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(54) **Titre** : METHODE D'OBTENTION DE CERAMIQUES FAITES D'OXYDES ET DE MATERIAUX MIXTES, PARTICULIEREMENT DESTINEES A LA FABRICATION DE MATRICES POUR DES PRODUITS HETEROGENES DE CERAMIQUE
(54) **Title**: A METHOD FOR PREPARING CERAMIC MIXED-OXIDE MATERIALS, PARTICULARLY INTENDED TO BE USED AS MATRIX MATERIAL IN COMPOSITE CERAMIC PRODUCTS

(57) **Abrégé/Abstract**:

The invention refers to a method for preparing ceramic mixed oxide materials, particularly intended to be used as matrix material in composite ceramic products, by mixing and co-milling of a metal and a ceramic oxide material and subsequent reaction-sintering in an oxidizing atmosphere. For obtaining an improved homogeneity between metal and oxide materials, the invention suggests that the metal is used in the form of an alloy with an element which is to be present in the final mixed-oxide material.

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(57) Abstract

The invention refers to a method for preparing ceramic mixed oxide materials, particularly intended to be used as matrix material in composite ceramic products, by mixing and co-milling of a metal and a ceramic oxide material and subsequent reaction-sintering in an oxidizing atmosphere. For obtaining an improved homogeneity between metal and oxide materials, the invention suggests that the metal is used in the form of an alloy with an element which is to be present in the final mixed-oxide material.

A method for preparing ceramic mixed-oxide materials, particularly intended to be used as matrix material in composite ceramic products.

The present invention refers to a method for preparing ceramic mixed-oxide materials, particularly intended to be used as matrix material in composite ceramic products, by mixing and co-milling of a metal and a ceramic oxide material and subsequent reaction-sintering in an oxidizing atmosphere.

In the preparation of ceramic oxide materials of the kind referred to by mixing and co-milling of a metal and a ceramic oxide material and subsequent reaction-sintering it has always been desirable to use the metal in a particulate form with as small particle size as ever possible. Therefore, in many cases it has been attempted to use milled aluminium of flake shape. A disadvantage has been, however, that said flakes smear and adhere to the milling bodies due to the softness of the metal and hence also mostly remain in flake shape. See e.g. Nils Claussen et al. "Low-shrinkage Reaction-Bonded Alumina", J. Europ. Ceram. Soc., 5, 1989, pages 29-35. It might also be referred to other articles of and with Nils Claussen and his research group such as "Tailoring of Reaction-Bonded Al_2O_3 Ceramics", Ceram. Eng. Sci. Proc., 11, pages 806-820, 1990.

Another way to achieve a better homogeneity between metal and oxide materials in the present connection has been suggested e.g. by the US firm Lanxide Corp., Newark, Del., USA and implies that an oxidation of the metal is carried out in melted form. See "Formation of Lanxide ceramic composite materials", J. Mater. Res., 1, 1986, pages 81-89. Furthermore it is to be referred to the

Swedish patent No. 8103269-0 which refers to a method in preparing shapes of silicon nitride based materials.

Summary of the invention

Since it thus is the fine-civision of the metal which in most cases constitutes the step which is difficult to surmount for achieving the goals aimed at, the present invention now suggests a different way of overcoming the difficulties and the feature essentially distinguishing the present invention is that the metal is used in the form of an alloy with an element which is to be present in the final oxide material.

In accordance with the present invention, that object is achieved with a method for preparing a ceramic mixed-oxide of at least two metals, the method comprising the steps of:

mixing an alloy including a metal selected from the group consisting of aluminum, calcium, lithium, magnesium, titanium, and yttrium, the alloy also including an element that is to be present in the ceramic mixed-oxide, the element being different from the metal and is selected from the group consisting of aluminum, silicon, and titanium, with a ceramic oxide that includes a metal that is to be present in the ceramic mixed oxide;

co-milling the alloy and ceramic oxide; and

reaction-sintering the mixed and co-milled alloy and ceramic oxide, thereby oxidizing the metal and element of the alloy to produce the ceramic mixed-oxide.

Preferably, this element is selected such that the alloy is brittle. In this connection it is a particular advantage of the invention when the element with which the metal is to be alloyed, is selected such that the alloy obtained becomes brittle so as to facilitate the milling. The subsequent reaction-sintering furthermore can be improved by adding a catalyst metal to the alloy.

Description of preferred embodiments

Thus the basic idea of the present invention is to mill, together with a suitable oxide compound, a brittle metal alloy into fine particle sizes. In the subsequent reaction-sintering the metal then is oxidized to its corresponding ceramic composition.

As examples thereof it can be referred to a test with an Al:Si-alloy (88:12), which together with Al_2O_3 was successfully milled to fine-size particles. Dry-pressed bodies of this composition were oxidized and it turned out that all of the Si together with a portion of Al formed mullite. Furthermore, this occurs already at a temperature below 1400°C in air atmosphere.

Other ceramic materials which can be manufactured according to the same principles are Al_2TiO_5, $3Y_2O_3 \cdot 5Al_2O_3$ (YAG), $Mg_2Al_4Si_5O_{18}$ (coerdirite), $MgAl_2O_4$ (spinel), $LiAlSi_2O_6$ (β-spodumene) and $CaZrO_3$ (T_m>2300°C).

By the invention it might thus be achieved that the milling of a pulverulent metal alloy with predetermined brittleness provides particles of sub-micron size (< 1μm). This provides for a really homogenous distribution of the metals in the alloy and hence reduces the temperature of the transformation to the corresponding ceramic composition. The homogenous distribution furthermore promotes this transformation. Moreover, when preparing an alloy powder having an added catalyst metal the reactivity might be further increased, e.g. by adding Mg to Al:Si. It also becomes possible to select the alloy such that an exactly correct ceramic composition is obtained. Owing to said correct ceramic composition the shrinkage during the oxidization also might be controlled and minimized. Should the metal be made still more brittle so as to promote the milling thereof a gas-atomized alloy powder may be produced having a certain quantity of added ceramic powder.

Example 1

Preparation of mullite

Two powder mixtures were prepared. One of them (reference AlSi) consisted of 30% by weight of Al:Si-alloy, weight ratio 88:12, (Johnson Matthey, <44 μm), 69% by weight of Al_2O_3 (Alcoa, A152SG, BET = 3,2 m^2/g) and 1% by weight of Mg (Merck, <1 mm), as auxiliary oxidization agent. The other (reference AlSi-ZrO_2) consisted of 30% by weight of Al:Si, 49% by weight of Al_2O_3, 20% by weight of ZrO_2 and 1% by weight of Mg. ZrO_2 was added as oxygen-diffusion-increasing agent. The two mixtures were milled in a ball mill with Si_3N_4-balls in an organic solvent to which was added dispersing and pressing agents. After milling the specific surface (BET) of AlSi had increased from 5,9 m^2/g to 10,0 m^2/g and for AlSi-ZrO_2 from 6,5 m^2/g to 10,5 m^2/g and studies in a scanning-electron microscope disclose that the alloys were milled into sub-micron particles. The organic solvent was removed in a thin-film evaporator and after that the mixtures were screen-granulated. The powder mixtures were subjected to cold isostatic pressing at 300 MPa to form green bodies with green densities of 71% of the theoretic density.

Oxidation tests were carried out in a thermo-gravimetric analyzing equipment (TGA). At 1400°C all Si with

2140259

a portion of Al had been oxidized to mullite ($Al_6Si_2O_{13}$), as proved by X-ray analyses and the density of said samples amounted to 84% of the theoretic value (valid for both AlSi and AlSi-ZrO_2). In AlSi-ZrO_2-samples ZrO_2 reacted with Si and was oxidized to $ZrSiO_4$ in the temperature range between 1100 and 1300°C, after which $ZrSiO_4$ reacted with Al_2O_3 so as to form mullite at 1400°C. The results also showed that in tests with ZrO_2-addition the oxidation rate of the alloy increased deeper in the inner of the body.

Example 2

Y_2Al (Alfa Products) was melted and spray-atomized. The powder obtained was weighed together with Al_2O_3 (Alcoa, A165G) in required quantities. The mixture was milled in a mill grinder with Al_2O_3-balls in an organic solvent with added dispersing and pressing agent. Studies in scanning-electron microscope showed that the alloy had been milled to sub-micron particles. The organic solvent was removed by means of a thin-film evaporator and after that the mixture was screen-granulated. The powder mixture was subjected to cold isostatic pressing at 300 MPa to form test bodies.

Oxidation tests were made in a thermo-gravimetric analyzing equipment (TGA) at 1400-1700°C. The resulting material consisted of yttrium-aluminium garnet (YAG), which was identified by means of X-ray diffraction.

Example 3

Ti_2Al-powder (Alfa Products) was weighed together with Al_2O_3 (Alcoa, A165G) in required quantities. The mixture was milled in a ball mill with Al_2O_3-balls in an organic solvent with added dispersing and pressing agents. Studies in scanning-electron microscope disclosed that the alloy had been milled to sub-micron particles. The organic solvent was removed by means of a thin-film evaporator and after that the mixture was screen-granulated. The powder mixture was subjected to cold isostatic pressing at 300 MPa to form green bodies.

Oxidation tests were carried out in a thermogravimetric analyzing equipment (TGA) at 1400-1500°C. The resulting material consisted of aluminium titanate (Al_2TiO_5), which was identified by means of X-ray diffraction.

CLAIMS

1. A method for preparing a ceramic mixed-oxide of at least two metals, said method comprising the steps of:

mixing an alloy including a metal selected from the group consisting of aluminum, calcium, lithium, magnesium, titanium, and yttrium, said alloy also including an element that is to be present in said ceramic mixed-oxide, said element being different from said metal and is selected from the group consisting of aluminum, silicon, and titanium, with a ceramic oxide that includes a metal that is to be present in said ceramic mixed oxide;

co-milling said alloy and ceramic oxide; and

reaction-sintering said mixed and co-milled alloy and ceramic oxide, thereby oxidizing said metal and element of said alloy to produce said ceramic mixed-oxide.

2. A method according to claim 1, wherein said ceramic mixed oxide is selected from the group consisting of mullite, yttrium aluminum garnet, aluminum titanate, spinel, coerdirite, and β-spodumene.

3. A method according to claim 1, wherein said metal in said ceramic oxide is selected from the group consisting of aluminum, silicon, and zirconium.

4. A method according to any one of claims 1 to 3, wherein said element is selected such that the alloy is brittle, thereby facilitating said co-milling.

5. A method according to any one of claims 1 to 4, further comprising the step of:

adding a catalyst metal to said alloy.

6. A method according to claim 5, wherein said catalyst metal is magnesium.

7. A method according to any one of claims 1 to 6, wherein a starting composition ratio of said metal and element in said alloy is selected to match exactly a final composition ratio of said metal and element in said ceramic mixed oxide.

8. A method according to claim 1, wherein said alloy is selected from the group consisting of alloys of aluminum and silicon, yttrium and aluminum, and titanium and aluminum.

9. A method according to claim 8, wherein said aluminum and silicon are present in said alloy in a ratio of 88 percent aluminum to 12 percent silicon.

10. A method according to claim 1, wherein said ceramic oxide is selected from the group consisting of Al_2O_3 and ZrO_2.

11. A method according to claim 1, wherein said ceramic mixed oxide is selected from the group consisting of Al_2TiO_5, $3Y_3O_35Al_2O_3$, $MgAl_2O_4$, $Mg_2Al_4Si_5O_{18}$, $LiAlSi_2O_6$, and $CaZrO_3$.

12. A method according to claim 1, wherein said alloy and ceramic oxide are milled to particles of submicron size.