pump from thermal shock when the pump is lowered into a high temperature liquid metal bath. Such pumps are used, for example, in processes which involve handling or treating aluminium. Pumps thus protected also resist thermal shock caused by cooling.

Ceramic materials produced as described herein are advantageously used in the manufacturing of moulds in an aluminium foundry because of the absence of shrinking or expansion of the material during manufacture of the mould. It is also possible using such ceramic materials, to produce moulds of all types, tubes, refractory bricks, liquid metal casting spouts, linings for furnaces, melting ladles, and ducts for hot liquids or gases which are particularly reactive.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Compound isotropic ceramic substance having high resistance to thermal shocks, said substance comprising randomly oriented ceramic fibres homogeneously dispersed in a proportion greater than 20% of the total weight of the final product in a hydraulic binding agent constituted by calcium aluminate.

2. The compound isotropic ceramic substance as claimed in Claim 1, wherein the dispersed ceramic fibres comprise alumina.

3. The compound isotropic ceramic substance as claimed in Claim 1, wherein the dispersed ceramic fibres comprise stabilised zirconia.

4. The compound isotropic ceramic substance as claimed in Claim 2, wherein the composition of the dispersed ceramic fibres comprise more than 85% of alumina and less than 15% of silica.

5. The compound isotropic ceramic substance as claimed in Claim 3, wherein the dispersed ceramic fibres comprise more than 98% of zirconia stabilised with yttrium oxide.

6. A method of producing a ceramic isotropic material comprising (i) forming an admixture comprising homogeneously distributed and randomly oriented ceramic fibres, a hydraulic binding agent comprising calcium aluminate, and water, in which admixture the weight of fibres is more than 20% of the combined weight of fibres and binding agent, and (ii) subjecting the admixture to elevated temperature to calcine the same and form the desired ceramic material.
7. The method as claimed in Claim 6, said method further comprising (i) agitating the fibres, the binding agent and excess water to produce a dispersion wherein the fibres are homogeneously distributed and randomly oriented, (ii) moulding the dispersion, (iii) vibrating the moulded dispersion to form the said admixture and excess water on the surface of the admixture, and (iv) removing the excess water from the surface of the admixture before subjecting the admixture to elevated temperature.

8. The method as claimed in Claim 6, wherein the admixture is formed by mixing together the fibres and the binding agent in the dry state and subsequently adding water.

9. The method as claimed in any one of Claims 6 to 8, wherein the weight of water agitated is at least equal to the weight of binding agent.

10. The method as claimed in any one of Claims 6 to 9, wherein the admixture is allowed to set before being subjected to elevated temperature.

11. The method as claimed in any one of Claims 6 to 10, wherein the admixture is subjected to elevated temperature by increasing the temperature by increasing the temperature at a rate of 20 degrees C per hour.

12. The method as claimed in any one of Claims 6 to 10, wherein the temperature is increased at a rate of 10 degrees C per hour.

13. The method as claimed in any one of Claims 6 to 12, wherein the admixture is calcined at a temperature of from 1000 to 1300°C.

14. The method as claimed in any one of Claims 6 to
13. wherein the fibres comprise alumina.

15. The method as claimed in Claim 14, wherein the fibres have a composition comprising more than 85% by weight of alumina and less than 15% by weight of silica.

16. The method as claimed in Claim 15, wherein the fibres have a composition comprising 88% by weight of alumina and 12% by weight of silica.

17. The method as claimed in any one of Claims 6 to 13 wherein the fibres comprise zirconia.

18. The method as claimed in Claim 17, wherein the fibres have a composition comprising at least 98% by weight of zirconia stabilised with yttrium oxide.

19. The method as claimed in any one of Claims 6 to 13, wherein the fibres comprise boron.

20. A method according to Claim 1 substantially as hereinbefore described with reference to the Example.

21. A compound isotropic ceramic substance, substantially as described herein and with reference to the Examples.


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