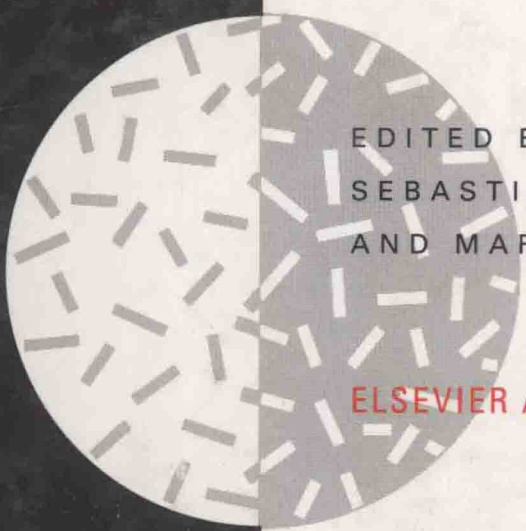
reinforced **ceramic** *composites*

A PATENT STUDY



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REINFORCED CERAMIC COMPOSITES

A Patent Study

INTRODUCTION

The present literature analysis on reinforced ceramics is the result of a comprehensive study of some hundreds of patents, patent applications from the United States, Western Europe and Japan, and other scientific and technical documents classified by the Netherlands Patent Office and the European Patent Office in Rijswijk, The Netherlands, according to the International Patent Classification System (IPC), class C 04 B 35/71 and subclasses thereof relating to artificial fibres, filaments and whiskers used in reinforcing ceramics.

From the study it became apparent that many attempts have been made in the past, since about 1920, to improve the properties of ceramics, such as their tensile strength, in order to use them for purposes other than, for example, chinaware.

In 1905 Bouvier discovered the strengthening effect of aluminium or silicon carbide crystals refractory ceramics.

Owing to the relatively low cost of raw materials used for the production of ceramic articles, many technologists have tried to make machine parts, such as bearings, heat exchangers and even cylinders of internal combustion engines, from ceramic material. Apart from the low cost considerations, some properties of ceramics, such as their low coefficient of expansion, their attractive moulding properties, their abrasion and pressure resistance, have given rise to attempts to apply them to mechanical parts usually made of metals.

In addition to their advantages, however, ceramics have some drawbacks resulting from their low tensile and impact strengths and their poor heat transition capacity. The latter disadvantage could be compensated by using ceramic parts as thin as possible, which may be acceptable, for example, for wafer-shaped heat exchangers which are usually not subjected to high tensile or impact loads, but not for high pressure or tensile stress loaded machine parts. It will therefore be obvious that technologists have made an approach to strengthen ceramic materials by fillers, such as fibres, filaments and whiskers.

The present book provides an insight into the development of various organic strengthening materials for ceramics since about 1960. The criterion chosen by the editors is the strengthening principle, with the exception of Chapter 8 which has to do with materials different from those discussed in the previous chapters, but which have strengthening features which are deemed of importance within the context of the present study.

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The editors owe their gratitude to the staff members of the Patent Information Division of TNO and to the officials of the Dutch and European Patent Offices, both in Rijswijk, as well as to the staff members of the library of the Technical University in Delft, who all were of great help in making pre-searches or in advising what IPC or library-entries had to be used to open the gate to the documents to be studied in the course of the present analysis.

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MARTEN TERPSTRA

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1.0 CERAMIC MATERIALS REINFORCED BY DENSIFICATION AND THE ADDITION OF PARTICLES.

General aspects

In preparing ceramic matrix composite materials by traditional methods several difficulties arise, especially in the densification step. Pressureless sintering can be difficult or impossible with particulate composites if the materials are not highly compatible. More importantly, it is impossible in most cases involving fibre composites, even when the materials are compatible, because the merging together of the particles is inhibited by the fibres which tend to prevent the necessary displacements of the densifying powder particles. These difficulties have been, in some cases, partially overcome by forcing the densification process through the application of external pressure at high temperature. However, this can generate many problems, including breakage of the reinforcing fibres, limitation of the capacity to produce complex shapes, and generally resulting in high costs caused by low productivity and the extensive finishing operations sometimes required.

Additionally, a uniform distribution of the second phase is hard to achieve. The resulting non-uniformities and/or undesired orientations of the reinforcing principle lead to loss in performance characteristics.

Another method for the formation of composites is by means of the reaction of gaseous species to form the desired ceramic (chemical vapour deposition).

This method is limited in its success, because the matrix deposition tends to occur on all of the composite second phase surfaces at once, such that matrix development only occurs until the growing surfaces intersect, with the trapping of porosity within the body being an almost inevitable consequence. Also the slow rate of matrix deposition makes such composites prohibitively expensive.

Another non-traditional approach involves the infiltration of the composite particles or fibres with a liquid organic material containing the necessary elements to form the desired matrix. Ceramic formation occurs by chemical reaction on heating the material. However, the elimination of the large amounts of volatile materials (necessary constituents of the initial flowable infiltrant composition) during the heating tends to leave behind a porous and/or cracked ceramic body.

US Patent No. 3 437 468 discloses composites made by a reaction process of molten aluminium with e.g. magnesium oxide, and silicon dioxide. However, the matrix constituents contain a large amount of magnesium aluminate, which has a low hardness and substantial amounts of silicon.

The European Patents No.s 155 831 and 169 067 disclose a method for producing a ceramic body by oxidation of a parent metal, which 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 reacts with a vapour-phase oxidant to form the oxidation reaction product.

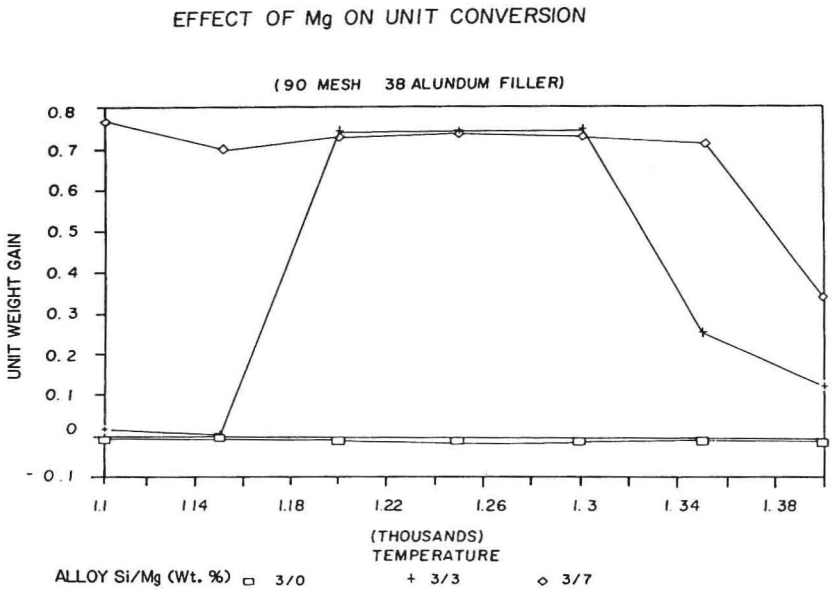
In certain cases one or more dopants, provided as alloying constituents of the parent metal, are required to facilitate growth of the ceramic body. Appropriate growth conditions for parent metals requiring dopants can be induced by externally applying layer(s) of dopant material to the surfaces of parent metals. Besides avoiding the necessity of alloying the dopant with the parent metal, it permits selective ceramic growth.

The aforementioned method of selective ceramic growth,in preparing composite materials, is extended by Newkirk M.S. et al. (**LANXIDE CORP.** (56.1)). It comprises the direction of the growth of a polycrystalline material resulting from the oxidation of a metal (the parent metal) towards a permeable mass of a filler, which is placed adjacent to the parent metal in the assumed path of the oxidation reaction product growth therefrom. The resulting matrix of polycrystalline material is simply grown around the filler material so as to embed the latter without substantially disturbing or displacing the array of filler material, or applying external forces. The growing polycrystalline matrix may also contain non-oxidized parent metal constituents.

Besides avoiding the costs involved with the extreme circumstances of hot pressing, it also avoids the damage resulting from high external forces. Additionally, the requirements of chemical and physical compatibility necessary for pressureless sintering to form ceramic composites are greatly reduced, or eliminated.

The reaction is continued for a time sufficient to embed at least a portion of the filler material within the oxidation product by growth of the latter. The resulting body is predominantly ceramic with respect to either composition or dominant properties although it may contain up to 40 vol.%, or more, metal.

Fig.1.1:



In figure 1.1, above, the unit weight gain (UWG) is shown for an aluminium parent metal, using a silicon carbide filler, having a diameter of less than 170 μm, as a function of the temperature and magnesium concentration. (UWG is the ratio of the final weight of the assembly minus the initial weight of the assembly divided by the initial weight of the parent metal ingot. Theoretically it can be as high as 0.89, indicating complete conversion of the aluminium to aluminium oxide.)

As parent metals titanium, zircon, silicon, tin, or aluminium may be used. When using aluminium or its alloys the polycrystalline material formed consists of α-aluminium oxide, and as an oxidant air of ambient atmospheric pressures may be used at temperatures of 900-1350 °C. The matrix contains preferably less than 10 wt.% magnesium aluminium oxidate spinel as an initiation surface, and 60-99 wt.% interconnected aluminium oxide or aluminium nitride.

The filler must be thermodynamically stable, and not volatile, under the temperature and oxidizing conditions as for example the oxides of rare earth metals, binary or higher order metallic compounds such as magnesium aluminium oxidate spinel ($MgO.Al_2O_3$) and stable refractory compounds. The filler materials may have diverse forms such as rods, bars, wires etc. Dopant materials are desirable to promote growth of the oxidation reaction product, and are important in controlling the microstructure. They may be

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chosen from a variety of compounds or mixtures thereof, as e.g magnesium, silicon, yttrium, and rare earth metals.
As oxidants all compounds able to remove electrons from metals, or sharing an electron under reaction circumstances are applicable.

A method for producing ceramic bodies having a predetermined geometry or shape is disclosed in the Commonly Owned Application Serial No. 861 025. The oxidation reaction product of a metal is infiltrated towards a defined surface boundary.
High fidelity is more readily achieved by providing the preform with a barrier means spaced from the metal for establishing a boundary or surface as disclosed in Commonly Owned Patent Application Serial No. 861 024.
Ceramic composites having a cavity with an interior geometry inversely replicating the shape of a positive mold or pattern are described in Commonly Owned Patent Application Serial No. 5 896 157.
All the aforementioned patent applications have in common that the ceramic body is produced by oxidation of a parent metal, which reacts with a vapour-phase oxidant to form the oxidation reaction product. The metal is heated to a temperature above its melting point, but below the melting point of the oxidation product. Filler materials may be incorporated and dopants can be employed to enhance the reaction. The composite contains between
1-40 wt.% of the parent metal.
Claar T.D. et al. (**LANXIDE TECHNOLOGY CO**. (56.4)) propose to produce a polycrystalline composite whereby the molten parent metal infiltrates a permeable mass of filler material and reacts in-situ with a vapour-phase oxidant. The respective rates of infiltration and oxidation reaction are controlled such that reaction takes place in at least a portion of the infiltrated filler mass. By means of such control the relative proportions of oxidized and non-oxidized parent metal within the composite microstructure can be varied to obtain desired end-use properties. Control of the process is achieved by:
i) Applying, when required, hydrostatic pressure to the molten parent metal.

ii) Regulating the inter-particle and the intra-particle pore size of the filler material. Pretreatment of the filler material to enhance wetting: removal of oxygen and/or moisture occluded on the surface of the filler material.
iii) Regulating the partial pressure of the oxidant in the vapour-phase, either by reduction of the ambient pressure, e.g. a vacuum, or diluting with an inert gas. Or applying, when required, pressure to 200 MPa, in order to increase the infiltration rate.
iiii) The use of dopants, which may be alloyed with the parent metal, coated on the surface of the parent metal, admixed in particulate form with the filler, or applied in a suspension as a coating of the filler.
As filler loose particles, 20-2000 μm in diameter, are suitable, having preferably a total porosity of 20-80 %, and an intra-particle pore size smaller than 5 μm. The particles may also be bonded together in a preform, or consist of whiskers, rods or platelets.
As parent metals silicon, aluminium or titanium can be used. If the composite should consist of the nitride of these metals, dopants such as copper, iron, and magnesium are applicable.
The process is controlled by the rates of metal infiltration and the oxidation or nitrification reaction. The treatment is carried out at 1500-1800 °C for 1-5 hrs.
Table 1.1, below,depicts the effect of the use of dopants in the densification of a silicon nitride polycrystalline composite produced from high purity silicon (Alpha grade Gn). The reaction conditions were in each case: a temperature of 1550 °C for 16 hrs, using 150-250 μm discrete agglomerate silicon nitride as a filler.

Table 1.1:

Test	Parent Metal	Weight Gain (% of Theoretical Maximum)
1	high purity Si	65
2	90% Si - 10% Fe	85
3	90% Si - 10% Cu	75

Silicon oxide can be converted into silicon nitride by a carbothermal reduction process in the presence of nitrogen. Silicon nitride has excellent intrinsic properties, but with the traditional ceramic fabrication techniques it could not be used to make dense bodies because of the highly covalent nature of the chemical bonding in this material and the corresponding low diffusion rates. Improvements were made by the discovery that aluminium could be incorporated. The materials thus formed were believed to be a single phase solid solution of aluminium oxide in silicon nitride. However, subsequently it was reported that this material was multi-phased, and the original formula incorrect. The solid solution existed between silicon nitride and aluminium oxynitride (Al_3ON_3).
The properties of the early materials were inferior to those of silicon nitride as a result of a residual grain boundary glass. The correct formula for aluminium substituted silicon nitride (ß-sialon) is: $Si_{6-z}Al_zN_{8-z}$, where $z \leq 4.2$ at 1750 °C.
Another non-oxide ceramic with excellent intrinsic properties is silicon oxynitride. This material has been used as a bonding phase for silicon carbide refractories. A limited replacement of silicon and nitrogen by aluminium and oxygen in silicon oxynitride (O-sialon) has been reported.
In the manufacture of silicon nitride and silicon carbide rice hulls can be used as raw material, disposing simultaneously of a waste problem. After the pyrolysis and subsequent ashing, a material containing in excess of 95 wt.% silicon can be obtained. However, a problem is that after the process unreacted silicon oxide can be present, which has to be removed. This usually involves leaching. The reaction rate can be increased with catalysts like iron. These additives are, however, detrimental to the product, impairing the mechanical properties and oxidation resistance, as well as promoting the decomposition of silicon nitride during sintering.
In US Patent specification 3 960 581 the production of ß-sialon is proposed, utilizing the reaction products of a carbothermal reduction. They were 15-70 wt.% aluminium, and 30-85 wt.% silicon nitride. But it is believed that the resulting ceramic material has inferior properties to those of silicon nitride and corresponding ß-sialons.
Trigg M. (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION (21)) formed a new ceramic product, composed of silicon nitride and silicon oxynitride, or aluminium substituted derivatives, and possible silicon carbide and fibre reinforcement, by a controlled carbothermal reduction process in the presence of nitrogen. The resulting material, which consists

of residual silicon oxide and silicon nitride, is fabricated into the desired shape of the product, followed by sintering in a nitrogen atmosphere at a temperature of 1400-2000 °C, with or without pressure.
It comprises 5-30 wt.% silicon, 3-10 wt.% aluminium, and 60-90 wt.% silicon nitride. The ceramic product comprises also silicon oxynitride. The silicon carbide content may vary up to 40 wt.%.
Sintering aids, which tend to go into the glassy phase, can be used to assist densification, in up to 20 wt.% of the product. Examples are lithium, beryllium, yttrium and members of the rare earth group.
The silicon oxide may be derived from pyrolysed rice hulls, which generally contains about 0.25 % aluminium in oxide form. After washing to remove foreign matter, rice hulls were heated under reflux conditions for 2 hrs. They were heated, after drying, in a nitrogen atmosphere and held at 700 °C for 2½ hrs to obtain silicon oxide and carbon. These products were heated in graphite crucibles in a tube furnace to 1450 °C, for 10 hrs to remove any remaining carbon.
The amount of silicon nitride produced will depend on the amount and type of impurities, reactivity of the reactants, rate at which gaseous reaction products leave the reaction zone, reaction temperature and time.
After mixing the powder, having a particle size of preferably less than 5 μm and an aspect ratio in the range of 5-22, with aluminium oxide, it was

Table 1.2:

SUMMARY OF HOT PRESSING

Specimen	Alumina Concentration (wt%)	Fired Density (g/cc)	MOR MPa	Vickers Hardness (GPa.)	Fracture Toughness ($MPa.m^{0.5}$)
A	1%	2.87	360	19.4	3.5
B	5%	2.91	300	19.1	3.4
C	9%	2.98	310	17.2	3.6

NOTES: Hot pressing conditions: (1) 1600°C for 15 minutes and 1800°C for 30 minutes; (2) 1600°C for 15 minutes and 1800°C for 40 minutes

isostatically pressed at 210 MPa, followed by hot-pressing at 35 MPa. Thus materials are obtained with a modulus of rupture (MOR) of 310-360 MPa, a Vickers hardness of 17.2-19.4 GPa, and fracture toughnesses of 3.4-3.6 $MPam^{\frac{1}{2}}$. (See the table 1.2, above.)

Ceramic composites can be made by infiltrating a molten matrix material into a compact filling material. There are, however, limitations to the applicability of this process. The molten matrix material may not have the requisite fluidity characteristic to function well as an infiltrant: the appropriate viscosity and melting temperature may not coincide with an economically feasible and non-destructive temperature and time.
Hillig W.B. (GENERAL ELECTRIC CO. (31.3)), provides a process which enables infiltration to be carried out at significantly lower temperatures, within commercially useful periods. It has the additional advantage that it is possible to fabricate a composite of the desired shape and size directly, so it needs little or no machining.
In the process a composite comprised of a matrix phase of 30-95 vol.%, and a ceramic filler phase of 5-70 vol.%, having a porosity of less than 10 vol.%, is made by forming a mixture of ceramic filler and a solid constituent of the abovementioned matrix, shaping it into a compact having an open porosity ranging from 30-90 vol.%, and contacting it with an infiltrant which is the remaining constituent of the matrix phase. (Any binder, lubricants or similar material used in production of the compact should be of the type which evapourates at temperatures of below 500 °C). The infiltrant has to have a liquidus temperature at least 100 °C lower as the matrix phase, and a maximum viscosity at least 50 % less than that of the matrix phase at infiltration temperature. Preferably, a layer of infiltrant is deposited on an as large as possible surface area of the compact to promote infiltration. Finally, the two components of the matrix phase are homogenized by heating at an appropriate homogenization temperature for less than 100 hrs.
The matrix material should have a particle size in the range of 2-200 μm, for control of the infiltrating rate of the filler. The particular ceramic filler used depends on the particular properties desired, its size should

be 0.5-25 μm. Examples are carbides, nitrides, borides and silicides, with particle sizes of 1000 μm or less; ceramic oxides are not useful.
The method is especially suited for metal aluminium oxidates, e.g. calcium aluminium oxidate ($CaO \cdot Al_2O_3$) or the alkaline earth aluminosilicon oxidates, e.g. strontium feldspar ($SrO \cdot Al_2O2SiO_{2)}$.
In an embodiment of the in situ formation of a cordierite phase, silicon carbide powder was mixed with a 3:2 molar blend of silicon oxide and aluminium oxide, with particles sizes between 2-5 μm. The mixture was pressed into a compact, which was placed on a carbon felt mat and its top surface was covered with a layer of magnesium silicon oxide granules. This was placed in a carbon mold and heated to 1650 °C, at 133 Pa for 10 min. A dense composite having no measurable open porosity was obtained.

Methods used in producing densified ceramic bodies as hot pressing in a rigid mold or hot isostatical pressing are not suitable for all kinds of sizes and shapes of articles. Undesirable density gradients as a result of non-uniform pressure distribution during pressing can cause fraction. Another problem can be adhesion of the sample to the mold.
Pechenik A. et al. (THE DOW CHEMICAL CO. (26)) suggest a process comprising heating the ceramic material between the lowest temperature at which sufficient deformation occurs in order to achieve the desired density and 2000 °C, and applying a pressure of 350-2400 MPa for less then 15 min.
The authors regard the process as applicable to many ceramic materials or combinations thereof. Zircon oxide, either or not in combination with a stabilizing agent is recommended as the most suitable material.
The temperature should be greater than that at which a pressure of 700 MPa will achieve at least 85 % of the theoretical density within 2 seconds, and at which recrystallization and grain growth occur. The rate of pressure increase should be greater than 700 $MPasec^{-1}$. The pressure, in the range of 700-1000 MPa, applied in a isostatically, must be sufficient to achieve the aforementioned 85 % density in less then about 5 seconds.
The process described allows, according to the authors, significantly lower temperatures and times for densification of ceramic bodies, thereby minimizing grain growth during densification.

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