EUROPEAN PATENT SPECIFICATION

Date of publication of patent specification: 11.11.92

Application number: 87630185.4

Date of filing: 10.09.87

Production of ceramic articles incorporating porous filler material.

Priority: 16.09.86 US 907939

Date of publication of application:
23.03.88 Bulletin 88/12

Publication of the grant of the patent:
11.11.92 Bulletin 92/46

Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

References cited:
EP-A- 0 193 292

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Description

This invention relates to the production of ceramic articles comprising oxidation reaction products as hereinafter defined. More particularly, it relates to methods of making such articles by oxidation reaction of a parent metal with a vapor-phase oxidant, thereby to form a ceramic matrix incorporating the porous filler, and to products of such methods.

There is substantial current commercial interest in the use of ceramic materials for a wide variety of industrial, mechanical, electrical, and structural components, owing to the advantageous attributes of these materials such as their hardness, ability to withstand high temperatures, chemical inertness, beneficial properties for electrical applications, and relatively light weight. Ceramics provide attractive alternatives to metals for many existing purposes, as well as enabling the development of diverse new types of components for which metals or other materials are unsuitable.

The production of ceramic components for technologically advanced applications is nevertheless attended with problems. Conventional ceramic-making methods have disadvantages including the high cost of sinterable powders, lack of batch-to-batch reproducibility of powder properties, substantial shrinkage on sintering, and susceptibility to retention of flaws produced by the forming procedure.

It is known to produce ceramics which are oxidation reaction products, viz. by reacting a precursor metal with an oxidant. As used herein, the term "oxidation reaction product" means one or more metals in any oxidized state wherein a metal (hereinafter "parent metal") has given up electrons to or shared electrons with another element, compound, or combination thereof (hereinafter "oxidant"). Accordingly, an "oxidation reaction product" under this definition includes the product of the reaction of one or more parent metals with an oxidant such as oxygen, nitrogen, halogen, sulphur, phosphorus, arsenic, carbon, boron, selenium, tellurium and compounds and combinations thereof, for example, methane, ethane, propane, acetylene, ethylene, propylene (as sources for carbon), and mixtures such as air, H₂/H₂O and CO/CO₂.

Examples of suitable parent metals include, without limitation, aluminum, zirconium, titanium, silicon, zinc, hafnium, and tin.

Commonly owned EP-A-0 155 831 describes a process for producing ceramic materials by oxidation reaction of a molten parent metal with a vapor phase oxidant, wherein the parent metal is heated to a temperature within a particular range (throughout which the parent metal is molten, but below the melting point of the oxidation reaction product) in the presence of an atmosphere comprising or containing the vapor-phase oxidant. Formation of an oxidation reaction product occurs and proceeds with the progressive transport of molten parent metal through its own already-formed oxidation reaction product, and concomitant progressive formation of additional oxidation reaction product, thereby affording a ceramic body of advantageous thickness, with or without included unoxidized metal. In some instances, a dopant (e.g., one or more materials used in conjunction with the parent metal) may be used to enable the ceramic-forming reaction to go forward in the desired progressive manner.

EP-A-193 292 describes a method for producing ceramic composites by infiltrating a permeable bed or preform of filler material by said oxidation reaction product. This filler material may have the same composition as the oxidation reaction product being formed or may differ in composition from the formed oxidation reaction product. A parent metal body is in extended surface contact with the permeable filler and the assembly is heated in the presence of a vapor-phase oxidant, with dopant present (where necessary or beneficial) either alloyed with the parent metal, or deposited on the surface of the parent metal body, or distributed through the filler body.

In these instances of producing ceramic composites, operating conditions are selected to achieve progressive infiltration and reaction, typically until infiltration of the permeable body with the oxidation reaction product is complete. If reaction proceeds to complete consumption of the parent metal, the produced article may be nearly all oxidation reaction product together with porosity and isolated nonoxidized metal plus any incorporated filler. If there is incomplete reaction of the parent metal, unreacted parent metal may be distributed through the produced article, and may comprise interconnected metal. The oxidation reaction product forms as a polycrystalline matrix incorporating the filler material, thereby providing a composite of the ceramic, optionally with unreacted metal and/or pores, and the filler material.

By such procedures, it is feasible to produce articles of near net shape. For instance, if a body of parent metal is surrounded by a permeable body of filler preform or particulate bed of substantially inert filler, and heated in the presence of oxidant until the metal has been completely oxidized, the resultant ceramic article will have an internal cavity conforming closely to the original external configuration of the initial parent metal body. If the permeable body itself has a defined external shape beyond which oxidation reaction product cannot occur, the produced ceramic article will have a corresponding external configuration.
With respect to these processes, it has been found that the filler may comprise particulate aggregates, wires, fibers, whiskers, woven lamina, and the like. Development work has proceeded with particulate aggregates owing to low cost and ease of making the preform. In the case of the particulate fillers, strength of the produced ceramic filler composite and many other mechanical properties are improved by reducing the particle size of the filler. However, it has been found in practice that green shapes (preforms) formed from very fine powders tend to contain forming flaws which are much larger than the maximum particle size and limit the strength of the material. Moreover, the gas permeability of the green shapes decreases with decrease of particle size, and hence the rate of the oxidation driven matrix penetration in the preform also decreases. In some cases, this oxygen starvation leads to formation of undesired constituents such as AlN which later hydrolyze and cause strength degradation.

Summary of the Invention

The present invention, in a first aspect, contemplates the provision of improvements in a method of making a self-supporting ceramic body having a filler material incorporated in a ceramic matrix of an oxidation reaction product, by disposing a body of parent metal and a permeable body comprising the filler material in relation to each other for growth and infiltration of the oxidation reaction product into the permeable body. The metal body is molten, and maintained in contact with an atmosphere comprising a vapor-phase oxidant that reacts with the molten parent metal to form the oxidation reaction product, and while in the appropriate temperature region, molten metal is progressively transported through the oxidation reaction product where it oxidizes on contact with the oxidant forming additional reaction product of a polycrystalline ceramic matrix. The improvement according to the present invention, in such a method broadly comprises using a permeable bed of a very fine filler material, having (i) a first pore system comprised of interparticle pores, preferably relatively coarse, and (ii) a second pore system comprised of intraparticle pores that are fine in relation to the interparticle pores and distributed throughout the mass. The filler material having intraparticle porosity is structurally stable during infiltration of the bed. This dual system of coarse and fine pores is found to insure effective concomitant infiltration of the oxidation reaction product and gas permeation of the permeable bed.

According to the present invention, said bed of filler material comprises porous agglomerates of stably cohered fine particles or crystallites. The finer porosity is defined by and between the constituent cohered fine crystallites within each agglomerate, and is referred to as "intraparticle porosity," while the coarser porosity is constituted of the interstitial space between agglomerates within the bed, and is referred to as "interparticle porosity." Illustratively, the bed may be an aggregate (e.g., a packed bed) of these agglomerates, or a green shape or preform made up of agglomerates which are bonded together as, for example, by partial sintering.

Illustrative filler material agglomerates suitable for use in the present invention, and currently commercially available, are generally spheroidal in shape with a size sufficient to afford ease of handling. Their porosity is such as to enable infiltration of the oxidation reaction product and vapor-phase oxidant; hence they do not limit the reaction rate, or cause formation of undesirable phases by oxygen starvation at the reaction front. Moreover, green shapes (preforms) constituted of such agglomerates are unground and advantageously free of large flaws or inhomogeneities. At the same time, the constituent crystallites of the agglomerates are of a very fine size; while they are held in the agglomerate structure against rearrangement during growth of the ceramic matrix in the present method, it is these fine crystallites that constitute the filler particles of the final product. Hence, use of the above-described agglomerates to constitute the permeable bed enables attainment of desired fineness of particle (i.e., crystallite) size yet without the difficulties and disadvantages that have heretofore been encountered with beds or preforms of very fine particles.

The constituent crystallites of the agglomerates may themselves be of any convenient shape, e.g., equiaxed or in the form of whiskers or platelets.

Further features and advantages of the invention will be apparent from the detailed description hereinbelow set forth, together with the accompanying drawing.

Brief Description of the Drawings

Fig. 1 is a simplified schematic elevational sectional view of a crucible, in a furnace, in illustration of the performance of an exemplary embodiment of the method of the invention:

Fig. 2 is a view similar to Fig. 1 illustrating a setup for performance of another exemplary embodiment of the invention;
Fig. 3 is a scanning electron micrograph of an unground alpha alumina particle suitable for use as a filler particle to constitute a porous bed or preform for the practice of the method of the invention; Fig. 4 is an optical micrograph of another unground alpha alumina particle suitable for use as a filler particle in the method of the invention; and Fig. 5 is a micrograph of an unground alpha alumina particle after infiltration with metal in the practice of the invention.

**Detailed Description**

The method of the invention will be described as embodied in a method wherein a ceramic article comprising filler material incorporated in a ceramic matrix of an oxidation reaction product is formed by orienting a body of a parent metal and a permeable mass of filler material relative to each other for infiltration of the oxidation reaction product into the permeable mass; in the presence of a vapor-phase oxidant, melting the parent metal body and reacting the molten metal with the oxidant (by heating to an appropriate temperature) to form oxidation reaction product, and at such temperature maintaining at least a portion of the oxidation reaction in contact with and between the body of molten metal and the oxidant, to progressively draw molten metal through the oxidation reaction product towards the oxidant and the filler material so that the oxidation reaction continues to form within the mass of filler material at the interface between the oxidant and previously formed oxidation reaction product and continuing the reaction for a time sufficient to infiltrate at least a portion of the mass of filler material, wherein (in accordance with the invention) the permeable mass comprises a first pore system constituted of interparticle porosity distributed throughout the mass and a second pore system constituted of intraparticle porosity also distributed throughout the mass, both systems of porosity being defined within or between portions of the filler material defining the second pore system being structurally stable, during infiltration of oxidation reaction product, in maintained pore-defining arrangement.

The present invention specifically contemplates the use, in this method, of a permeable body (filler material bed or preform) comprising an aggregate or preformed body of particles of any composition that is substantially functionally inert to the parent metal under the conditions of the process of the present invention. Each particle itself comprises a porous agglomerate of stably cohered crystallites which may be equi-axed or in the form of whiskers or platelets. Some examples of such particles include the following:

(i) Calcined unground aluminum trihydrate, the particles of which retain the outer size and shape of the low density alumina trihydrate, but internally recrystallized to an intergrown network of alpha-alumina platelets. As the density of the trihydrate is approximately 2.4 g/cm³ while that of alpha alumina is approximately 4 g/cm³, these particles are typically 50% porous. The diameter of the alpha alumina platelets varies from 0.5 to 5 microns, depending on the calcination temperature schedule and mineralizer additions.

(ii) Spray dried or agglomerated and partially sintered particles of any chemical composition that is substantially functionally inert to the parent metal under the conditions of the process of the present invention. In this case, for equi-axed dense powder, the typical initial open porosity of the individual spray-dried particles is approximately 40-50%. The porosity can be reduced to approximately 10-15% by a calcination procedure leading to partial sintering. Below 10-15% porosity, the pores are isolated and no longer accessible to the parent metal or its oxidation products.

(iii) Spray dried or agglomerated metal powder particles which are then reaction bonded either by nitridation or oxidation. Silicon and aluminum nitride powders are commercially produced by grinding of such nitrided metal particles. Porosities of such reaction bonded particles can vary widely, depending on the exact details of the oxidation process.

(iv) Particles formed by carbothermic reduction of spray dried or agglomerated particles of oxide precursors, etc. Boride, carbide and nitride powders and whiskers are commercially produced in this way. Carbides are produced under vacuum or inert atmosphere. Nitrides are formed by carbonitridation in ammonia, forming gas, or nitrogen. To make borides, B₂C or B₃O₃ are used as boron precursors. In this case, large volume fractions of intraparticle porosity are achievable because of the release of CO/CO₂ gas reaction product. A wide variety of crystalite shapes ranging from equi-axed to high aspect ratio whiskers are obtainable. In the case of TiB₂, open sponge-like particle structures are observed, which are particularly well suited for reactive infiltration.

It will be appreciated that in each of the foregoing instances, the permeable body in accordance with the invention is characterized by a first pore system of interconnected relatively coarse pores, and a second pore system of interconnected finer pores, both distributed throughout the body. The first pore system comprises the void spaces or interparticle porosity (between adjacent agglomerates in the bed or preform)
and the second pore system comprises the intraparticle porosity, within each agglomerate, defined between the constituent crystallites of that agglomerate. Also, in each case, the portions of the filler material defining the second pore system are structurally stable so as not to undergo pore-closing rearrangement during the infiltration step of the method; thus the individual crystallites of each agglomerate are stably cohered together in pore-defining arrangement with each other.

The filler is substantially functionally inert but may contain a minor fraction of a compound reducible by the parent metal; for example, in the case of Al parent metal, the filler may contain SiO₂ or Si₃N₄. The reducible siliceous compound may be added as a powder to the functionally inert filler (e.g. Al₂O₃ or SiC) in the form of quartz sand or an aluminosilicate mineral such as kaolin clay.

The reducible compound may be distributed as a mineral constituent of the filler material, for example, the Na₂O content of Al₂O₃ which is typically between 0.05 and 0.6%, or the SiO₂ content of aluminosilicate minerals such as clays or feldspars which vary from 40-60%. In the latter case, the SiO₂ content of the filler would be reduced to 50% or less (i.e., a minor amount) by mixing with an inert material. The reducible compound may also be formed as a coating on the functionally inert filler either by precipitation from solution by any of the well-known sol-gel routes or by partial oxidation of the filler material, e.g. air oxidation of SiC at 1,300 °C to form an SiO₂ coating on all the filler particles.

The presence of a reducible compound in the filler promotes uniform and rapid initiation of the infiltration reaction and a uniform reaction infiltration front. The reducible compound(s) may be distributed uniformly throughout the filler bed, or concentrated at the interface between the filler and the parent metal.

Further minor additions to the filler can be made to alter its wetting characteristics with respect to the molten parent metal under the reaction conditions. For example, additions of alkali metal compounds tend to promote the wetting of the filler by the parent metal. Na, Li and K compounds are particularly suitable.

Referring to Fig. 1, in the illustrative embodiment of the present method there represented, a body of a parent metal (which, for example, may comprise aluminum, silicon, zirconium, hafnium, tin or titanium) and a permeable body in accordance with the invention (as defined above) are positioned adjacent each other and oriented with respect to each other so that growth of the oxidation reaction product will be in a direction toward the filler material of the permeable body in order that the filler material, or a part thereof, will be infiltrated by the growing oxidation reaction product and embedded therein. This positioning and orientation of the parent metal and filler material with respect to each other may be accomplished within a graphite or like crucible 10 by simply embedding a body of parent metal 11 within a permeable body comprising a bed 12 of particulate filler material as illustrated in Fig. 1 or by positioning one or more bodies of parent metal within, or on adjacent a permeable body comprising a bed or other assembly (e.g. a porous green shape or preform) of the filler material. The assembly is, in any case, arranged so that a direction of growth of the oxidation reaction product will be toward the filler material, and the oxidation reaction product will permeate or engulf at least a portion of the filler material such that void space between filler particles will be filled by the grown oxidation reaction product matrix.

When one or more dopant materials (described below) are required or desirable to promote or facilitate growth of the oxidation reaction product, the dopant may be used on and/or in the parent metal and, alternatively or in addition, the dopant may be used on, or incorporated in, the bed or preform of filler material.

In the case of employing aluminum or its alloys as the parent metal and an oxygen-containing gas as the oxidant in the process of the present invention, the appropriate amounts of dopants can be alloyed into or applied to the parent metal, as described below in greater detail. The parent metal body is then placed in the crucible 10 or other refractory container with the metal surface exposed to the adjacent or surrounding mass of permeable filler material 12 in the container and in the presence of an oxidizing atmosphere (typically air at ambient atmospheric pressure). The resulting assembly is then heated within a furnace 14 to elevate the temperature thereof into the region typically between about 850 °C and about 1,450 °C, or, more preferably, between about 900 °C and about 1,350 °C, depending upon the filler material, dopant or the dopant concentrations, or the combination of any of these whereupon the parent metal transport begins to occur through the oxide skin normally protecting the aluminum parent metal.

The continued high temperature exposure of the parent metal to the vapor-phase oxidant allows the continued oxidation of parent metal to form a polycrystalline reaction product layer of increasing thickness. This growing oxidation reaction product progressively impregnates the permeable adjacent filler material with an interconnected oxidation reaction product matrix which also may contain nonoxidized parent metal constituents, thus forming a cohesive composite. The growing polycrystalline matrix impregnates or permeates the filler material at a substantially constant rate (that is, a substantially constant rate of thickness increase over time), provided sufficient air (or oxidizing atmosphere) interchange is allowed in the furnace to keep a relatively constant source of oxidant therein. Interchange of oxidizing atmosphere, in the case of air,
can be conveniently provided by vents 15 and 16 in the furnace 14. Growth of the matrix continues until at least one of the following occurs: (1) substantially all of the parent metal is consumed; (2) the oxidizing atmosphere is replaced by nonoxidizing atmosphere, is depleted of oxidant, or evacuated, or (3) the reaction temperature is altered to be substantially outside the reaction temperature envelope, e.g., below the melting point of the parent metal. Usually, the temperature is reduced by lowering the furnace temperature, and then the material is removed from the furnace.

In the illustrative embodiment of Fig. 1, the initial parent metal body is a solid body of quatrefoil-shaped cross section, and is buried in a permeable body comprising a packed bed of porous filler agglomerates. Fig. 1 shows conditions obtaining part way through the infiltration step. The starting parent metal body has melted and oxidation reaction product has infiltrated a zone 18 of the permeable body 12, leaving the volume 20 initially occupied by the solid parent metal body only partially filled with residual molten parent metal 11. The zone 18 constitutes a product shape comprised of the oxidation-reaction-product-infiltrated filler material, surrounding and defining a cavity (volume 20) which approximately replicates the original shape of the starting parent metal body.

The product of this method is a rigid, integral solid article constituted of the initial inert filler material of the permeable body, together with polycrystalline oxidation reaction product formed interstitially therein during the heating step as well as any unreacted parent metal that may be present. Preferably, in at least many instances, the quantity of metal in the initial parent metal body is so selected, in relation to the interstitial or pore volume of the permeable body, that at the completion of the reaction the latter volume is completely filled with the reaction product (with or without unreacted parent metal); thus, the produced article is a dense, self-bonded, essentially pore-free body constituted of the inert filler material of the initial permeable body incorporated in a polycrystalline matrix of the oxidation reaction product formed during the heating step and any unreacted metal that may be present.

The excess metal, in the latter case, may be either isolated or interconnected. Macroscopically excess metal may also be present on some external surfaces of the ceramic body providing a well-bonded metal-ceramic interface. In this manner, ceramic-surfaced metallic components may be produced deriving strength from their metallic core, and hardness, erosion resistance and/or other properties from the ceramic surface layer.

The present method, utilizing a porous preform or bed of filler material, enables ceramic components of near net shape to be readily achieved. The external surface configuration of the produced article may be determined by appropriately defining the initial external surface configuration of the permeable body, for example, if the latter body is a packed bed of particles by confining the packed bed within a suitable shape-defining barrier that limits the growth of reaction product. Assuming that the quantity of metal in the initial parent metal body is so proportioned to the interstitial volume of the permeable body that the latter becomes completely infiltrated with oxidation reaction product during the heating step, and that the heating step is continued until such complete infiltration has occurred, and further assuming that the permeable body surrounds or substantially surrounds the parent metal body, the produced article will have a void or cavity corresponding to the spatial volume originally occupied by the parent metal body and replicating the external surface configuration of the parent metal body. Assuming that the quantity of parent metal is sufficient to achieve complete filling of the interstitial volume of the permeable body with oxidation reaction product, the produced article will be a uniform, solid body (with or without pores) having the external shape of the initial permeable body.

Fig. 2 illustrates an alternative embodiment of the present method for producing an article similar to that produced by the embodiment of Fig. 1. In Fig. 2, within the refractory crucible 10 there is supported a permeable body 12a comprising a filler material preform in accordance with the invention, corresponding in configuration to the desired product article shape. The preform may, for example, be a body of porous agglomerates of filler material crystallites, the agglomerates being bonded together (e.g. by sintering) to form the selected shape, which in this case defines an internal, initially empty cavity 18a of quatrefoil cross section. A body of parent metal 11a is initially supported within a refractory well 24 above the crucible and communicating downwardly with the preform cavity 18a through an opening 26 in register with a port 28 in the preform. Fig. 2 shows the starting set-up for this procedure, with the crucible 10 disposed in the furnace 14 (already described with reference to Fig. 1) but before heating is commenced.

As heating proceeds, with continuing circulation of air or other vapor-phase-oxidant atmosphere through vents 15 and 16 so as to permeate the preform, the metal 11a metals and fills the preform cavity, with the result that oxidation reaction product infiltrates the preform body. Dopant material, if needed or desired, may either be alloyed into the parent metal body or be coated on the internal surface of the preform or distributed throughout the preform. The final product, as before, is a rigid ceramic article incorporating the preform filler material in a matrix of oxidation reaction product with or without unreacted metal and/or pores.
To exemplify further the method of the invention, in specific (and, for particular purposes, especially preferred or convenient) embodiments, there is employed a permeable body (filler material bed or preform) comprising an aggregate of unground porous alpha alumina particles produced by calcination of metallurgical grade alumina trihydrate and each constituted of an agglomerate of alpha alumina crystallites. Such particles are commercially available, and are exemplified by the products sold under the trade name "Alcan C-70 Series" aluminas, viz. C-70, C-71, C-72, C-73 and C-75 alumina. Fig. 3 is a scanning electron micrograph of an unground porous particle of Alcan C-70 alumina, and Fig. 4 is an optical micrograph of an unground porous particle of Alcan C-72 alumina. Properties of the Alcan C-70 Series aluminas are given in the following table:

**PROPERTIES OF ALCAN C-70 SERIES UNGROUND CALCINED ALUMINAS**

<table>
<thead>
<tr>
<th>CHEMICAL PROPERTIES</th>
<th>C-70</th>
<th>C-71</th>
<th>C-72</th>
<th>C-73</th>
<th>C-75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O, %</td>
<td>0.40</td>
<td>0.18</td>
<td>0.13</td>
<td>0.12</td>
<td>0.05</td>
</tr>
<tr>
<td>max</td>
<td>0.60</td>
<td>0.30</td>
<td>0.20</td>
<td>0.20</td>
<td>0.08</td>
</tr>
<tr>
<td>Leachable Na₂O, %</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>max</td>
<td>0.06</td>
<td>0.06</td>
<td>0.05</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>SiO₂, %</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>max</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe₂O₃, %</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>max</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.06</td>
</tr>
</tbody>
</table>

 Specific Surface Area, m²/g 0.5-0.7 0.5-0.7 0.5-0.7 0.3-0.5 0.5-0.7  
 Ultimate Crystal Size, μm 2-3 2-3 2-3 3-5 3-5  
 Bulk Density Loose, g/cm³ (lb/cu ft) 0.8 (50) 0.8 (50) 0.8 (50) 1.0 (62) 0.7 (44)  
 Bulk Density Packed, g/cm³ (lb/cu ft) 1.1 (69) 1.1 (69) 1.1 (69) 1.3 (80) 1.3 (80)  
* Green Density, g/cm³ 2.10 2.10 2.10 2.30 2.20  
* Fired Density @ 1620°C, g/cm³ 3.65 3.70 3.71 3.60 3.80  
* Linear Shrinkage, % 14 14 14 12 16  

 Cumulative Particle Size Distribution -

- >0.494 mm (+ 60 mesh) 10%
- >0.044 mm (+ 200 mesh) 60%
- >0.044 mm (+ 325 mesh) 97%
- <0.044 mm (- 325 mesh) 3%

(* ) These properties of alumina are determined as follows:

125 g alumina is ground with 4000 g of (1 inch) alumina grinding balls in a (1.3 gal) mill rotating for 4 h at 62 rpm. Green density is determined on a 10 g disk pressed at (5000 psi) in a (1 inch) die without binder. Fired density and shrinkage are determined by Alcan Method 1074-71. Specific surface area is determined by the BET method.

The Alcan C-70 Series aluminas, all of which are suitable for the practice of the present process, are produced by calcining Bayer process alumina trihydrate (more correctly aluminum trihydroxide) in rotary kilns. The starting trihydrate is in particulate form. During calcination, the combined water is driven off and the oxide formed passes through several intermediate phases until the stable alpha-alumina structure is
reached. Addition of small amounts of mineralizer during calcination accelerates the conversion to alpha alumina and promotes the growth of the alpha crystals. Particle size of the alumina is determined during the hydrate precipitation stage of the Bayer process, but crystal size of alpha alumina is developed during the calcination process. Although the alumina trihydrate precursor is a nonporous particle of specific gravity 2.42 g/cm³ and bulk density of about 1.3 g/cm³, the resulting unground alpha alumina is a porous aggregation (open lattice structure) of monocrystal platelets (crystallites) with a specific gravity of 3.98 g/cm³ and a bulk density of about 1 g/cm³. These aluminas are 95-100% alpha alumina and have less than 0.1% loss on ignition. Any nonleachable soda present is in the form of beta alumina, Na₂O·11Al₂O₃. The fine aluminas of the C-70 series differ from each other in crystal size and soda content, reduction in soda content being effected (in all but C-70 alumina) by appropriate treatment during calcination.

Although typical present-day commercial uses for such aluminas involve grinding the as-calcined porous particles, the use of the particles in unground condition contributes importantly to the attainment of the advantages of the present invention. Each of these unground particles is a stable, generally spheroidal, multocrystallite structure of, say, several tens of μm in size, cohered together, with an open network of substantially uniformly distributed pores, the pores being of similar size to the crystallites. Each unground particle is thus a porous agglomerate of crystallites, within the meaning of the term agglomerate as used herein. The unground porous particles are easily handled and readily assembled into packed beds or porous preforms free of large flaws or inhomogeneities. The stably cohered crystallite structure of the individual unground particles maintains the individual crystallites against rearrangement prior to and during matrix (oxidation reaction product) growth and preserves the open porosity of the assembled bed or preform for assured adequate permeation of vapor phase oxidant until matrix formation is complete.

In the practice of the present and like methods, the scale of the grown polycrystalline matrix microstructure is refined by reduction of filler particle size in the bed or preform. Hence, for a fine matrix microstructure, a very fine filler particle size is desirable. The minute individual crystallites of alpha alumina in the unground porous alumina particles exemplified by Alcan C-70 Series aluminas constitute such fine filler particles, for the purpose of determining fineness of grown matrix microstructure, notwithstanding that each unground particle of the filler bed or preform is a much larger agglomerate of multiple crystallites, held in an open structure. Thus, use of the described unground porous particles to constitute the bed or preform affords both the particle fineness required for fine matrix microstructure and the maintained permeability and homogeneity (freedom from gross flaws) usually associated with larger particles.

The size of the unground porous particles can be tailored by choice of size of the trihydrate precursor, and the alpha crystallite size by the calcination schedule and mineralizer additions, as will be apparent to persons skilled in the art. Also, while it is satisfactory in many cases to provide (in the present method) a filler bed or preform consisting essentially of an aggregate of the unground porous alpha alumina particles described above, the aggregate may also include a minor proportion of smaller porous or nonporous inert powder particles, e.g. a proportion of fines selected to fill the interstices (typically about 10 to 20 μm in size) between the larger unground particles. Similarly in the use of other permeable bodies embraced within the invention, such minor proportions of fines may be incorporated.

Referring again to Fig. 1, then, in an illustrative instance of the practice of the present method, a body of aluminum metal 11, e.g. alloyed or coated with minor proportions of suitable dopants such as Mg and Si or coated with a thin powder layer of suitable dopant such as MgO and/or silica, is embedded in a packed bed 12 of Alcan C-70 unground porous alpha alumina particles, and heated in air (oxidant) to a temperature at which the metal is molten and at which progressive ceramic (alpha-Al₂O₃) growth into the packed bed occurs. Fig. 5 is a micrograph of unground Alcan C-72 alpha alumina after such infiltrating ceramic growth. Heating is continued until the oxidation reaction product fully permeates the packed bed. The resultant article is a rigid, self-sustaining article comprising alpha alumina crystallites of the filler particles distributed through the intergrown polycrystalline alpha alumina matrix, with or without unreacted metal present.

In an actual test, preforms were produced by slip casting ground Alcan C-70 Series aluminas. When it was attempted to grow a matrix of Al₂O₃ into these preforms using molten aluminum in the presence of air as oxidant, it was found that growth was very slow. In contrast to these results, such matrix growth into a bed of unground Alcan C-70 Series alumina particles was substantial, under generally comparable process conditions. Significantly, in the bed of unground particles, the Al₂O₃ matrix growth and any metallic constituents present completely filled the interior of the porous particles, affording a dense, fine microstructure suitable for structural component applications.

In specific embodiments, the method of the invention involves a particular utilization or modification of more general techniques for producing a self-supporting ceramic body by oxidation of a parent metal to form an oxidation reaction product, as heretofore disclosed in the aforementioned EP-A-155 831. More specifically, in these techniques the parent metal is heated to an elevated temperature above its melting
point but below the melting point of the oxidation reaction product in order to form a body of molten parent metal which reacts upon contact with a vapor-phase oxidant to form the oxidation reaction product. The oxidation reaction product, or at least a portion thereof which is in contact with and extends between the body of molten parent metal and the oxidant, is maintained at the elevated temperature, and molten metal is drawn through the polycrystalline oxidation reaction product and towards the oxidant, and the transported molten metal forms oxidation reaction product upon contact with the oxidant. As the process continues, additional metal is transported through the polycrystalline oxidation reaction product formation thereby continually "growing" a ceramic structure of interconnected crystallites. Usually, the resulting ceramic body will contain therein inclusions of nonoxidized constituents of the parent metal drawn through the polycrystalline material and solidified therein as the ceramic body cooled after termination of the growth process. As explained in one or more of the aforementioned patent applications, resultent novel ceramic materials are produced by the oxidation reaction between a parent metal and a vapor-phase oxidant, i.e., a vaporized or normally gaseous material, which provides an oxidizing atmosphere. In the case of an oxide as the oxidation reaction product, oxygen or gas mixtures containing oxygen (including air) are suitable oxidants, with air usually being preferred for obvious reasons of economy. However, oxidation is used in its broad sense, as herein, and refers to the loss of, or sharing of electrons by a metal to an oxidant which may be one or more elements and/or compounds. Accordingly, elements other than oxygen may serve as the oxidant. In certain cases, the parent metal may require the presence of one or more dopants in order to favorably influence or facilitate growth of the ceramic body, and the dopants may be provided as alloying constituents of the parent metal. For example, in the case of aluminum as the parent metal and air as the oxidant, dopants such as magnesium and silicon, to name but two of a larger class of dopant materials, were alloyed with the aluminum alloy utilized as the parent metal. Alternatively, and as previously disclosed in EP-A-169 067, appropriate growth conditions as described above, for parent metals requiring dopants, can be induced by externally applying a layer of one or more dopant materials to the surface or surfaces of the parent metal, thus avoiding the necessity of alloying the parent metal with dopant materials, e.g., metal oxides such as those of magnesium, zinc and silicon, in the case where aluminum is the parent metal and air is the oxidant.

Thus, the foregoing techniques enable the production of oxidation reaction products readily "grown" to desired thicknesses heretofore believed to be difficult, if not impossible, to achieve with conventional ceramic processing techniques. The underlying metal, when raised to a certain temperature region above its melting point, and in the presence of dopants (if required) is transported through its own otherwise impervious oxidation reaction product, thus exposing fresh metal to the oxidizing environment to thereby yield further oxidation reaction product. The result of this phenomenon is the progressive growth of a dense, interconnected ceramic optionally containing some nonoxidized parent metal constituents distributed throughout the growth structure.

The specific type of procedure with which the present invention is concerned is described in EP-A-193 282 and is a method for producing a self-supporting ceramic composite structure comprising (1) a ceramic matrix obtained by oxidation of a parent metal, e.g., an aluminum alloy, to form a polycrystalline material consisting essentially of (i) the oxidation reaction product (e.g., alpha-aluminum oxide) of the parent metal with a vapor-phase oxidant (e.g., oxygen) and, optionally, (ii) one or more nonoxidized constituents of the parent metal; and (2) a filler embedded by the matrix.

Generally, this procedure is based upon the discovery that the growth of a polycrystalline material resulting from the oxidation of a parent metal by the above-described techniques can be directed towards a permeable mass of functionally inert filler material, sometimes herein referred to simply as "filler," which is placed adjacent the parent metal. The filler is engulfed and embedded within the growth of polycrystalline material to provide a composite ceramic structure. Under suitable process conditions, the molten parent metal oxidizes outwardly from its initial surface (i.e., the surface exposed to the oxidant) towards the oxidant and the filler by migrating through its own otherwise impermeable oxidation reaction product structure. The oxidation reaction product grows into the permeable mass of filler, which may comprise an aggregate of divided solid filler material. This results in novel ceramic matrix composite structures comprising a dense matrix of a ceramic polycrystalline material embedding the filler materials.

The mass or aggregation of filler material or materials is positioned adjacent the parent metal in the assumed path of the oxidation reaction product growth therefrom. The filler material can comprise either a loose or bonded array or arrangement of materials, which array has interstices, openings, intervening spaces, or the like, to render it permeable to the oxidant and to the oxidation reaction product growth. Further, the filler material may be homogeneous or heterogeneous, and may have a chemical composition identical to or different from the grown oxidation reaction product matrix. A matrix of the polycrystalline material resulting from the oxidation reaction product growth is simply grown around the filler material so as to embed the latter without substantially disturbing or displacing it. Thus, no external forces are involved
which might damage or disturb the arrangement of the filler material and no awkward and costly high
temperature, high pressure processes and facilities are required as in known conventional processes to
achieve a dense composite ceramic structure. In addition, the stringent requirements of chemical and
physical compatibility necessary for pressureless sintering to form ceramic composites are greatly reduced
or eliminated.

In the ceramic matrix growth process, the parent metal is heated to a temperature above its melting
point but below the melting point of the oxidation reaction product thereby forming a body of molten parent
metal which is reacted with the oxidant to form the oxidation reaction product. At this temperature or within
this temperature range, the body of molten metal is in contact with at least a portion of the oxidation
reaction product which extends between the body of molten metal and the oxidant. Molten metal is drawn
through the oxidation reaction product towards the oxidant and towards the adjacent filler material to sustain
the continued formation of oxidation reaction product at the interface between the oxidant and previously
formed oxidation reaction product. The reaction is continued for a time sufficient to embed at least a portion
of the filler material within the oxidation reaction product by growth of the latter, which optionally has therein
inclusions of non-oxidized constituents of parent metal, to form the composite structure.

The products of such procedures generally are adaptable or fabricated, such as by machining,
polishing, grinding, etc., for use as articles of commerce which, as used herein, are intended to include,
without limitation, industrial, structural and technical ceramic bodies for applications where electrical, wear,
thermal, structural or other features or properties are important or beneficial; and it is not intended to
include recycled or waste materials such as might be produced as unwanted by-products in the processing
of molten metal.

As used herein, reference to an "oxidant," "vapor-phase oxidant," or the like, which identifies the 
oxidant as containing or comprising a particular gas or vapor, means an oxidant in which the identified gas
or vapor is the sole, or predominant, or at least a significant oxidizer of the parent metal under the
conditions obtaining in the oxidizing environment utilized. For example, although the major constituent of air
is nitrogen, the oxygen content of air is the sole or predominant oxidizer for the parent metal because oxygen is a significantly stronger oxidant than nitrogen. Air is therefore an "oxygen-containing gas" oxidant but not a "nitrogen-containing gas" oxidant within this definition.

The term "parent metal" as used herein refers to that metal, e.g., aluminum, which is the precursor of
the polycrystalline oxidation reaction product and includes that metal or a relatively pure metal, a
commercially available metal having impurities and/or alloying constituents therein, and an alloy in which
that metal precursor is the major constituent. Although the invention is described herein with particular
emphasis on aluminum as the parent metal, other metals which meet the criteria of the invention are also
suitable, such as silicon, titanium, tin, zinc and zirconium.

The term "ceramic" as used herein is not limited to a ceramic body in the classical sense, that is, in the
sense that it consists entirely of non-metallic and inorganic materials but, rather, it refers to a body which is
predominantly ceramic with respect to either composition or dominant properties, although the body may
contain substantial amounts of one or more metals derived from the parent metal, most typically within a
range of from about 1-40% by volume, but may include still more metal.

As further set forth in one or more of the above-cited applications, certain parent metals under specific
conditions of temperature and oxidizing atmosphere meet the criteria necessary for the oxidation phenom-
enum of the present invention with no special additions or modifications. However, dopant materials used in
combination with the parent metal can favorably influence or promote the oxidation reaction process.

Useful dopants for an aluminum parent metal, particularly with air as the oxidant, include, for example,
magnesium metal and zinc metal, in combination with each other or in combination with other dopants
described below. These metals, or a suitable source of the metals, may be alloyed into the aluminum-based
parent metal at concentrations for each of between about 0.1-10% by weight based on the total weight of
the resulting doped metal. The concentration range for any one dopant will depend on such factors as the
combination of dopants and the process temperature. Concentrations within this range appear to initiate the
ceramic growth, enhance metal transport and favorably influence the growth morphology of the resulting
oxidation reaction product.

Other dopants which are effective in promoting polycrystalline oxidation reaction product growth for
aluminum-based parent metal systems using air or oxygen as oxidant are, for example, silicon, germanium,
tin and lead, especially when used in combination with magnesium or zinc. One or more of these other
dopants, or a suitable source of them, is alloyed into the aluminum parent metal system at concentrations
for each of from about 0.5 to about 15% by weight of the total alloy; however, more desirable growth
kinetics and growth morphology are obtained with dopant concentrations in the range of from about 1-10%
by weight of the total parent metal alloy. Lead as a dopant is generally alloyed into the aluminum-based
parent metal at a temperature of at least 1,000 °C so as to make allowances for its low solubility in aluminum; however, the addition of other alloying components, such as tin, will generally increase the solubility of lead and allow the alloying materials to be added at a lower temperature.

One or more dopants may be used depending upon the circumstances, as explained above. For example, in the case of an aluminum parent metal and with air as the oxidant, particularly useful combinations of dopants include (a) magnesium and silicon or (b) magnesium, zinc and silicon. In such examples, a preferred magnesium concentration falls within the range of from about 0.1 to about 3% by weight, for zinc in the range of from about 1 to about 6% by weight, and for silicon in the range of from about 1 to about 10% by weight.

The function or functions of the dopant material can depend upon a number of factors other than the dopant material itself. These factors include, for example, the particular parent metal, the end product desired, the particular combination of dopants when two or more dopants are used, the use of an externally applied dopant in combination with an alloyed dopant, the concentration of the dopant, the oxidizing environment, and the process conditions. The dopant or dopants (1) may be provided as alloying constituents of the parent metal, (2) may be applied to at least a portion of the surface of the parent metal, or (3) may be applied to the filler or a part of the filler bed, or any combination of two or more techniques (1), (2) and (3) may be employed.

By way of further illustration of the invention, reference may be made to the following examples:

Example I

Al alloy (10% Si-up to 3% Mg) was disposed for growth of oxidation reaction product into an Alcan C-72 unground alumina bedding (crystallite size 1.5 μm to 5 μm diameter, agglomerated into a particle of size 45 μm to 150 μm diameter) in an atmosphere of air (up to 100% oxygen has been used). Reaction time and temperatures varied as follows:

- Time (hours to soak temperature): 2
- Time (hours at soak temperature): 0 to 100
- Temperature (°C): 1,100 to 1,250 °C
- Alloy: Al + 10% Si + (0.0 to 3.0%) Mg

The experimental set-up was either as a cube of metal sitting in the bedding with the top surface of the metal exposed to the reactive gas or as a cube of metal completely buried in the bedding (all metal surfaces in contact with the bedding).

Fig. 5 shows an optical micrograph of a cross section of the resulting growth. The experimental conditions used to obtain this sample were: 100 hours at 1,150 °C, alloy Al-10% Si with MgO applied as a slurry to the surface of the metal to serve as an external dopant. The figure shows an alumina particle infiltrated with aluminum alloy. The particle is surrounded by Al metal/aluminum oxide growth product.

Example II

The experimental setup employs two concentric thick walled crucibles formed from the same mix and by the same process. The outer crucible has a 3.8 cm outer diameter and a 2.5 cm inner diameter. An aluminum alloy slug of nominal composition Al-3% Mg-10% Si is placed into the larger crucible and the 2.5 cm outer diameter inner crucible is then inserted. The inner crucible acts as a floating lid thereby preventing growth from the slug into free air. Thus the oxidation reaction product growth is directed into the ceramic preform.

Crucibles with various densities were fabricated by mixing various proportions of ground and unground Alcan C-72 aluminas. Ground C-72 alumina consists of individual crystallites liberated from the unground agglomerate particles. It is in the form of platelets up to 5 μm in diameter and about 1 μm thick. These powder mixtures were then mixed with a 5 weight % polyvinyl alcohol solution using only enough binder solution to allow the mix to flow when vibrated in the rubber molds. Generally speaking, as the proportion of unground alumina increased, so did the amount of binder solution necessary to permit flow. The vibration of the mold was stopped when air bubble evolution was no longer observed. The molds were then placed in a freezer overnight to permit removal of the casting from the mold. Immediately thereafter, the cast crucibles were placed in a drying oven at 90 °C to drive off the excess water and set the organic binder. Finally, the crucibles were given a bisque firing at 1,300 °C for two hours to drive off the organic binder and impart sufficient high temperature strength to allow the subsequent exposure to molten aluminum at 1,250 °C.

The metal slugs and lightly sintered crucibles were assembled and heated to 1,250 °C for 24 hours in air.
Where MgO was used as a dopant, it was applied after the bisque firing by filling the containment crucible to the height of the metal slug with a water-based MgO slurry and immediately removing the excess. Where Si dopant was used as an accelerator, it was added in the form of 100 mesh powder to the C-72 alumina mixture.

Results, expressed as average percent weight gain on aluminum versus average preform density, are set forth in the following table:

**SUMMARY OF PREFORM INFILTRATION RESULTS FOR CONCENTRIC CRUCIBLE EXPERIMENTS**

<table>
<thead>
<tr>
<th>Ground/Unground Ratio</th>
<th>Silicon In Pref orm (%)</th>
<th>MgO</th>
<th>Average Porosity (%)</th>
<th>Average Density (g/cc)</th>
<th>Average Wt. Gain on Al (I)</th>
<th>Range of Wt. Gain on Al (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:7</td>
<td>No</td>
<td>64.9</td>
<td>1.4</td>
<td>10.6</td>
<td>10.0 - 11.0</td>
<td></td>
</tr>
<tr>
<td>5:5</td>
<td>No</td>
<td>64.9</td>
<td>1.4</td>
<td>7.2</td>
<td>4.3 - 10.9</td>
<td></td>
</tr>
<tr>
<td>7:3</td>
<td>No</td>
<td>54.9</td>
<td>1.8</td>
<td>10.1</td>
<td>4.4 - 24.6</td>
<td></td>
</tr>
<tr>
<td>10:0</td>
<td>No</td>
<td>47.4</td>
<td>2.1</td>
<td>17.0</td>
<td>13.2 - 17.9</td>
<td></td>
</tr>
<tr>
<td>3:7</td>
<td>4.8</td>
<td>72.4</td>
<td>1.1</td>
<td>72.0</td>
<td>40 - 90#</td>
<td></td>
</tr>
<tr>
<td>5:5</td>
<td>4.8</td>
<td>62.4</td>
<td>1.5</td>
<td>8.8</td>
<td>8.3 - 9.8</td>
<td></td>
</tr>
<tr>
<td>7:3</td>
<td>4.8</td>
<td>54.9</td>
<td>1.8</td>
<td>32.5</td>
<td>28.7 - 35.1</td>
<td></td>
</tr>
<tr>
<td>10:0</td>
<td>4.8</td>
<td>49.8</td>
<td>2.0</td>
<td>18.6</td>
<td>14.2 - 23.3</td>
<td></td>
</tr>
<tr>
<td>3:7</td>
<td>Yes</td>
<td>69.0</td>
<td>1.2</td>
<td>85.5</td>
<td>85.0 - 86.1</td>
<td></td>
</tr>
<tr>
<td>5:5</td>
<td>Yes</td>
<td>61.2</td>
<td>1.5</td>
<td>65.6</td>
<td>54.7 - 81.0</td>
<td></td>
</tr>
<tr>
<td>7:3</td>
<td>Yes</td>
<td>50.9</td>
<td>1.9</td>
<td>40.3</td>
<td>20.3 - 57.0</td>
<td></td>
</tr>
<tr>
<td>10:0</td>
<td>Yes</td>
<td>45.7</td>
<td>2.1</td>
<td>14.6</td>
<td>11.1 - 23.3</td>
<td></td>
</tr>
<tr>
<td>3:7</td>
<td>4.8</td>
<td>69.0</td>
<td>1.2</td>
<td>82.1</td>
<td>79.3 - 86.8</td>
<td></td>
</tr>
<tr>
<td>5:5</td>
<td>4.8</td>
<td>61.2</td>
<td>1.5</td>
<td>49.2</td>
<td>37.2 - 60.3</td>
<td></td>
</tr>
<tr>
<td>7:3</td>
<td>4.8</td>
<td>50.9</td>
<td>1.9</td>
<td>35.4</td>
<td>28.9 - 42.4</td>
<td></td>
</tr>
<tr>
<td>10:0</td>
<td>4.8</td>
<td>48.3</td>
<td>2.0</td>
<td>39.8</td>
<td>37.3 - 43.3</td>
<td></td>
</tr>
</tbody>
</table>

* Contains some estimated values.

The results indicate that in all cases, higher weight gains corresponding to the formation of the oxidation reaction product were obtained with more porous, less dense filler mixtures produced with higher proportions of the unground alumina.

**Example III**

Slugs of Al-10% Si alloy were completely buried in beds of unground Alcan C-74 alumina particles, heated from 20°C to 1,150°C over two hours, held at 1,150°C for 100 hours, and cooled to ambient temperature over about 14 hours. In one test, no dopant was employed, and no visible growth was observed. In a second test, the metal slug was coated with MgO in water. Extensive, non-uniform growth was observed.

**Example IV**

Slugs of Al-10% Si-3% Mg alloy were completely buried in beds of unground Alcan C-72 alumina particles, and the samples (slug plus bed) were subjected to heating at 1,150°C for 24 hours. Initial and final weights of the samples, and dopants employed, were as follows:
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Starting Weight (grams)</th>
<th>Dopant Used</th>
<th>Final Weight (grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.570</td>
<td>none</td>
<td>2.679</td>
</tr>
<tr>
<td>2</td>
<td>3.111</td>
<td>painted with aqueous solution of Na$_2$Si$_2$O$_5$</td>
<td>6.960</td>
</tr>
<tr>
<td>3</td>
<td>2.970</td>
<td>painted with aqueous solution of Na$_2$Si$_2$O$_5$ &amp; MgO</td>
<td>6.578</td>
</tr>
<tr>
<td>4</td>
<td>2.794</td>
<td>painted with aqueous solution of water &amp; MgO</td>
<td>6.394</td>
</tr>
</tbody>
</table>

**Claims**

1. A method for incorporating a very fine filler material into a ceramic composite article comprising a substantially functionally inert filler material in a ceramic matrix of an oxidation reaction product, said ceramic composite article being made by a process including the steps of
   (a) orienting a body of a parent metal and a permeable bed or preform of filler material relative to each other for the infiltration of an oxidation reaction product of the parent metal with an oxidant into the permeable bed or preform of filler material, said permeable bed or preform of filler material comprising a first pore system of coarser inter-particle porosity or interstices distributed throughout the permeable bed or preform of filler material particles;
   (b) in the presence of a vapor phase oxidant, melting the parent metal body and reacting the molten metal with the oxidant to form oxidation reaction product, by heating to a predetermined temperature and at said temperature maintaining at least a portion of said oxidation reaction product in contact with and between said body of molten metal and said oxidant, to progressively draw molten metal through the oxidation reaction product towards the oxidant and the filler material so that oxidation reaction product continues to form within said bed or preform of filler material at the interface between the oxidant and previously formed oxidation reaction product and continuing said reaction for a time sufficient to infiltrate at least a portion of the said bed or preform of filler material, characterized in that the individual very fine particles of the filler material to be incorporated into the ceramic composite article are provided in the form of coarser porous agglomerates of stably cohered fine crystallites within which agglomerates a second pore system constituted by interconnected intraparticle porosity exists, said second pore system being constituted by pores being of similar size to the crystallites and being structurally stable during infiltration of the permeable bed or preform of filler material with oxidation reaction product in maintained pore-defining arrangement.

2. A method according to claim 1, wherein said agglomerates are selected from the group consisting of unground porous particles of alpha-alumina produced by calcination of alumina trihydrate and each constituted of a multiplicity of very fine alpha-alumina crystallites having a crystal size in the range of from 0.5 to 5 μm, spray dried or agglomerated and partially sintered particles of an inert filler material, spray dried or agglomerated metal powder particles being reaction bonded by nitration or oxidation and carbothermically reduced spray dried or agglomerated particles of oxide precursors.

3. A method according to claim 2, wherein said bed or preform of filler material comprises a major proportion by weight of said agglomerates in the form of said unground particles and a minor proportion by weight of particles, smaller than said unground particles, of functionally inert material.

4. A method according to claim 3, wherein the proportion of said smaller particles is such that said smaller particles substantially fill the interstices between the agglomerates, said interstices being part of
5. A method according to any of the preceding claims, wherein said preform is a preform of self-sustaining shape constituted by bonding said agglomerates together.

6. A method according to any of the preceding claims, wherein said parent metal comprises aluminum.

7. A method according to claim 6, wherein said oxidant comprises atmospheric oxygen and said oxidation reaction product comprises alpha-alumina optionally containing nonoxidized constituents of the aluminum parent metal.

8. A method according to claim 1, wherein said oxidation reaction product also forms within at least a portion of said second pore system.

9. A method according to claim 1, wherein said second pore system is at least partially infiltrated by said molten parent metal.

10. A method according to claim 1, wherein said second pore system is at least partially infiltrated by both said oxidation reaction product and said molten parent metal.

11. An article as obtained by a method according to any of the preceding claims.

Patentansprüche

1. Verfahren zur Inkorporierung eines sehr feinen Füllstoffmaterials in einen keramischen Verbundgegenstand, der ein im wesentlichen funktionell inertes Füllstoffmaterial in einer keramischen Matrix eines Oxidationsreaktionsprodukts aufweist, wobei der keramische Verbundgegenstand nach einem Verfahren hergestellt wird, das die Schritte umfaßt:

(a) Orientieren eines Körpers aus einem Grundmetall und einem permeablen Betts oder einer Vorform aus Füllstoffmaterial so relativ zueinander, daß die Infiltration eines Oxidationsreaktionsprodukts des Grundmetalls mit einem Oxidationsmittel in das permeable Bett oder die Vorform des Füllstoffmaterials erfolgt, wobei das permeable Bett oder die Vorform des Füllstoffmaterials ein erstes Porensystem aus einer groberen Zwischenteilchenporosität oder aus Zwischenräumen aufweist, durch das das permeable Bett oder die Vorform der Füllstoffmaterialteilchen verteilt sind;

(b) in Gegenwart eines Dampfphasenoxidationsmittels Schmelzen des Grundmetallkörpers und Umsetzen des schmelzflüssigen Metalls mit dem Oxidationsmittel unter Bildung von Oxidationsreaktionsprodukte durch Erhitzen auf eine vorgegebene Temperatur, und bei dieser Temperatur Halten wenigstens eines Teils des genannten Oxidationsreaktionsprodukts in Kontakt mit und zwischen dem Körper aus schmelzflüssigem Metall und dem Oxidationsmittel, um fortschreitend schmelzflüssiges Metall durch das Oxidationsreaktionsprodukt zu dem Oxidationsmittel und dem Füllstoffmaterial zu saugen, so daß sich fortgesetzt Oxidationsreaktionsprodukt innerhalb des genannten Betts oder der Vorform des Füllstoffmaterials an der Grenzfläche zwischen dem Oxidationsmittel und vorher gebildetem Oxidationsreaktionsprodukt bildet, und Fortsetzen der genannten Umsetzung für eine Zeit, die ausreicht, um wenigstens einen Teil des genannten Betts oder der Vorform des Füllstoffmaterials zu infiltrieren, dadurch gekennzeichnet, daß die individuellen sehr feinen Teilchen des Füllstoffmaterials, die in den keramischen Verbundgegenstand inkorporiert werden sollen, in Form von groberen porösen Agglomeraten aus stabil zusammenhängenden feinen Kristalliten eingesetzt werden, innerhalb welcher Agglomerate ein zweites Porensystem existiert, das von einer untereinander verbundenen Infrateilchenporosität gebildet wird, wobei das genannte zweite Porensystem von Poren gebildet wird, die eine ähnliche Größe wie die Kristallite aufweisen und die während der Infiltration des permeablen Betts oder der Vorform des Füllstoffmaterials mit dem Oxidationsreaktionsprodukt strukturell stabil in einer aufrechterhaltenen porenden definierenden Anordnung sind.

2. Verfahren nach Anspruch 1, bei dem die genannten Agglomerate ausgewählt sind aus der Gruppe, die besteht aus nichtverformten porösen Teilchen von alpha-Aluminiumoxid, die durch Calcinieren von Aluminiumoxidtrihydrat hergestellt wurden und jeweils aus einer Vielzahl von sehr feinen alpha-
Aluminiumoxidkristalliten mit einer Kristallgröße im Bereich von 0,5 bis 5 um gebildet werden, aus sprühgetrockneten oder agglomerierten und teilweise gesinterten Teilchen eines inerten Füllstoffmaterials, aus sprühgetrockneten oder agglomerierten Metallpulverteilchen, die durch Nitrieren oder oxidationsreaktionsgebunden sind, und aus carbothermisch reduzierten sprühgetrockneten oder agglomerierten Teilchen von Oxidvorläufern.

3. Verfahren nach Anspruch 2, bei dem das genannte Bett oder die Vormasse aus Füllstoffmaterialteilchen einen Haupt-Gewichtsanteil der genannten Agglomerate in Form der genannten nichtvermahlten Teilchen sowie einen geringeren Gewichtsanteil von Teilchen, die kleiner sind als die genannten nichtvermahlten Teilchen, aus einem funktionell inertem Material aufweist.

4. Verfahren nach Anspruch 3, bei der der Anteil der genannten kleineren Teilchen ein solcher ist, daß die genannten kleineren Teilchen im wesentlichen die Zwischenräume zwischen den Agglomeraten füllen, welche Zwischenräume Teil des ersten groberen Porensystems sind.

5. Verfahren nach irgendeinem der vorausgehenden Ansprüche, bei dem die genannte Vormasse eine Vormasse von selbsttragender Form ist, die dadurch gebildet wird, daß man die Agglomerate aneinander bindet.


8. Verfahren nach Anspruch 1, bei dem das genannte Oxidationsreaktionsprodukt sich auch innerhalb wenigstens eines Teils des genannten zweiten Porensystems bildet.


11. Ein Gegenstand, wie er nach einem Verfahren nach irgendeinem der vorausgehenden Ansprüche erhalten wird.

Revendications

1. Procédé pour incorporer une charge très fine dans un article composite céramique comprenant une charge principalement inerte du point de vue fonctionnel dans une matrice céramique d’un produit réactionnel d’oxydation, dit article composite céramique étant obtenu par un procédé qui comprend les étapes consistant :
   (a) à orienter un corps d’un métal-mère et un lit perméable ou une préforme de matière constituant une charge l’un par rapport à l’autre en vue de l’infiltration d’un produit réactionnel d’oxydation du métal-mère avec un oxydant dans le lit ou la préforme perméable de charge, le lit ou la préforme perméable de charge comprenant un premier système de pores formé d’une porosité inter-particulaire ou d’interstices assez grossiers distribués dans tout le lit ou la préforme perméable de particules de charge ;
   (b) en présence d’un oxydant en phase vapeur, à faire fondre le corps de métal-mère et a faire réagir le métal fondu avec l’oxydant pour former un produit réactionnel d’oxydation, par chauffage à une température prédéterminée et, à ladite température, à maintenir au moins une portion du produit réactionnel d’oxydation au contact du corps de métal fondu et de l’oxydant et entre eux, de manière à attirer progressivement du métal fondu à travers le produit réactionnel d’oxydation en direction de l’oxydant et la charge afin que du produit réactionnel d’oxydation continue de se former dans le lit ou la préforme de charge à l’interface entre l’oxydant et le produit réactionnel d’oxydation.
précédemment formé et à poursuivre ladite réaction pendant une durée suffisante pour imprégner une portion au moins du lit ou de la préforme de charge,
caractérisé en ce que les très fines particules individuelles de charge devant être incorporées dans l'article composite céramique sont prévues sous forme de masses agglomérées poreuses assez grossières de fines cristallites à cohésion stable, masses agglomérées dans lesquelles existe un second système de pores constitué d'une porosité intraparticulaire interconnectée, ce second système de pores étant constitué de pores de diamètre semblable à celui des cristallites et de structure stable pendant l'infiltration du produit réactionnel d'oxydation dans le lit ou la préforme perméable de charge, avec maintien d'un agencement définissant des pores.

2. Procédé suivant la revendication 1, dans lequel les masses agglomérées sont choisies dans le groupe comprenant des particules poreuses non broyées d'alpha-alumine produites par calcination de trihydrate d'alumine et constituées chacune d'une multiplicité de très fines cristallites d'alpha-alumine ayant un diamètre des cristaux dans la plage de 0,5 à 5 \( \mu \text{m} \), de particules d'une charge inerte séchées par pulvérisation ou agglomérées et partiellement frittées, de particules de poudre métallique séchées ou pulvérisées ou agglomérées, liées par réaction de nituration ou d'oxydation et de particules de précurseurs d'oxyde, carbo-thermiquement réduites, séchées par pulvérisation ou agglomérées.

3. Procédé suivant la revendication 2, dans lequel le lit ou la préforme de particules de charge comprend une proportion dominante en poids des corps agglomérés sous forme de desrites particules non broyées et une proportion secondaire en poids de particules plus petites que les particules broyées, d'une matière fonctionnellement inerte.

4. Procédé suivant la revendication 3, dans lequel la proportion desdites particules plus petites est telle que ces particules plus petites remplissent principalement les interstices entre les masses agglomérées, ces interstices faisant partie du premier système de pores assez grossiers.

5. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la préforme est une préforme de configuration auto-portante constituée par liaison des masses agglomérées entre elles.

6. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le métal-mère comprend de l'aluminium.

7. Procédé suivant la revendication 6, dans lequel l'oxydant comprend de l'oxygène atmosphérique et le produit réactionnel d'oxydation comprend de l'alumine alpha contenant facultativement des constituants non oxydés du métal-mère à base d'aluminium.

8. Procédé suivant la revendication 1, dans lequel le produit réactionnel d'oxydation se forme aussi dans une partie au moins du second système de pores.

9. Procédé suivant la revendication 1, dans lequel le métal-mère fondu est au moins partiellement infiltré dans le second système de pores.

10. Procédé suivant la revendication 1, dans lequel le produit réactionnel d'oxydation et le métal-mère fondu sont tous deux au moins partiellement infiltrés dans le second système de pores.

11. Article obtenu par un procédé suivant l'une quelconque des revendications précédentes.
FIG. 4