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HIGHLY REFRACTORY BUILDING MATERIAL AND METHOD OF MAKING SAME

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It is known to manufacture refractory building materials which contain substantial amounts of tricalciumsilicate, Ca_3SiO_5, or in which tricalciumsilicate is the main constituent. For instance, such refractory materials have been manufactured from dolomite, special care being taken that the building material shall be as free as possible from uncombined calciumoxide and from calcium orthosilicate, Ca_2SiO_4, in order that the building material on the one hand should be stable with regard to the action of water and on the other hand that it should not be destroyed by the polymorphic transformation of Ca_2SiO_4. It is known to manufacture such building materials from dolomite, adding fluxing agents which contain silicon, aluminum, iron and chromium. In such manner refractory building materials have been made which apart from tricalciumsilicate, contain aluminates, ferrites, and alumoferrites which crystallize separately, as has been found by means of observations on the microstructure of those materials.

A great difficulty in the industrial utilization of such materials which have been manufactured from dolomite or from limestone, consists in that these materials are subject to softening at comparatively low temperatures for instance it is known that such materials break down under a load of 2 kg/cm² at a temperature of not more than 1600° C.

This difficulty can be understood, if one considers that the ferrites and aluminates of calcium are melting already at temperatures of 1425° C.–1536° C., wholly or in part, and that the melting temperatures of mixtures of $Ca_4Al_2Fe_2O_{10}$ aand tricalciumsilicate, which are melting still more easily, are still lower namely about 1350° C. A building material which contains substantial amounts of such ferrites and aluminates in separate crystals is partly liquified already at temperatures between 1400° C.–1500° C., and by means of that liquification it looses its mechanical strength and softens.

While until now the compounds of trivalent metals in refractory products from dolomite were found predominatingly in the form of independent crystals which are relatively easily fusible, the present invention is based upon the principle that one manufactures refractory building materials in which calcium trisilicate and the compounds of calcium and the trivalent metals form mixed crystals (solid solutions) which are very much more refractory than the mechanical mixtures of tricalciumsilicate and aluminates, ferrites and the like. From these mixed crystals one can manufacture highly refractory materials which can be used under load, even at temperatures of 1700° C., and which are extremely stable against the action of moisture, and which are not subject to any objectionable transformation, such as caused by the presence of Ca_2SiO_4.

The manufacture of refractory mixed crystals from tricalciumsilicate and the compounds of calcium oxide with the oxides of trivalent metals, such as aluminum, iron and chromium, may be suitably carried out according to the following methods. First one has to regulate the chemical composition of the raw materials in such a manner that the compounds of calcium and trivalent metals, for instance $Ca_3Al_2O_6$, $Ca_2Fe_2O_5$, $Ca_4Al_2Fe_2O_{10}$ can be dissolved at high temperatures, for instance 1330–1560° C., in the solid state in the tricalciumsilicate which is present, or that they can in any case form highly refractory mixed crystals with the tricalciumsilicate. Secondly, the raw materials have to be mixed so intimately that during firing the desired refractory mixed crystals can be formed relatively rapidly. Thirdly, the raw materials must be subjected to a process of sintering (vitrification) at elevated temperatures, that is to say, formation of a clinker, or a dense mass which contains a predominating amount of the desired mixed crystals, which process leads to the formation of the refractory mixed crystals. Fourthly, one can manufacture shaped bodies, starting from these refractory products, such shaped bodies being for instance bricks of special shapes which equally have the favourable properties of the sintered product, especially the high refractoriness at elevated temperatures and the stability against water or moisture.

The first step consists in regulating the amounts of SiO_2, Al_2O_3, Fe_2O_3, Cr_2O_3 in proportion to the amount of CaO, in such a manner that the desired formation of mixed crystals between the tricalciumsilicate and the compounds of trivalent metals can take place without the formation of objectionable amounts of easily fusible crystals, such as $Ca_4Al_2Fe_2O_{10}$, Ca_2FeO_5, $Ca_3Al_2O_6$. On the other hand a certain minimum amount of Al_2O_3, Fe_2O_3, Cr_2O_3 ought to be present in order to make possible the manufacture of the building material, chiefly as fluxing agents and possibly also for stabilizing the tricalciumsilicate, Ca_3SiO_5, by the formation of mixed crystals.

It has been found that the necessary conditions for the manufacture of a highly refractory product can be expressed by giving the amounts of SiO_2, Al_2O_3, Fe_2O_3, Cr_2O_3 in proportion to the percentage of CaO of the building material. Hitherto one has often tried to fix the most favourable amounts of the substances added in proportion to the total weight of crude dolomite or limestone used; however, only the proportion to the percentage of CaO is of importance.

Calculating the amounts of trivalent metals, it has to be noted that the effect of one unit of weight Al_2O_3 corresponds to about double the weight of Fe_2O_3 and Cr_2O_3, according to numerous practical trials.

For each 100 parts by weight of CaO the quantity by weight of

$$Al_2O_3+\frac{Fe_2O_3+Cr_2O_3}{2}$$

shall not be less than about 6 and not more than about 15, preferably it shall be about 7–12%. If the trivalent metals substantially consist of chromium and iron, the higher amounts, for instance 15–17 parts by weight for each 100 parts by weight of CaO may be used. The amount by weight of SiO_2, calculated in proportion to 100 parts by weight of CaO ought not to be lower than about 20 parts and ought not to be in excess of about 33 parts, preferably it should be about 22–29 parts of SiO_2.

Calculating these amounts, one has to take into consideration not only the percentage of SiO_2, Al_2O_3, Fe_2O_3, Cr_2O_3 in the materials added, such as quartz, talc, kaolinite, clay, iron ores and chrome iron ore, but also the percentage of SiO_2 and of trivalent metals in the raw materials used, such as dolomite and limestone.

Manufacturing according to the present invention, the raw material containing the calcium, for instance the limestone or the dolomite, is very finely crushed, preferably together with the added materials, until a grain size of 0.12 mm or less is obtained, preferably by wet milling. It is very advantageous to add a dispersing agent during the wet milling. One can use inorganic or organic dispersing agents. Very advantageously one can use for that purpose soluble compounds of sodium, especially those which have an alkaline reaction, such as for instance soda, sodium silicates, such as sodium metasilicate, borax; also certain compounds without alkaline reaction can be used, such as sodium phosphate, sodium pyrophosphate, sodium oxalate. Likewise one can use humates and tannates of sodium or ammonium. By using compounds of sodium in amounts corresponding to from 0.1 to 1.5 parts by weight of Na_2O, preferably about 0.5 parts by weight, for 100 parts by weight of CaO, one obtains at the same time the important advantage that the compounds of sodium are very useful as fluxing agents with regard to the sintering (vitrification) of the building material.

For substances of addition which contain silicon, aluminium, iron, chromium, one can for instance use quartz, bauxite, kaolinite, clay, chrome iron ore, or mixture of such substances.

The crushed product, if necessary is dried, eventually moulded into lumps, and then preferably in a neutral or oxidising atmosphere is subjected to a process of sintering (vitrification), at a temperature sufficiently high to calcine the dolomite and the limestone and to obtain the desired formation of refractory mixed crystals; the temperature of vitrification is preferably very much higher than the melting temperature of the aluminates, ferrites, alumoferrites and chromites of calcium which enter into their constitution. In the utilization of ferrites the sintering temperatures ought to be in excess of 1425° C. which is the melting point of $Ca_2Fe_2O_5$, preferably they ought to be above 1500° C.; in utilizing aluminates they ought to be in excess of 1536° C., which is the temperature of partial melting of $Ca_3Al_2O_6$, preferably they ought to surpass even 1600° C. A very important phenomenon which can be observed in the process of sintering, according to the invention, is the following:

The mixture of substances at a temperature between for instance 1500° C. and 1600° C. shows first a very distinct softening, which apparently is due to the fact that at these temperatures part of the mixture is being melted, especially the ferrites and aluminates of calcium; by means of the action of that fused liquid the refractory mixed crystals are then formed which mixed crystals contain jointly in the same crystals calcium, silicon and the oxides of trivalent metals in a form which is refractory against fusion. These refractory mixed crystals are the most important constituent of the building material according to the invention. If one uses dolomite or other raw materials rich in magnesium, such as mixtures of dolomite and magnesite as the most important constituent of the raw material, then the sintered building material contains considerable amounts of magnesium. In the sintered product the magnesium is present chiefly in the form of uncombined MgO (periclase); in small amounts, however, it can be present in other compounds; for instance it is even possible that it is found also in the refractory mixed crystals which consist predominatingly of calcium silicate and in subordinate amounts of aluminate or ferrite of calcium.

The sintering of the material can be effected periodically in kilns, such as chamber furnaces or ring furnaces, or it can be very well effected in continuously operating furnaces, such as rotating kilns, analogous to the kilns used for the manufacture of cement. At a firing temperature of 1600° C., an exposure to burning of for instance 6 hours is quite sufficient for the process of sintering.

During cooling of the sintered product a partial separation of the components of the mixed crystals can take place; but during the utilization of the products at high temperatures the mixed crystals are regenerated.

The refractory sintered products according to the present invention can be worked up according to methods known in the industry of refractories, for obtaining moulded bodies, for instance bricks, bricks for arched roofs and the like; however, in many cases one uses directly the sintered product for obtaining a dense mass, for furnaces bottoms and the like.

In the manufacture of shaped products one proceeds advantageously as follows. The sintered product, having a yellowish-brown colour, if aluminates are being used, and a predominating green colour, if ferrites or alumoferrites are being used, and which has the constitution of a dense clinker, is crushed, for instance by means of crushing devices, to produce as much as possible of sharply edged grains. The crushed material, for instance with a maximum grain size of 4 mm. is worked up in such a manner that the finely divided fraction is used as a bonding agent; for instance, a material with grain size less than 0.15 mm. is used in an amount of preferably 15–20% by weight of the building material, but also higher percentages of finely divided materials can be utilized. From the batches, if desired moistened with water or with aqueous solutions, one can produce shaped bodies, for instance by means of an hydraulic press, such moulded bodies being afterwards dried and subjected to a process of firing preferably in a neutral or oxidising atmosphere, and preferably at temperatures above 1400° C., for instance at 1500–1550° C. At these temperatures the finely divided mass is densified, which improves the stability of the shaped material against moisture, and at the same time the mixed crystals are better homogenized which improves the refractoriness.

Using the chemical composition given in the present invention and by means of the process of sintering described above, it is even possible to heat the moulded shapes to a temperature in excess of the melting temperatures of the compounds of calcium and the oxides of trivalent metals, without partial fusion and without softening of the moulded bodies taking place.

The moulded bodies manufactured according to the invention are extremely refractory and under a load of 2 kg/cm² at a temperature of 1700° C they are subject to a deformation amounting to only 1–3% or less. They are extremely stable against the action of moisture or water and can be kept immersed in water for months, without being hydrated in an objectionable manner; they even resist a treatment of 2 hours in autoclaves with superheated water at 170° C.

Examples

(1) As raw material, a dolomite of the following composition was used: 30.65% by weight of CaO, 20.23% MgO, 1.10% Al_2O_3, 1.46% FeO_3, 0.58% SiO_2, 45.98% CO_2. To 100 parts by weight of the dolomite were added 6.50 parts by weight of quartz (with 99.9% SiO_2) and 1.00 part by weight of Fe_2O_3 and 1.80 parts by weight of Na_2CO_3. 30 parts by weight of water were added and the material crushed in a ball mill until a degree of sub-division below 0.12 mm (2500 openings per cm², or 120 mesh English), dried by evaporation of the water and sintered at a temperature of 1520° C. for 6 hours in an oxidizing atmosphere. The sintered products were crushed to a grain size of 4 mm. The fine dust, with a particle size of less than 0.15 mm was separated by means of a sieve, and was used as an amount of 20 percent by weight of fines, together with 80 percent by weight of coarse granular material (0.15–4.0 mm). As a liquid for the batch a solution of 15% of syrup in water was used. To 20 parts of fine material there were added 2 parts of liquid, while to 80 parts of coarse granular material there were added 3 parts of liquid; the fines and the coarse grains were mixed and then moulded in a hydraulic press under a pressure of 200 kg/cm², after which they were dried and subjected to firing at cone 18 for 24 hours. The shaped bodies which were manufactured in such a manner had a refractoriness under a load of 2.8 kg/cm² at 1590° C, and at 1750° C under the same load a linear compression of only 2%. The products were extremely stable against water. In this example the ratio by weight of SiO_2:CaO is 23:100 and

$$Al_2O_3+\frac{Fe_2O_3}{2}:CaO=7.5:100$$

(2) As raw material a dolomite of the following composition was used: 28.80% CaO, 22.70% MgO, 0.10% SiO_2, 0.40% Al_2O_3, 0.40% Fe_2O_3, 47.70% CO_2.

To 100 parts by weight of the dolomite were added the following substances: 14 parts by weight of a refractory clay of the following composition: 59.60% SiO_2, 29.30% Al_2O_3, 1.40% Fe_2O_3, 0.10% CaO, 0.10% MgO, 1.40% Na_2O+K_2O, 8.10% H_2O, as well as 1 part by weight of Na_2CO_3. The mixture was milled with the addition of 20 percent by weight of water to 100 parts by weight of dry substance until all passed through a sieve with 4900 openings per cm² (180 mesh English), corresponding to a maximum particle size of 0.088 mm. The substance was sintered at 1620° C for 6 hours, cooled down, crushed to a maximum grain size of 4 mm, and then worked up to obtain moulded bodies as in example 1. The shaped bodies had a refractoriness under a charge of 2 kg/cm² as follows: begin of softening at 1560° C; breakdown under the same load takes place at 1690° C. The stability of the material against water was excellent. One could use the sintered material in the crushed state or in unbroken state for lining of furnaces for melting iron and steel without previous manufacturing of shaped bodies.

In this example the ratio by weight of SiO_2:CaO is 21:100 and

$$Al_2O_3+\frac{Fe_2O_3}{2}:CaO=12.5:100$$

Such dolomite refractories as described in example 2, relatively rich in Al_2O_3, are especially well suited for such uses as for linings of soda ovens, even if these refractories are somewhat less resistive against load under extremely high temperatures than those which contain less amounts of Al_2O_3. They are very resistive against alkaline fluxes.

(3) The same dolomite as in example 1 was used. To 100 parts by weight of the dolomite were added 6 parts by weight of quartz and 4 parts by weight of chrome iron ore of the following composition: 51% Cr_2O_3, 16% FeO, 12% Al_2O_3, 16% MgO and 5% SiO_2. To the mixture was further added 1 part of Na_2CO_3, and the material was worked up as in example 1. Again a highly refractory product, entirely stable against water is obtained. In this example the ratio by weight of SiO_2:CaO is 22.1:100 and

$$Al_2O_3+\frac{Fe_2O_3+Cr_2O_3}{2}:CaO$$

is 13.7:100.

(4) A limestone containing 55.50% CaO, 1.00% SiO_2, 43.50% CO_2 and 0.10% Al_2O_3 was worked up. To 100 parts of limestone were added 11.50 parts by weight of quartz, as well as 5 parts by weight of Fe_2O_3 and 5 parts by weight of a clay containing 60% SiO_2, 30% Al_2O_3 and 10% H_2O; further to 126.5 parts by weight of the mixture were added 2 parts by weight of crystallized borax as well as 25 parts by weight of water. The material was finely milled, dried by means of evaporation, and then sintered at 1650° C for 4 hours. A refractory product was obtained which could be used as well for ramming masses as for the manufacture of moulded bodies. In this example the ratio by weight of SiO_2:CaO is 27.9:100 and

$$Al_2O_3+\frac{Fe_2O_3}{2}:CaO=7.40:100$$

The examples given demonstrate that by following the conditions described one obtains products the properties of which are highly superior to those of water resisting dolomites known hitherto. For instance concerning the refractoriness under a load of 2 kg/cm^2, one has hitherto for water resisting dolomites usually quoted a temperature of beginning of softening (ta) 1500° C, while for the temperature of breakdown under load (te) one has quoted 1600° C; that demonstrates that an important technical progress is made, if one follows the instructions according to the present invention.

The refractoriness under load of the new products is also very much better than that of those magnesites which have generally been used hitherto, and for which the beginning of softening under a load of 2 kg/cm^2 is found at about 1500° C.

In the same manner, according to the method described, one can obtain highly refractory products, characterized by mixed crystals of tricalciumsilicate on the one hand and aluminates, ferrites etc. of calcium on the other hand starting from mixtures of dolomite, limestone, magnesite with additional substances consisting of silicates or oxides; one can also utilize such natural raw materials the composition of which leads directly to the formation of the desired mixed crystals, for instance dolomite or limestone which themselves contain corresponding amounts of SiO_2, Al_2O_3, iron compounds. In working up such raw materials, eventually after homogenizing by means of fine crushing of the raw material, one can again effect a sintering at such elevated temperatures that softening takes place and the desired mixed crystals are formed, which later on can be worked up, such as described in the foregoing.

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