



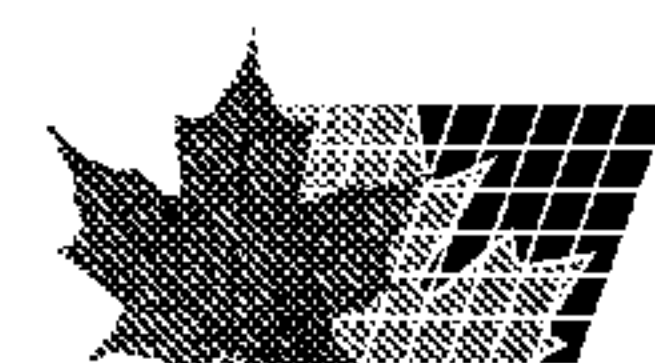
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(54) Titre : PROCEDE DE FABRICATION D'UN MATERIAU COMPOSITE CERAMIQUE
(54) Title: A METHOD FOR MANUFACTURING A CERAMIC COMPOSITE MATERIAL

(57) **Abrégé/Abstract:**

The invention refers to a method of manufacturing a ceramic composite material comprising matrix and reinforcing materials and an intermediate weak interface material, said composite material being particularly intended for use at temperatures above 1400 °C and in oxidizing environment, the matrix and reinforcing materials consisting of the same or different ceramic oxides having a melting point above 1600 °C, and the interface material providing in combination with said materials a stress field liable to micro-cracking. The invention now suggests that the reinforcing fibre material is immersed into a powder slurry containing carbon (C) and ZrO₂ so as to be coated thereby and then dried, after which the composite material is subjected to green forming and densification steps as known per se, and finally a heat-treatment in air leaving a porous structure of the interface material.



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(54) Title: A METHOD FOR MANUFACTURING A CERAMIC COMPOSITE MATERIAL (57) Abstract The invention refers to a method of manufacturing a ceramic composite material comprising matrix and reinforcing materials and an intermediate weak interface material, said composite material being particularly intended for use at temperatures above 1400 °C and in oxidizing environment, the matrix and reinforcing materials consisting of the same or different ceramic oxides having a melting point above 1600 °C, and the interface material providing in combination with said materials a stress field liable to micro-cracking. The invention now suggests that the reinforcing fibre material is immersed into a powder slurry containing carbon (C) and ZrO₂ so as to be coated thereby and then dried, after which the composite material is subjected to green forming and densification steps as known per se, and finally a heat-treatment in air leaving a porous structure of the interface material.		

A method for manufacturing a ceramic composite material

The present invention refers to a method of manufacturing
5 a ceramic composite material comprising matrix and reinforcing
materials and an intermediate weak interface material, said
composite material being particularly intended for use at tem-
peratures above 1400°C and in an oxidizing environment, the ma-
trix and reinforcing materials consisting of the same or dif-
10 ferent ceramic oxides having a melting point above 1600°C, and
the interface material providing in combination with said mate-
rials a stress field liable to micro-cracking.

For obtaining an intentional cracking behaviour of such
ceramic composites various suggestions have been made, for in-
15 stance according to WO 93/22258 to the Applicant. In practice,
however, it has turned out that an interface layer of ZrO_2 pro-
vides a bonding which mostly is too strong. On the other hand,
carbon provides a suitably weak bonding between the reinforcing
material and the matrix but degrades the fibre material. Over
20 ZrO_2 , also HfO_2 , fulfils the requirements as to a weak interface
zone but in many connections a still weaker interface is desir-
able.

Therefore, the main object of the present invention is to
suggest a method by which an even weaker interface is obtained.
25 In one aspect of the invention, the reinforcing fibre material
is immersed into a powder slurry containing carbon and ZrO_2 so
as to be coated thereby and then dried, after which the compos-
ite material is subjected to green forming and densification
steps as known per se, and finally a heat-treatment in air
30 leaving a porous structure of the interface material. In an-
other aspect of the invention, the reinforcing fibre material
is immersed into and coated with a first powder slurry contain-

ing ZrO_2 and then dried and immersed into and coated with a second powder slurry containing carbon and dried, after which the composite material is subjected to green forming and densification steps as known per se, and finally a heat-treatment in
5 air leaving a gap between the reinforcing material and the matrix. It is advantageous to use a powder slurry technique, in which thus rather great particles are used which create a stable porous layer when a coating is used including C/ZrO_2 .

By the present invention it is thus possible to obtain a
10 weak interface securing the necessary crack deflection and fibre pullout behaviour during fracture of the composite.

The coating formed on fibres of which the reinforcing material consist and which are immersed in the slurry has proved to be adherent and strong enough to survive green forming and
15 densification processes. After densification the C is removed by heat treatment in air, leaving a gap or porosity in the oxide interface. The volume fraction of C can be varied to achieve the desired interface strength. The interface made by this invention is stable at high temperatures for long times
20 because the pores have got the right size, i.a. are large enough.

According to the further aspect of the invention, there is provided, however, another way to obtain an interface weak enough, namely to add a fugitive layer. In this method, the re-
25 inforcement is first immersed in a C powder slurry, dried and then immersed in an oxide (ZrO_2) powder slurry, forming a double or sequential coating. Again, this coating is strong and adherent enough to survive green forming and densification. After densification the C is removed by heat treatment leaving a
30 gap between the reinforcing material and the oxide interface. Surface roughness of the reinforcing and matrix materials is sufficient to give load transfer between reinforcing material

and matrix material. The absence of bonding between the oxide interface and the reinforcing material will ensure effective crack deflection. The degree of load transfer and frictional sliding resistance between reinforcing material and matrix controlling the fibre pullout behaviour can be varied by varying the thickness of the fugitive C layer.

The presence of an oxide interface will prevent a possible carbothermal reduction of the surface of the reinforcing fibre material of single crystal Al_2O_3 fibres (to Al_4C_3) which would degrade the mechanical properties by defects created. The presence of oxide interface (especially in the case of a C/ ZrO_2 mixture) will locally raise the partial pressure of oxygen and thus prevent the carbothermal reduction to take place.

Example 1

Single crystal fibres of Al_2O_3 (from Saphikon Inc., USA) were covered with a thin layer of C/ ZrO_2 mixture. This was made by immersing the fibres in a slurry of C/ ZrO_2 -powder in water. The volume proportions of C to ZrO_2 was 1/1. After drying the coated fibres were stacked to a fibre preform in a plaster mould. A Al_2O_3 powder slurry was poured thereon and a pressure gradient was applied to give good infiltration of the fibre preform.

After drying the green bodies were sintered by hot-pressing at 1400°C , 10 MPa for 70 minutes. The C was burnt out by heat treatment at 1250°C for 10 hours leaving a porous ZrO_2 layer. After sintering and heat treatment the porous ZrO_2 was about 3 μm thick. The porous ZrO_2 layer provided crack deflection and fibre pullout which was proved by bending tests. Furthermore, the porous ZrO_2 layer was stable at 1400°C for 1000 hours and still provided crack deflection and fibre pullout after this heat treatment which was proved by bending tests.

Example 2

Example 1 was repeated however using HfO_2 instead of ZrO_2 .

Example 3

5 Single crystal fibres of Al_2O_3 (from Saphikon Inc., USA) were covered with a thin double layer of C and ZrO_2 . This was made by first immersing the fibres in a slurry of ZrO_2 -powder in water and then immersing the fibres in a slurry of C-powder in water. After drying the coated fibres were stacked to a
10 fibre preform in a plaster mould. An Al_2O_3 powder slurry was poured thereon and a pressure gradient was applied to give good infiltration of the fibre preform.

After drying the green bodies were sintered by hot-pressing at 1400°C , at 10 MPa for 70 minutes. The C was burnt
15 out by heat treatment at 1250°C for 10 hours leaving a gap of about 1 μm between the zirconia layer and the Al_2O_3 matrix. After sintering and heat treatment the ZrO_2 layer was about 3 μm of thickness and not bonded to the matrix. The gap between fibre and ZrO_2 layer provided crack deflection and fibre pullout
20 which was proved by bending tests. (Furthermore, the ZrO_2 layer was stable at 1400°C for 1000 hours and still provided crack deflection and fibre pullout after this heat treatment which was proved by bending tests.)

Example 4

25 Example 3 was repeated however using HfO_2 instead of ZrO_2 .

Example 5

Example 3 was repeated, however with the steps in slightly reversed order, i.e. by first immersing the fibres in a slurry of C-powder in water and then in a slurry of ZrO_2 -
30 powder, with similar advantageous result.

CLAIMS

1. A method of manufacturing a ceramic composite material comprising matrix and reinforcing materials and an intermediate weak interface material, said composite material being for use at temperatures above 1400°C and in oxidizing environment, the matrix and reinforcing materials consisting of the same or different ceramic oxides having a melting point above 1600°C, and the interface material providing in combination with said materials a stress field liable to microcracking, characterized in that a reinforcing fibre material is immersed into a powder slurry containing carbon (C) and ZrO₂ so as to be coated thereby and then dried, after which the resulting composite material is subjected to green forming and densification steps, and finally a heat-treatment in air leaving a porous structure of the interface material.

2. A method of manufacturing a ceramic composite material comprising matrix and reinforcing materials and an intermediate weak interface material, said composite material being for use of temperatures above 1400°C and in oxidising environment, the matrix and reinforcing materials consisting of the same or different ceramic oxides having a melting point above 1600°C, and the interface material providing in combination with said materials a stress field liable to microcracking, characterized in that a reinforcing fibre material is immersed into and coated with a first powder slurry containing ZrO₂ and then dried and immersed into and coated

with a second powder slurry containing carbon and dried, after which the resulting composite material is subjected to green forming and densification steps, and finally a heat-treatment in air leaving a gap between the reinforcing material and the matrix.

3. A method according to claim 2, characterized in that the reinforcing material, after having been covered with carbon is again immersed into the first slurry so as to be provided with an outermost ZrO_2 coating.