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(54) Title: REFRACTORY CERAMIC PRODUCT, USE OF HOLLOW SPHERES OF MAGNESIA SPINEL, BATCH FOR PRODUCING A REFRACTORY CERAMIC PRODUCT, METHOD FOR PRODUCING A REFRACTORY CERAMIC PRODUCT, KILN FOR PRODUCING CEMENT CLINKER OR LIME AND METHOD FOR PRODUCING CEMENT CLINKER OR LIME

(57) Abstract: The invention relates to a refractory ceramic product, a use of hollow spheres of magnesia spinel, a batch for producing a refractory ceramic product, a method for producing a refractory ceramic product, a kiln for producing cement clinker or lime and a method for producing cement clinker or lime.

Refractory ceramic product,
use of hollow spheres of magnesia spinel,
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D e s c r i p t i o n

The invention relates to a refractory ceramic product, a use of hollow spheres of magnesia spinel, a batch for producing a refractory ceramic product, a method for producing a refractory ceramic product, a kiln for producing cement clinker or lime and a method for producing cement clinker or lime.

Refractory ceramic products are products that can withstand high temperatures. The term “refractory product” in the sense of the invention refers in particular to refractory materials with an operating temperature above 600°C and preferably to refractory materials in accordance with DIN 51060:2000-06, i.e., materials with a pyrometric cone equivalent >SK17. The pyrometric cone equivalent can be determined in particular in accordance with DIN EN 993-12:1997-06.

As is well known in the art, the term “ceramic” refractory product refers to a refractory product that is comprised of ceramic material, i.e., particles which are sintered together.

Further, as well known in the prior art, a “batch” for producing a refractory ceramic product is comprised of components from which a refractory ceramic product can be produced by firing.

A typical field of application for refractory ceramic products is their use in kilns for the production or firing of cement clinker and lime. Such kilns may be rotary kilns or shaft kilns in particular. Such kilns are lined with refractory ceramic products that can withstand the high temperatures in such kilns.

Typically, such refractory ceramic products by which such kilns for the production of cement clinker and lime are lined are based on magnesia, i.e., a refractory material based on the oxide MgO.

In principle, such refractory ceramic products based on magnesia have proven to be suitable for lining such kilns. However, it is a permanent task to improve such refractory ceramic products in terms of their insulating capacity and strength. Thus, it is a constant goal to give such refractory ceramic products a good insulating effect with a high strength at the same time. However, the increase of an insulating effect in prior art refractory ceramic products is usually accompanied by a reduction in strength. A main reason is that an improved insulating effect is associated with increased porosity, which leads to a reduction in strength. Furthermore, increased porosity, which in particular is also associated with increased open porosity, can lead to a deterioration in the corrosion resistance of the refractory ceramic product, since components can penetrate the open porosity, resulting in corrosion of the product.

In rotary kilns and shaft kilns for burning cement clinker and lime, temperatures in the range of up to 1,400 to 1,500°C regularly prevail. However, this is regularly not the temperature to which the refractory ceramic products lining the kilns are subjected to. This is due to the fact that on the hot side of the refractory ceramic products, the fired material, i.e., clinker or lime, usually presents some barrier to the furnace atmosphere. Further, the temperature within the refractory ceramic products decreases from the hot side to the cold side. The average temperature within the refractory ceramic products is therefore well below the aforementioned temperatures and often in the range of about 800°C. It is therefore desirable that the refractory ceramic products have good strength and a good insulating effect at 800°C.

It is an object of the invention to provide a refractory ceramic product that has a good insulating effect and a high strength. At the same time, the refractory ceramic product should

preferably also have a high corrosion resistance. In particular, the refractory ceramic product should have a good insulating effect at about 800°C and further a good strength.

It is a further object of the invention to provide a batch for producing such a refractory ceramic product, as well as a method for producing such a refractory ceramic product.

To solve the problem, according to the invention there is provided a refractory ceramic product, comprising the following features:

- a matrix of particles sintered together;
- the particles sintered together comprise first particles and second particles;
- the first particles are particles based on magnesia;
- the second particles are hollow spheres of magnesia spinel;
- the proportion of the second particles is in the range from 1 to below 10% by mass, based on the total mass of the matrix.

Surprisingly, it has been found in the context of the invention that a refractory ceramic product having the above features has at the same time both a good insulating capacity, i.e., a low thermal conductivity, and a good strength, and in particular a low thermal conductivity at 800°C.

Of particular importance for these properties of the refractory ceramic product according to the invention are the second particles in the form of the hollow spheres of magnesia spinel, which are present in the matrix in a proportion of 1 to below 10% by mass.

With respect to the thermal conductivity of the refractory ceramic product according to the invention, it has been found within the scope of the invention that a proportion of second particles in the proportion according to the invention makes it possible to provide a refractory ceramic product with an excellent insulating capacity, i.e., a low thermal conductivity, in particular a thermal conductivity at 800°C of less than 3.9 W/m·K. In particular, however, it has been surprisingly found in the context of the invention that this low thermal conductivity is only slightly further reduced at a proportion of hollow spheres of 10% by mass and above, but at the same time the strength is greatly reduced. In particular, the cold crushing strength (CCS) decreases dramatically when hollow spheres of magnesia-spinel are present in proportions of 10% by mass and above. For numerous applications, however, it is desirable

that magnesia-based refractory ceramic products for lining kilns, especially for lining kilns for the production of cement clinker and lime, have a cold crushing strength above 60 MPa. According to the invention, however, it has surprisingly been found that such strength values usually cannot be achieved when the hollow spheres of magnesia-spinel are present in a proportion of 10% by mass and above in the matrix. According to the invention, it is therefore envisaged to provide the hollow spheres of magnesia spinel in a proportion of less than 10% by mass in the matrix.

It is also of particular importance for the invention that the hollow spheres consist of magnesia spinel, i.e., of a material based on magnesia spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$, MgAl_2O_4). According to the invention, this has been found to allow the use of elastifiers in the refractory ceramic product without thereby damaging the integrity of the refractory ceramic product or degrading its properties. Elastifiers are known to be components added to magnesia-based refractory ceramic products to lower the brittleness of the product or reduce its modulus of elasticity. Usually, such elastifiers are spinel-type materials, for example materials based on magnesia spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$, MgAl_2O_4), hercynite ($\text{FeO} \cdot \text{Al}_2\text{O}_3$, FeAl_2O_4) or pleonaste ($(\text{Mg}, \text{Fe})(\text{Al}_2\text{O}_4)$). By using hollow spheres made of magnesia spinel, however, a reaction of the hollow spheres with such elastifiers is suppressed, so that the integrity of the hollow spheres and thus their effect in the refractory ceramic product is not impaired.

It is well known that hollow spheres, sometimes also referred to as "microspheres" in the prior art, are small hollow spheres or balloons consisting of an essentially dense shell filled with a gas, in particular air. Since the shell is very small in relation to the total volume of the hollow spheres, such hollow spheres have only an extremely low bulk density. The use of such hollow spheres in refractory ceramic products can therefore greatly reduce the thermal conductivity of such products. Usually, hollow spheres are produced by first providing a melt of the material of the hollow spheres, i.e., in the present case a melt of magnesia spinel. The melt is then blown through nozzles to form molten hollow spheres, which are then cooled either in a fluid, in particular water, or in a gas, in particular air, causing them to cool and solidify. Small hollow spheres are then obtained, which are referred to as hollow spheres. The size of the spheres can be adjusted, in particular, by the temperature of the melt, the nozzle shape, and the parameters during blowing through the nozzle. A method for producing hollow spheres is described, for example, in WO 2012/122745 A1 (PCT/CN2011/075096).

A particular advantage with regard to the use of hollow spheres for adjusting the thermal conductivity of the refractory ceramic product according to the invention also lies, in particular, in the fact that these have a substantially dense surface, with the effect that the refractory ceramic product has only a relatively low open porosity. This makes it possible to provide a refractory ceramic product according to the invention with very good corrosion properties.

According to the invention, it was found that the refractory ceramic product according to the invention can exhibit excellent strength, in particular an excellent cold crushing strength of over 60 MPa, when the hollow spheres are present in a proportion of about 5% by mass. Further, the refractory ceramic product according to the invention exhibits an excellent ratio of thermal conductivity to strength when the hollow spheres are present in a proportion of about 5% by mass in the product. Preferably, therefore, it may be provided that the second particles are present in the matrix in a proportion as close as possible to a proportion of 5% by mass. At the same time, it was found that the thermal conductivity of the refractory ceramic product according to the invention decreases only to a small extent when the second particles in the form of hollow spheres of magnesia spinel are present in the product in a proportion of more than about 5% by mass, i.e., in a proportion in the range from 5 to below 10% by mass. According to a preferred embodiment, it may therefore be provided that the second particles are present in the refractory ceramic product in a proportion of at most 9% by mass, more preferably at most 8% by mass, even more preferably at most 7% by mass, and even more preferably at most 6% by mass, in each case based on the total mass of the matrix. It may further be provided that the second particles are present in a proportion of at least 2% by mass, more preferably in a proportion of at least 3% by mass and even more preferably in a proportion of at least 4% by mass in the refractory ceramic product according to the invention, again each based on the total mass of the matrix. Furthermore, it may preferably be provided that the proportion of the second particles is present in the range from 2 to 9% by mass, more preferably in the range from 3 to 8% by mass, even more preferably in the range from 4 to 7% by mass and even more preferably in the range from 4 to 6% by mass in the refractory ceramic product according to the invention, again in each case based on the total mass of the matrix.

Surprisingly, it has been found in the context of the invention that the size or diameter of the hollow spheres of magnesia spinel can have a significant influence on the properties of the

refractory ceramic product according to the invention. Thus, according to the invention, it has been surprisingly found that the refractory ceramic product according to the invention has particularly low thermal conductivity and high strength when the hollow spheres have a diameter not exceeding 3 mm. Furthermore, it has been found that the thermal conductivity can be increasingly reduced and the strength increasingly increased, the greater the proportion of hollow spheres made of magnesia spinel with a diameter not exceeding 1 mm becomes. This finding is all the more surprising in view of the fact that the ratio of volume to mass decreases with an increasingly smaller diameter of the hollow spheres and therefore it would actually be expected that the insulating capacity of a product decreases insofar as it comprises hollow spheres with an increasingly smaller diameter. The reason for the fact that the properties of the refractory ceramic product with regard to its thermal conductivity can be increasingly improved insofar as the proportion of hollow spheres is increasingly less than 1 mm has not yet been conclusively clarified. The inventors assume that hollow spheres with a diameter of more than 3 mm are largely destroyed and with a diameter in the range of 1 to 3 mm at least in a relevant proportion are destroyed during the manufacturing process of the refractory ceramic product, as a result of which the strength of the product decreases and at the same time the destroyed hollow spheres can no longer develop their insulating effect in the product. According to a preferred embodiment, it is provided in this respect that the hollow spheres have a diameter not above 3 mm, even more preferably a diameter not above 2 mm and particularly preferably a diameter not above 1 mm.

Furthermore, according to the invention, it has been found that the thermal conductivity of the refractory ceramic product can be reduced only slightly by the hollow spheres if the hollow spheres have a diameter below 100 μm . According to a preferred embodiment, it is therefore provided that the hollow spheres have a diameter in the range from 100 μm to 3 mm, more preferably in a range from 100 μm to 2 mm and particularly preferably in a range from 100 μm to 1 mm.

The diameter of the hollow spheres is determined according to the standard ISO 1927-3. The diameter of the hollow spheres in the refractory product can, e.g., be determined using electron microscopy.

The hollow spheres of magnesia spinel are based on the mineral magnesia spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$, MgAl_2O_4). The magnesia spinel does not necessarily have to be present with stoichiometric proportions of the oxides MgO and Al_2O_3 .

According to one embodiment, the hollow spheres have a chemical composition comprising the following oxides in the following mass proportions, each relative to the total mass of the hollow spheres:

MgO : 25 to 34% by mass;

Al_2O_3 : 66 to 75% by mass.

According to the invention, it has been surprisingly found that the refractory ceramic product has particularly good properties in terms of its thermal conductivity and strength, insofar as the magnesia spinel of the hollow spheres is present with a superstoichiometric proportion of Al_2O_3 . A stoichiometrically composed magnesia spinel has a proportion of Al_2O_3 of 71.67% by mass and MgO of 28.33% by mass. According to a preferred embodiment of the invention, it may be provided that the magnesia spinel of the hollow spheres has a chemical composition comprising the following oxides in the following mass proportions, each based on the total mass of the hollow spheres: MgO : 25 to 28% by mass and Al_2O_3 : 72 to 75% by mass, more preferably MgO : 25 to 27% by mass and Al_2O_3 : 73 to 75% by mass and even more preferably MgO : 25 to 26.5% by mass and Al_2O_3 : 73.5 to 75% by mass.

According to one embodiment, the hollow spheres have a bulk density in the range from 0.5 to 1.0 g/cm^3 , based on the total mass of the hollow spheres.

The refractory ceramic product according to the invention, like any ceramic product, comprises a matrix of particles sintered together. These particles further comprise, in addition to the second particles of hollow spheres of magnesia spinel, first particles based on magnesia.

Such particles based on magnesia may in principle be any particles of a material based on magnesia known in the prior art for refractory ceramic products. For example, the particles based on magnesia may comprise at least one of the following: Particles of sintered magnesia or particles of fused magnesia. According to a particularly preferred embodiment, the particles based on magnesia are in the form of particles of sintered magnesia.

According to a particularly preferred embodiment, the particles based on magnesia are particles of low-iron magnesia. Particularly preferably, the low-iron magnesia has a chemical composition with an Fe_2O_3 content of at most 1% by mass.

According to a preferred embodiment, the particles sintered together comprise the first particles, the second particles and third particles, and wherein the third particles are particles based on at least one spinel-type material.

Such further particles in the form of spinel-type material can, in particular, act as elastifiers by which the ductility of the refractory ceramic product according to the invention can be reduced.

According to a preferred embodiment, the third particles are particles of at least one of the following spinel-type materials: magnesia spinel, magnesia spinel coated magnesia, hercynite or pleonaste. Even more preferably, the third particles are particles of at least one of the following spinel-type materials: magnesia spinel, hercynite or pleonaste. Even more preferably, the third particles are particles of magnesia spinel.

According to a preferred embodiment, it may be provided that the third particles are present in a proportion in the range from 0 to 20% by mass, more preferably in the range from 1 to 20% by mass, more preferably in the range from 3 to 17% by mass and even more preferably in the range from 5 to 15% by mass.

According to a preferred embodiment, it is provided that the first particles are present in a proportion that complements the proportion of the second particles to 100% by mass, based on the total mass of the matrix.

According to a preferred embodiment, to the extent the matrix comprises third particles, it is provided that the first particles are present in a proportion that complements the proportion of the second particles and the third particles to 100% by mass, based on the total mass of the matrix.

According to one embodiment, it is provided that the first particles are present in a proportion in the range from 99 to above 70% by mass, more preferably in the range from 98 to above 70% by mass and more preferably in a proportion in the range from 90 to 80% by mass, in each case based on the total mass of the matrix.

As previously stated, the second particles exhibit a particularly good effect with respect to the thermal conductivity and the strength of the product if the first particles comprise, in addition to the particles based on magnesia, particles based on a spinel-type material in the form of magnesia spinel, since in this case the hollow spheres of the second particles prove to be particularly stable and, in particular, a reaction with the components of the refractory ceramic product can be suppressed.

Preferably, the refractory ceramic product according to the invention is based on magnesia. Particularly preferably, the refractory ceramic product has a chemical composition based on magnesium oxide (MgO). In this respect, magnesium oxide in the matrix of the refractory ceramic product according to the invention preferably represents the oxide that is present in the highest mass fraction, relative to the total mass of the oxides according to the chemical composition of the matrix.

According to a preferred embodiment, the matrix has a chemical composition comprising the following oxides in the following mass percentages, each based on the total mass of the matrix:

MgO: 82 to 94% by mass;
Al₂O₃: 4 to 14% by mass;
further oxides: 0 to 6% by mass.

Further preferably, the matrix has a chemical composition comprising the following oxides in the following mass percentages, each based on the total mass of the matrix:

MgO: 84 to 90% by mass;
Al₂O₃: 8 to 13% by mass;
further oxides: 1 to 4% by mass.

The above "further oxides" preferably are at least one of the following oxides: SiO₂, CaO, Fe₂O₃.

Further preferably, the matrix has a chemical composition comprising the following oxides in the following mass percentages, each based on the total mass of the matrix:

MgO: 82 to 94% by mass;

Al₂O₃: 4 to 14% by mass;

Fe₂O₃: 0.3 to 1% by mass;

further oxides: 0 to 5% by mass, wherein the "further oxides" preferably are at least one of the following oxides: SiO₂, CaO.

Further preferably, the matrix has a chemical composition comprising the following oxides in the following mass percentages, each based on the total mass of the matrix:

MgO: 84 to 90% by mass;

Al₂O₃: 8 to 13% by mass;

Fe₂O₃: 0.3 to 1% by mass;

further oxides: 1 to 3% by mass, wherein the "further oxides" preferably are at least one of the following oxides: SiO₂, CaO.

Further preferably, the matrix has a chemical composition comprising the following oxides in the following mass percentages, each based on the total mass of the matrix:

MgO: 84 to 90% by mass;

Al₂O₃: 8 to 13% by mass;

Fe₂O₃: 0.3 to 1% by mass;

SiO₂: 0.2 to 1.3% by mass;

CaO: 0.8 to 1.8% by mass.

Accordingly, the matrix of the refractory ceramic product comprises mainly the oxides MgO and Al₂O₃, the content of the oxide Fe₂O₃ being preferably extremely low and preferably in a proportion of at most 1% by mass.

The chemical composition of the matrix of the refractory ceramic product may be determined in particular by X-ray fluorescence analysis (XRF), and in particular according to the standard ISO 12677:2011.

The refractory ceramic product according to the invention may have a very low thermal conductivity and thus a good insulating effect. According to a preferred embodiment, the refractory ceramic product has a thermal conductivity at 800°C of less than 5.0 W/m·K and particularly preferably below 4.5 W/m·K.

The thermal conductivity is determined according to the standard ISO 8894-2:2007.

Despite this only low thermal conductivity, the refractory ceramic product according to the invention can at the same time nevertheless exhibit good strength, in particular very good cold crushing strength (CCS). In particular, the refractory ceramic product according to the invention can have a cold crushing strength of at least 60 MPa. According to a preferred embodiment, the refractory ceramic product according to the invention has a cold crushing strength of above 60 MPa.

The cold crushing strength is determined according to the standard ISO 10059-1:1992.

Thus, the refractory ceramic product according to the invention can be provided with an exceptionally good ratio of thermal conductivity to cold crushing strength.

According to a preferred embodiment, the matrix of the refractory ceramic product according to the invention has a density in the range of 2.8 to 2.9 g/cm³, determined according to the standard ISO 5017:2013.

Despite this relatively low density, the refractory ceramic product according to the invention can nevertheless have only a low apparent porosity, in particular an apparent porosity of at most 18.5% by volume. This only low apparent porosity with a simultaneously low density can be realized in particular by using hollow spheres in the matrix to give the product a low density without creating a porous matrix.

According to a preferred embodiment, the matrix of the refractory ceramic product according to the invention has an open apparent in the range of 17 to 18.5% by volume, determined according to the standard ISO 5017:2013.

It is also an object of the invention to use hollow spheres of magnesia spinel to reduce the thermal conductivity of a magnesia-based refractory ceramic product, wherein the hollow spheres of magnesia spinel are used with the proviso that the magnesia-based refractory ceramic product comprises a proportion of the hollow spheres of magnesia spinel in the range from 1 to below 10% by mass, based on the total mass of the magnesia-based refractory ceramic product.

In other respects, the use of the hollow spheres of magnesia spinel according to the invention may be made with the provisos according to the features of the invention disclosed herein.

"Magnesia-based" according to the use according to the invention means that the refractory ceramic product comprises MgO as the main oxide.

According to another aspect of the invention, a batch for producing a refractory ceramic product is provided, comprising the following features:

- a first component and a second component;
- the first component is at least one raw material based on magnesia;
- the second component are hollow spheres of magnesia spinel;
- the proportion of the second component is in the range from 1 to below 10% by mass, based on the total mass of the first and second component.

The batch is preferably used to produce the refractory ceramic product according to the invention.

According to one embodiment, the batch further comprises a third component which is a raw material based on at least one spinel-type material.

It is also an object of the invention to provide a method for producing a refractory ceramic product, comprising the following steps:

- providing a batch according to the invention;
- firing the batch.

The method is preferably used to produce the refractory ceramic product according to the invention.

By firing the batch, the first particles of the refractory ceramic product according to the invention are formed from the first component of the batch according to the invention, and the second particles of the refractory ceramic product according to the invention are formed from the second component. To the extent the third component is present in the batch, the third particles of the refractory ceramic product according to the invention are formed from the third component. The first component is thereafter such that the first particles of the refractory ceramic product can form therefrom, the second component is such that the second particles of the refractory ceramic product can form therefrom, and the third component is such that the third particles of the refractory ceramic product can form therefrom.

The composition of the first component may thereafter preferably correspond to the composition of the first particles, i.e., comprise in particular the proportions of particles based on magnesia as disclosed above. Their proportions in the batch may correspond to the proportions of these particles in the matrix of the refractory ceramic product according to the invention.

Further, the hollow spheres of magnesia spinel of the second component may have the characteristics of the hollow spheres of magnesia spinel of the second particles and may be present in the batch in the proportions in which the proportions of the second particles are present in the matrix of the refractory ceramic product according to the invention.

Further, the third component may thereafter preferably correspond to the composition of the first particles, i.e., comprise in particular the proportions of particles based on a spinel-type material as disclosed above.

Firing the batch according to the method of the invention is for such a duration and at such a temperature that the first component, the second component and, to the extent it is comprised in the batch, the third component sinter together and form a matrix of particles sintered together. For example, the firing may be carried out for a duration in the range of 3 to 8 hours at a temperature in the range of 1,500 to 1,800°C.

It is also an object of the invention to provide a kiln for producing cement clinker or lime, comprising the following features:

- the kiln comprises a lining of refractory products;
- the refractory products comprise refractory ceramic products according to the invention.

The kiln according to the invention can preferably be a rotary kiln or a shaft kiln, particularly preferably a rotary kiln.

It is also an object of the invention to provide a method for producing cement clinker or lime, comprising the following steps:

- providing a kiln according to the invention;
- providing raw materials from which cement clinker or lime can be produced through firing;
- firing the raw materials in the kiln.

The method for producing cement clinker or lime can further be carried out in accordance with the technologies known from the prior art.

Further features of the invention are apparent from the claims and the exemplary embodiments of the invention described below.

All features of the invention may, individually or in combination, be combined with each other as desired.

Exemplary embodiments

First, exemplary embodiments of batches according to the invention were provided for producing exemplary embodiments of refractory ceramic products according to the invention.

The exemplary embodiments of the batches each comprise a first component, a second component and a third component.

The first component was a raw material in the form of sintered magnesia. The chemical composition of the sintered magnesia was as follows:

MgO: 96.7% by mass;
Al₂O₃: 0.2% by mass;
Fe₂O₃: 0.8% by mass;
SiO₂: 0.8% by mass;
CaO: 1.4% by mass;
Others: 0.1% by mass.

The third component was a raw material in the form of fused magnesia spinel, acting as an elastifier. The chemical composition of the fused magnesia spinel was as follows:

MgO: 32.5% by mass;
Al₂O₃: 62.9% by mass;
Fe₂O₃: 0.6% by mass;
SiO₂: 0.4% by mass;
CaO: 0.8% by mass;
Others: 2.8% by mass.

The second component was present in the form of hollow spheres of magnesia spinel. These hollow spheres of magnesia spinel had the following chemical composition:

MgO: 24.6% by mass;
Al₂O₃: 74.0% by mass;
Fe₂O₃: 0.2% by mass;
SiO₂: 0.4% by mass;
Others: 0.8% by mass.

The bulk density of the hollow spheres was 1 g/cm³.

Subsequently, three batches were produced from these components, which are designated V1 to V3 in Table 1 below. According to this, the three batches V1 to V3 were identical with respect to their first component. With regard to the second component, the V1 to V2 batches each had a proportion of 5% by mass of the second component. However, the hollow spheres in the V1 batch were exclusively present in a grain size of 1 mm or less, while in the V2 batch they were present in a grain size of up to 1 mm and up to 2 mm, respectively. In the

V3 batch, the hollow spheres were present in a proportion of 8 % by mass and with a grain size of up to 1 mm and up to 2 mm.

Table 1

Component	Raw material	V1	V2	V3	V4	V5
First component	Sintered magnesia >3-5 mm	13	13	13	13	13
	Sintered magnesia >1-3 mm	27	27	27	27	27
	Sintered magnesia >0,1-1 mm	20	20	20	20	20
	Sintered magnesia >0-0,1 mm	24	24	24	24	24
Third component	Fused magnesia-spinel >0-5 mm	11	11	8	0	16
Second component	Hollow spheres of magnesia-spinel >1-2 mm	-	2	3.2	6.4	-
	Hollow spheres of magnesia-spinel >0,2-1 mm	5	3	4.8	9.6	-

All data on the proportion of components in Table 1 are given in % by mass.

Batches V4 and V5 are examples of batches not according to the invention. Batch V4 comprises hollow spheres, but in a proportion above 10 % by mass, namely, in a proportion of 16 % by mass. Batch V5 comprises the first component alone and thus no second component in the form of hollow spheres of magnesia spinel.

In order to have a similar chemical composition for all batches V1 to V5, different amounts of fused magnesia spinel having a chemical composition almost identical to the hollow spheres and a grain size of up to 5 mm were added as a third component to the batches. The third component was added into an extent so that all batches contained the sum of the second and third component in a proportion of 16% by mass.

According to an exemplary embodiment of a method according to the invention, the batches V1 to V3 were each mixed with a binder in the form of lignosulfonate in a proportion of 4 % by mass, based on the mass of the batch without the binder.

Subsequently, green bodies were pressed from the batches at a pressure of 140 MPa.

The pressed green bodies were then fired for a period of 5 hours at 1,600°C in a tunnel kiln.

After firing, exemplary embodiments of refractory ceramic products according to the invention made from the V1 to V3 batches have been provided.

Batch V4 not according to the invention was produced in the same way, and the batch V5 not according to the invention was fired in the same way to produce a refractory ceramic product.

As a result of the firing, the particles of the first and second components of the respective batches sintered together and formed a matrix of particles sintered together. The particles of the first component of the respective batches formed the first particles of the refractory ceramic product, and the particles of the second component formed the second particles of the refractory ceramic product. The material and grain size of the first component of the respective batches thereafter corresponded to the material and grain size of the first particles of the refractory ceramic product made therefrom. Accordingly, the material and grain size of the hollow spheres of magnesia spinel of the second component of the respective batch corresponded to the hollow spheres of magnesia spinel according to the second particles in the refractory ceramic product made therefrom. Table 2 below shows chemical and physical properties of the refractory ceramic products made from the V1 to V5 batches, respectively, where in Table 2 the V1 to V5 products are designated according to the batches from which they are made, respectively.

Table 2

	V1	V2	V3	V4	V5
Chemical composition					
MgO	86.9	86.7	86.1	84.1	86.9
Al ₂ O ₃	10.3	10.5	11.2	12.7	10.3
Fe ₂ O ₃	0.8	0.8	0.6	0.8	0.8
SiO ₂	1.4	0.7	0.8	1.0	0.7
CaO	0.6	1.3	1.3	1.4	1.3
Physical properties					
Density [g/cm ³]	2.86	2.87	2.83	2.74	2.95
Open porosity [Vol.-%]	18.4	18.7	19.7	22.1	16.2
CCS [MPa]	74	70	61	49	84
V-Modulus [MPa]	3212	2390	2603	2460	4690

CMoR [MPa]	5.2	4.3	4.3	4.1	6
Heat conductivity at 200°C [W/m·K]	4.62	4.76	5.82	4.23	6.50
Heat conductivity at 400°C [W/m·K]	3.93	4.45	5.02	3.62	5.66
Heat conductivity at 600°C [W/m·K]	3.67	4.09	4.53	3.39	5.42
Heat conductivity at 800°C [W/m·K]	3.64	3.93	4.40	3.33	5.16

The exemplary embodiments of refractory ceramic products according to V1 to V3 of Table 2 show a particularly low thermal conductivity at 800 °C of only 3.64, 3.93 and 4.40 W/m·K, respectively.

Despite this only low thermal conductivity, the products according to V1 to V3 simultaneously exhibit an excellent cold crushing strength of 74, 70 and 61 MPa, respectively.

Furthermore, despite the only very low density of 2.86, 2.87 and 2.83 g/cm³, respectively, the products according to V1 to V3 exhibit only a relatively low open porosity of 18.4, 18.7 and 19.7 % by volume, respectively.

Table 2 shows that even though product V4, due to its high proportion of hollow spheres of 16% by mass, also has a low thermal conductivity which is in the region of the thermal conductivity of the products V1 to V3, at the same time has a drastically reduced CCS, due to which this product is not usable for many applications.

The products V1 to V3 produced according to the exemplary embodiment can be excellently used for lining a cement rotary kiln for burning cement clinker.

Claims

1. A refractory ceramic product, comprising the following features:
 - 1.1 a matrix of particles sintered together;
 - 1.2 the particles sintered together comprise first particles and second particles;
 - 1.3 the first particles are particles based on magnesia;
 - 1.4 the second particles are hollow spheres of magnesia spinel;
 - 1.5 the proportion of the second particles is in the range from 1 to below 10% by mass, based on the total mass of the matrix.
2. The refractory ceramic product according to claim 1, wherein the hollow spheres have a diameter not above 3 mm.
3. The refractory ceramic product according to at least one of the preceding claims, wherein the hollow spheres have a diameter in the range from 100 μm to 3 mm.
4. The refractory ceramic product according to at least one of the preceding claims, wherein the hollow spheres have a chemical composition comprising the following oxides in the following mass proportions, each relative to the total mass of the hollow spheres:

MgO: 25 to 34% by mass;

Al₂O₃: 66 to 75% by mass.

5. The refractory ceramic product according to at least one of the preceding claims, wherein the hollow spheres have a bulk density in the range from 0.5 to 1.0 g/cm³, relative to the total mass of the hollow spheres.
6. The refractory ceramic product according to at least one of the preceding claims, wherein the particles sintered together comprise the first particles, the second particles and third particles, and wherein the third particles are particles based on at least one spinel-type material.
7. The refractory ceramic product according to claim 7, wherein the third particles are particles of at least one of the following spinel-type materials: magnesia spinel, magnesia spinel coated magnesia, hercynite or pleonaste.
8. The refractory ceramic product according to at least one of the preceding claims, having a proportion of the first particles that complements the proportion of the second particles and the third particles to 100% by mass, based on the total mass of the matrix.
9. The refractory ceramic product according to at least one of the preceding claims, wherein the matrix has a chemical composition comprising the following oxides in the following mass proportions, each relative to the total mass of the matrix:

MgO: 82 to 94% by mass;
Al₂O₃: 4 to 14% by mass;
further oxides: 0 to 6% by mass.
10. The refractory ceramic product according to at least one of the preceding claims, having a thermal conductivity at 800°C of less than 5.0 W/m·K.
11. Use of hollow spheres of magnesia spinel to reduce the thermal conductivity of a magnesia-based refractory ceramic product, wherein the hollow spheres of magnesia spinel are used with the proviso that the magnesia-based refractory ceramic product comprises a proportion of the hollow spheres of magnesia spinel in the range from 1 to

below 10% by mass, based on the total mass of the magnesia-based refractory ceramic product.

12. A batch for producing a refractory ceramic product, comprising the following features:
 - 12.1 a first component and a second component;
 - 12.2 the first component is at least one raw material based on magnesia;
 - 12.3 the second component are hollow spheres of magnesia spinel;
 - 12.4 the proportion of the second component is in the range from 1 to below 10% by mass, based on the total mass of the first and second component.
13. A method for producing a refractory ceramic product, comprising the following steps:
 - A. providing a batch according to claim 12;
 - B. firing the batch.
14. A kiln for producing cement clinker or lime, comprising the following features:
 - 14.1 the kiln comprises a lining of refractory products;
 - 14.2 the refractory products comprise refractory ceramic products according to at least one of claims 1 to 10.
15. A method for producing cement clinker or lime, comprising the following steps:
 - A. providing a kiln according to claim 14;
 - B. providing raw materials from which cement clinker or lime can be produced through firing;
 - C. firing the raw materials in the kiln.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/067417

A. CLASSIFICATION OF SUBJECT MATTER INV. C04B35/043 C04B35/64 C04B35/66 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C04B Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LIU ZHENYING ET AL: "Effect of hollow spheres on the properties of lightweight periclase-magnesium aluminate spinel refractories", INTERNATIONAL JOURNAL OF APPLIED CERAMIC TECHNOLOGY, vol. 20, no. 5, 10 May 2023 (2023-05-10), pages 3194-3205, XP093112372, US ISSN: 1546-542X, DOI: 10.1111/ijac.14409 the whole document -----	1 - 15
A	CN 115 611 614 A (ANHUI HAILUO SIAM REFRACTORY MAT CO LTD) 17 January 2023 (2023-01-17) examples; tables ----- - / - -	1 - 15
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 18 September 2024		Date of mailing of the international search report 26/09/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Munro, Brian

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/067417

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	<p>CN 113 443 898 A (MARVELS REFRACTORIES ANSHAN CO LTD) 28 September 2021 (2021-09-28) whole document - see examples, table & the claims</p> <p>-----</p>	1 - 15

INTERNATIONAL SEARCH REPORT

Information on patent family members

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CN 115611614	A	17-01-2023	NONE	

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