

A METHOD FOR PRODUCING OXIDE COMPOUNDS 03 NOV 1999**FIELD OF THE INVENTION**

The present invention relates generally to a method for the production of ceramic materials. More particularly, the invention relates to a method for producing ceramic materials
5 involving a low temperature heat treatment of powdered particles.

BACKGROUND OF THE INVENTION

Ceramic materials contain both metallic and non-metallic elements, e.g. oxygen and due to their wide range of mechanical and physical properties find application in pottery, bricks, tiles, cooking ware, glass, refractories, magnets, electrical devices, fibres and abrasives.

10 Spinel, mullite, and calcium aluminate cements are used to produce refractory materials that are widely used as linings in furnaces in steel, glass and other industries. Spinel, mullite and cordierite are mainly used to make refractory bricks and unshaped refractories, while calcium aluminates are commonly used as binders for refractory castables. Some of these oxide compounds are used in large quantities. For instance, China alone consumes about
15 1,500-2,000 tons of spinel and mullite respectively and about 2,000 - 3,000 tons of calcium aluminate cements every year. Several tens of thousand tons of these cements are consumed worldwide annually.

Synthesis of these high temperature ceramic materials are not only difficult but also energy consuming. Commercial oxide compounds are currently produced by either fusion or
20 sintering method, as briefly described below:

(a) Fusion method

In the fusion process, the following steps are carried out:

Raw materials → mixing → electric fusion → crushing (and grinding)

Raw materials of magnesia, calcia, alumina and bauxite are electrically fused at temperatures
25 above their melting temperatures ranging from 1800°C to 2200°C. Bulk spinels, mullite and

calcium aluminate cements can be fabricated only after the fusion process. Since spinels, mullite and calcium aluminate cements are to be used in the powder form, crushing and grinding have to be performed to turn them into powders. Several steps of crushing and grinding are taken to obtain different size of powder particles. In general, powder particles
5 of micron size are obtainable only with this method.

High temperature fusion and later crushing and grinding not only consume a large amount of energy but also pollute the environment.

(b) Sintering method:

In the sintering process, the following procedures are generally carried out:

Raw materials (crushing and grinding) → mixing → compaction → sintering
(1600~1950°C) → crushing (and grinding)

The powder mixture is firstly mixed according to its chemical ratio. Compaction of the mixed powder into small pellets is performed to obtain mechanical bonding from interdiffusion among the different powder particles. After compaction, the pellets are further sintered between 1600 to 1950°C. Diffusion between different constitutions takes place, giving rise to the desired compounds during high temperature sintering. Since the powder is sintered in a compact form, the diffusion process causes diffusion bonding between the particles, resulting in the formation of bulk materials after sintering. To get back to the powder form, the sintered bulk material must undergo crushing and grinding process again.

20 The fusion and sintering methods described above are carried out at high temperatures (about 1600°-2200°C) and consume large amount of energy and, inevitably, bring about severe problems in air pollution. In addition, since the fused bulk materials and sintered pellets are hard and strong, usually, the life of the grinding mills is significantly shortened due to severe wear and tear. Contamination of the processed materials often takes place due
25 to the material worn off the crushing machines and grinding mills.

Accordingly, there exists a need for methods, with reduced energy requirements, for producing ceramic materials such as those which may be suitable for use as refractory materials.

DESCRIPTION OF THE FIGURES

Figure 1 shows the X-ray diffraction spectra of the mixtures after milling for different durations and annealing alumina and magnesium hydroxide at 1100°C for 1 hour.

Figure 2 shows the X-ray diffraction patterns of the mixtures after different milling durations
5 and annealing alumina and clay at 1300°C for 3 hours.

Figure 3 shows the X-ray diffraction patterns of the mixtures after milling for different durations and annealing calcium hydroxide and alumina at 1100°C for 1 hour.

DISCLOSURE OF THE INVENTION

Throughout this specification and the claims which follow, unless the context requires
10 otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The ceramic materials of particular relevance to the present invention are "mixed metal
oxides" which contain at least two different metal atoms, or metal atoms of differing valency,
15 and oxygen. These materials may find use as refractory materials for use in linings for furnaces in the steel, glass and other industries, or as binders or cements for refractory castables, or as fuel elements in nuclear reactors, and may be referred to as refractory oxides.

The present inventors have now found that a mixture of the precursor components in powdered or milled form can be subjected to a heat or annealing treatment at temperatures
20 lower than those previously used to fuse or sinter the components. Advantageously, this method may allow for the production of powdered ceramic materials which eliminates or reduces the need for further crushing or grinding following heat treatment.

Accordingly, the present invention provides a method of producing a ceramic material, which method comprises subjecting a mixture of milled precursor components to a heat treatment of
25 less than about 1600°C for a time and under conditions sufficient to form said ceramic material.

One type of ceramic material contemplated by the method of the invention are the class of

- materials referred to as spinels. Spinel-type materials have the general stoichiometric formula of AB_2O_4 wherein A represents a divalent metal ion such as Mg^{2+} , Fe^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} or Ni^{2+} and B represents a trivalent metal ion such as Al^{3+} , Fe^{3+} , Cr^{3+} , Ga^{3+} , Co^{3+} and Mn^{3+} . Classic spinel has the formula $MgOAl_2O_3$, however other spinels of the formula AB_2O_4 include gahnite [$ZnOAl_2O_3$], pleonaste [(Mg, Fe) Al_2O_3], picotite [(Mg, Fe) O ($AlCr_2$) O_3], chromite [$FeOCr_2O_3$], hercynite [$FeOAl_2O_3$] and magnetite [$FeOFe_2O_3$]. A preferred spinel is $MgOAl_2O_3$. It is to be understood that the ceramic material, whilst consisting substantially of the stoichiometric spinel, may also be enriched in one or other of the precursor components, for example Al_2O_3 - rich spinel or MgO-rich spinel.
- Other ceramic materials include: mullites ($3Al_2O_3 \cdot 2SiO_2$), including stoichiometric and Al_2O_3 -rich; cordierites [(Mg, Fe) $_2 Al_4Si_5O_{18}$]; olivines including ($2FeOSiO_2$) and forsterite ($2MgOSiO_2$); zircon ($ZrO_2 \cdot SiO_2$), wollastonite ($CaSiO_3$), beryl ($Be_3Al_2Si_6O_{18}$), enstatite ($MgSiO_3$) and calcium aluminates including $CaAl_2O_4$, $CaAl_4O_7$, $Ca_{12}Al_{14}O_{33}$. Non-stoichiometric ceramic materials may be prepared by enriching the precursor component mixture in one or the other of the precursor components. Mixtures of any two or more compounds are also contemplated. Other types of ceramic oxide materials which may be prepared by the methods of the invention will be apparent to the skilled person.

The precursor components of the mixed metal ceramic material are subjected to mechanical attrition i.e., milling, prior to subjecting to the heat (firing) treatment. The milled precursor components are in powder form and typically have a particle size in the range of about 100 nm to about 5 μm , for example, about 100 nm to about 3 μm . Typically the powdered precursors may be intimately mixed, for example in a blender, before milling although it will be recognised that the individual components may be separately milled and then mixed prior to firing. Mechanical milling or attrition of the precursor components is preferably carried out by high energy milling, such as in a high energy planetary ball mill or horizontal ball mill.

In a ball mill, the weight ratio of ball to precursor powder may be from about 5:1 to about 50:1, preferably about 10:1 to about 40:1, typically about 20:1 for a planetary ball mill. The ball size may range from about 10 to 25 mm diameter, for example 15-20 mm however, larger or smaller balls and other ball: powder ratios may also be used to achieve particulate size. These may be determined by routine testing. Al_2O_3 or ZrO_2 vials may be used to avoid contamination by iron from use of iron vials.

Typically, the duration of milling is sufficient to result in substantial formation of the desired

ceramic material following subsequent annealing. The duration of milling may be carried out for a period of between about 30 minutes and 30 hours, preferably for between 1 hour and 10 hours, for example about 2-5 hours.

Optionally, to obtain a further smaller particle size, the milled precursors can be further ball
5 milled by wet or dry milling at low milling energy.

The milled precursor mixture may optionally be compacted into the desired shape or form such as bricks, tiles or sheets prior to annealing treatment. Compaction may be effected under pressures of about 200 to about 1000MPa. The presence of a binder is optional.

The reduced temperature heat treatment comprises annealing or firing of the milled precursor
10 mixture at temperatures below those commonly used in sintering and fusion processes, i.e., less than 1600°C, e.g., less than about 1500°C, preferably in the range of about 800 to about 1400°C, for example at about 1000 to about 1300°C. The skilled addressee will recognise that the duration of the annealing treatment will vary with the temperature employed and with the degree of milling the precursor powder components were subjected to, for example, longer
15 periods of mechanical attrition, resulting in reduced powder particle size, may reduce the time and temperature of the annealing treatment. Typically annealing may be carried out for a duration of about 30 minutes to about 20 hours such as about 1 to about 5 hours depending on the annealing temperature and the extent of prior milling or particle size of the precursor components. The duration and temperature of firing may also depend on the source of
20 precursor compounds and the skilled addressee will be readily able to determine suitable conditions through routine testing. Optionally the annealing process may be carried out in an oxidizing atmosphere. The skilled person will also recognise which precursor components may be used in the production of the desired ceramic material. Suitable precursors include natural raw materials such as bauxite (containing $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and natural
25 clays, for example kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and montmorillonite ($\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_2$). Other precursor components include common industrial raw materials such as alumina (Al_2O_3), magnesium hydroxide ($\text{Mg}(\text{OH})_2$), and calcium hydroxide ($\text{Ca}(\text{OH})_2$). The skilled person will recognise that other metal-oxygen containing precursors may be employed such as hydroxides, carbonates and oxides of suitable metals.

30 Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood

that the invention includes all such variations and modifications which fall within the spirit and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

- 5 The invention will now be described with reference to the following non-limiting examples which are illustrative of the invention and are not intended to supercede the generality of the above description.

EXAMPLES

Example 1.

10 Synthesis of spinel

- Alumina and magnesium hydroxide in a ratio of 1:1 in powder form were used as raw materials. The raw materials were stoichiometrically mixed in a V-blender for one hour and milled in a Fritsch 5 planetary mill. The ball to powder weight ratio was 20:1, and the rotational speed of the sun-disk was 250 rpm. The rotational ratio of the vial to the sun-disk is 2.17. Mechanical ball milling was carried out in air atmosphere for 1 to 5 hours. After mechanical ball milling, the milled powder was annealed in an electric heating furnace at 1100°C in air for different durations. For comparison purposes, mixtures of powders with the same composition but without milling were compacted at 400 MPa. After compaction, the compacts were annealed in the same manner as the mechanically ball milled powder.
- 15 is 2.17. Mechanical ball milling was carried out in air atmosphere for 1 to 5 hours. After mechanical ball milling, the milled powder was annealed in an electric heating furnace at 1100°C in air for different durations. For comparison purposes, mixtures of powders with the same composition but without milling were compacted at 400 MPa. After compaction, the compacts were annealed in the same manner as the mechanically ball milled powder.
- 20 Phase compositions of the annealed mixtures were studied with a Shimadzu Lab XRD-6000 X-ray diffractometer.

- Figure 1 shows the X-ray diffraction spectra of the mixtures after milling for different durations and annealing of alumina and magnesium hydroxide at 1100°C for 1 hour. It can be seen that for powder mixture without milling, after annealing only a very small amount of spinel has been formed, while the mixture after 1 hour of milling and followed by annealing composes mainly of spinel and little unreacted MgO and Al₂O₃. Residual MgO and Al₂O₃ in the annealed mixtures decrease with increase in milling time and completely disappear after milling for 5 hours. With longer mechanical attrition, the
- 25 amount of spinel has been formed, while the mixture after 1 hour of milling and followed by annealing composes mainly of spinel and little unreacted MgO and Al₂O₃. Residual MgO and Al₂O₃ in the annealed mixtures decrease with increase in milling time and completely disappear after milling for 5 hours. With longer mechanical attrition, the

system could be achieved with lower annealing temperature and/or shorter annealing time.

Example 2.

Synthesis of mullite

- 5 The raw materials for synthesis of mullite were a 1:1 ratio of natural clay and alumina. The synthesis processing is the same as described in Example 1. Figure 2 shows the X-ray diffraction patterns of the mixtures after different milling durations and annealing of alumina and clay at 1300°C for 3 hours. For the mixture without milling, although visible amount of mullite is formed in the annealed mixture, a large amount of Al_2O_3 and SiO_2 still remains
- 10 unreacted. When the mixture is milled for 1 hour followed by annealing at 1300°C for 3 hours, little residual Al_2O_3 and SiO_2 was detected. The annealed powder consists mainly of mullite. Residual Al_2O_3 and SiO_2 in the annealed mixtures decrease with increase in milling duration and disappear after milling for 5 hours.

Example 3.

- 15 Synthesis of calcium aluminates

Calcium aluminate (CaAl_2O_4) was produced with a 1:1 ratio of alumina and calcium hydroxide as raw materials. The synthesis process is the same as described in Example 1. Figure 3 shows the X-ray diffraction patterns of the mixtures after milling for different durations and annealing calcium hydroxide and alumina at 1100°C for 1 hour. For the un-

20 milled powder mixture, after annealing, only a small quantity of CaAl_2O_4 has been formed. Large amount of Al_2O_3 and CaO still exists. The mixture after 2 hours of milling and followed by annealing composes mainly of CaAl_2O_4 with very little unreacted CaO and Al_2O_3 . Both CaO and Al_2O_3 are not detected in the mixtures after milling for 5 hours and annealing at 1100°C for 1 hour.



CLAIMS:

1. A method of producing a ceramic material, which method comprises subjecting a mixture of milled precursor components to a heat treatment of less than about 1600°C for a time and under conditions sufficient to form said ceramic material.
2. A method according to claim 1 further comprising prior subjecting the precursor components to high energy milling.
3. A method according to claim 1 wherein the precursor components are milled together as a mixture of components.
4. A method according to claim 2 or 3 wherein the precursor components are milled for a duration of about 30 minutes to about 30 hours, such as between about 1 to about 5 hours.
5. A method according to claim 2 or 3 wherein the milling is carried out in a high energy ball mill or horizontal ball mill.
6. A method according to claim 5 wherein the weight ratio of ball to precursor components is about 5:1 to about 50:1, preferably about 10:1 to 40:1.
7. A method of producing a ceramic material, which method comprises subjecting a mixture of precursor components having a particle size in the range of about 100 nm to about 5 μ m to a heat treatment of less than about 1600°C for a time and under conditions sufficient to form said ceramic material.
8. A method according to claim 1 or claim 7 wherein the heat treatment is carried out at a temperature of between about 800°-1400°C, preferably about 1000°C to about 1300°.
9. A method according to claim 1 or claim 7 wherein the heat treatment is carried out in an oxidizing atmosphere.
10. A method according to claim 1 or claim 7 wherein the ceramic material is a spinel,

such as classic spinel, mullite, cordierite, forsterite or a calcium aluminate, such as CaAl_2O_4 , CaAl_4O_7 or $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$.

11. A method according to claim 1 or claim 7 wherein the milled precursor mixture is compacted into a desired shape or form prior to heat treatment.
12. A method according to claim 1 or claim 7 further comprising crushing or grinding the ceramic material resulting from heat treatment.

