

T U H H - A D V A N C E D C E R A M I C S G R O U P

REACTION-BONDED Al_2O_3 (RBAO) AND RELATED TECHNOLOGY

Novel Technology developed by the Advanced Ceramics Group of TUHH for the Manufacturing of Low-Shrinkage, High-Strength α - Al_2O_3 , β/β'' - Al_2O_3 and other Al_2O_3 -Based Ceramics

Introduction

Reaction-formed ceramics exhibit several advantages when compared to conventionally manufactured ceramics; e.g., low to zero shrinkage, clean grain boundaries and suitability as matrix for composite fabrication. Until recently, R + D activities have concentrated on reaction-bonded Si_3N_4 (RBSN), reaction-bonded SiC (RBSC), CVD-based processes and self-propagating high-temperature synthesis (SHS). Newer developments represent directed oxidation of molten metals (DMO) and polymer-derived ceramics, such as active-filler controlled pyrolysis (AFCOP).

On a larger scale, only the DMO process (LANXIDE) renders ceramic composites based on Al_2O_3 , the most important high-performance engineering ceramic. Due to the fact that the Advanced Ceramics Group of TUHH has been carrying out research on AFCOP, RBSN and DMO for quite a while, we recently succeeded in developing a process to manufacture Al_2O_3 (α and β/β'') and Al_2O_3 -based composites essentially by oxidizing Al powder to Al_2O_3 followed by sintering. The process shows some analogies to both RBSN and DMO technology, however, higher densities and strengths are exhibited by RBAO than are true for RBSN, and the process usually is faster, more versatile, and reproducible and easier to control than DMO. It might have been obvious to utilize the oxidation of Al powder to make Al_2O_3 , however, the pyroforicity of fine Al powder has so far prevented successful application of RBSN-type technology.

The RBAO Process

Al metal powder, usually 10 to 200 μm in dia., flaky or globular, and Al_2O_3 is attrition milled in a fluid like acetone or isopropanol. Tetragonal ZrO_2 (TZP) milling media are especially

suitable because the ZrO_2 wear (3 to 5 %) stimulates the reaction bonding process. When Al_2O_3 milling balls are used, some ZrO_2 should be added to enhance the reaction sintering process. Si, Cr, Zr powder, zircon sand, forsterite, mullite, silica, SiC or Si_3N_4 can be added to modify the reaction bonding process and correspondingly the product. During milling, the Al metal as well as the ceramic particles are converted to a homogeneous, mostly submicron powder mixture with parts of the second phases finely dispersed, i. e., mechanically alloyed into the Al metal. This mixture can easily be dried and safely handled in air because of partial passivation of the Al particles (ca. 15 - 35 % of the Al metal is oxidized on milling, essentially into $\gamma'-Al_2O_3$).

Any P/M forming technique, e.g., isopressing, slip and tape casting, extrusion or injection molding can be applied to compact and shape the green bodies. Due to the presence of metallic Al, the friction is reduced, green strength is enhanced (up to 50 MPa when isopressures of 600 MPa are applied) and green bodies can be further shaped even by EDM. Hence, the green bodies can also be used as machinable preforms.

The type of heat-treatment cycle in air (also humid air or oxygen) represents the base for a variety of unique microstructures:

For fully oxidized bodies or matrices, a slow heating rate or rather a two-step cycle is preferred if no or only small amounts of ZrO_2 (< 5 %) are present. In the first cycle at 800 to 1100°C, Al particles (or other mechanically alloyed elements, such as Zr, Cr, Si, Ti, etc.) are oxidized. About 30 to 50 % of Al is oxidized on heating below the melting point of Al. Therefore, at temperatures above the melting point, no melt coagulation or sweating out takes place due to the confining oxide skin. This fact leaves reactive second-phase particles or fibers unattacked by molten Al. Further oxidation of Al occurs by O_2 diffusion along the grain boundaries of nanometer-sized freshly formed Al_2O_3 crystals. The expansion associated with the Al - Al_2O_3 reaction (28 %) is compensated for in the second heating step at temperatures > 1200°C by sintering. Freshly formed submicron crystals are the reason for the low sintering temperatures. In a modified version of the RBAO process, SiC or Si additives, for

instance, are fully reacted to mullite, or zircon (ZrSiO_4) is partially dissociated and reacted also to mullite. Fine ($\sim 1 \mu\text{m}$) SiC particles, e.g., added as 5 to 15 μm abrasive particles to facilitate comminution of Al, are first oxidized (associated with 108 % volume increase) and then converted fully or partially into mullite. In Si-free composites, glassy phases have not been observed at grain boundaries. With the addition of other alloying elements, such as Zr or Cr, further expansion on oxidation (i. e., 49 % ZrO_2 , 102 % Cr_2O_3) further compensates for the shrinkage on sintering and, thus, allows for enhanced near-net-shape processing.

When larger amounts of ZrO_2 (also formed from Zr metal) are present, e. g., 5 to 20 vol%, fast reaction times can be realized, possibly due to the oxygen conductivity of ZrO_2 and a catalytic effect of Zr or ZrO_2 . Even one-step reaction sintering, hence, conventional type sintering is possible leading to full oxidation and high densities. Furthermore, ZrO_2 -toughening becomes available.

Fast heating to temperatures $> 1300^\circ\text{C}$ leads to bodies with a white dense Al_2O_3 coat with a cermet-type Al/ Al_2O_3 core. The thickness of the oxide coat can be controlled by the heating rate. This allows the manufacturing of functionally graded materials. Only ZrO_2 contents $> 20 \text{ vol}\%$ enable full oxidation and sintering under rapid heating conditions.

As a consequence of the small Al_2O_3 -crystal size, fully and partially sintered RBAO bodies can be shaped superplastically at relatively low temperatures, an opportunity for dense composite formation.

Composite Formation

The RBAO process is not only suitable to fabricate monolithic Al_2O_3 or Al_2O_3 -containing bodies, but also renders an ideal matrix for a variety of different composite types. Especially due to the low shrinkage, large (non-shrinking) second-phase particulates (e.g., fibers, platelets, etc.) can easily be incorporated into an RBAO matrix. When low sintering temperatures ($\sim 1300^\circ\text{C}$) are used, a

fine (0.1 to 0.7 μm dia.) open porosity can be obtained which is suitable for metal infiltration or filter application. Such porous RBAO bodies have been pressure infiltrated (e.g., by gas pressure or squeeze casting) with Al leading to strong enhancement of mechanical properties. Metal infiltration of composites leads to DMO-type microstructures with very homogeneous microstructures. For instance, RBAO composites with up to 40 vol% SiC particles (28 to 400 μm) have been manufactured.

Mechanical Properties

Fully oxidized RBAO with e.g. 4 % linear shrinkage (93 % TD) exhibits an average 4-point bending strength of ~ 600 MPa and a toughness of ~4 MPa/m, comparable to conventionally sintered high-density (> 99 % TD) Al_2O_3 . ZrO_2 -containing RBAO shows strengths of > 700 MPa under equivalent processing conditions and strengths of > 1200 MPa after consecutive HIP'ing. Al-infiltrated, Al_2O_3 platelet containing RBAO composites easily exceed 700 MPa and 8 MPa/m. Reaction bonded mullite consisting of 95 % mullite (rest Al_2O_3 , ZrO_2) has been fabricated by RBAO technology with zero shrinkage (97 % TD) and 4-point bend strengths > 300 MPa, using fine SiC powder. It must be pointed out though that, up to now, no microstructure and property optimization has been carried out.

Advantages of RBAO Process and Product

1. All ceramic and P/M compaction and forming techniques can be applied. Due to the presence of metallic Al, green strength is high, the friction is reduced and EDM may be used to perform precision green machining (if necessary).
2. Cheap and impure (e.g., SiO_2 containing Al_2O_3) raw materials can be used to achieve high-quality products.
3. Low reaction bonding and sintering temperatures are required.
4. Additions of ZrO_2 lead to both reduced reaction times and transformation toughening.
5. Intergranular glassy phases are only found in Si-containing RBAO. Most silicious phases are crystallized to either mullite or zircon.
6. RBAO bodies exhibit small to zero dimensional changes during heat treatment, i.e. near net-shape fabrication is possible.

7. The strength of RBAO bodies is higher than that of conventionally sintered Al_2O_3 at given porosities (e.g. 600 MPa at 93 % TD).
8. RBAO technology can be modified by a variety of additives, such as Zr, Cr, Nb, Si, SiC, etc. to yield composite oxides, mullite, etc. These modifications offer enhanced near-net shape capabilities.
9. An interesting RBAO-modification can be made by adding Na_2O or Na_2CO_3 (plus small amounts of Li_2O and MgO) to produce $\beta/\beta''\text{-Al}_2\text{O}_3$ of high mechanical strength (> 300 MPa) and high β''/β -ratios.
10. The size of the pores in fully reacted bodies is small (0.1 to $< 1 \mu\text{m}$) and their distribution is very homogeneous. The pore structure (open/closed) is adjustable by the heat-treatment used.
11. Open-porosity RBAO ceramics are suitable for filtration purposes and for metal infiltration.
12. Metal infiltrated RBAO can be precision machined by EDM, it furthermore facilitates joining to metal parts.
13. Bodies with cermet-type core structure coated by a dense Al_2O_3 layer can be prepared by partial reaction followed by sintering.
14. RBAO technology is ideally suited to fabricate a great variety of composites comprising small to very large second-phase particulates (e.g. platelets, whiskers, fibers, etc.).
15. Fully and partially sintered RBAO bodies can be used as superplastically shapable preforms.

Further Research

Presently one senior scientist, two Ph.D students (Topics: "ZrO₂-toughened RBAO" and "In situ whisker formation in Nb-RBAO") and several M.S. students (Topics e.g.: "Extension of RBAO technology to mullite and other oxide ceramics", "Application of RBAO Technology to $\beta''/\beta\text{-Al}_2\text{O}_3$ " and "Slip casting of RBAO composites") are performing research in the field of RBAO. A cooperative research project (with M. Rühle, MPI Stuttgart) on high-resolution TEM of RBAO and RBAO composites is being carried out. Further cooperation on RBAO-type mullite is being performed with A.H. Heuer, Case Western University, Ohio, USA. Due to the broad

variability of RBAO technology, however, much further research is needed.

Patent and License Situation

A German patent filed on April 4, 1988, has been granted on August 24, 1989 under DE 38 12 266 C1. A European equivalent (PCT/EP89/00382) has been positively examined and published under No. 0412975 on February 20, 1991. The regional phase of this application has been filed on April 9, 1990 under No. 89 904 545.4. The US application has been filed on September 27, 1990 and positively examined (No. 585,119) and the Japanese application on October 11, 1990 (No. 01-504100) with an examination request filed March 14, 1991, both on the base of PCT/EP/00382 with the priority of April 04, 1988. The international examination report, issued June 13, 1990 by the European Patent Office has confirmed a) the novelty of the application PCT/EP 89/00382, b) the inventive creativity and c) the commercial usefulness.

Furthermore, an extension of RBAO technology to mullite and mullite/ Al_2O_3 bodies has been filed on May 29, 1990 as German patent application DE 40 17 262.7 and a further extension under DE 40 39 530.8 on December 11, 1990 (PCT equivalent PCT/EP 91/00986, published December 12, 1991 under WO 91/18846, US and Japanese applications have been filed). RBAO technology using Zr metal alloy additions and consequent ZrO_2 -toughening of RBAO has been applied on December 11, 1990 under DE 40 39 531.6 and DE 41 26 782 (PCT, European (No. 91 120 788), US (No. 786,196) and Japanese (No. 325 481/91) applications have been filed. A new German patent (No. 41 19 705) on functionally graded ZrO_2 -toughened RBAO has been applied for. Therefore, RBAO product and process can now be licensed to the ceramic industry. Due to pronounced differences both in processing and in mechanisms, infringement of Lanxide technology related patents is not possible [See comparison of DMO (Lanxide) and RBAO process].

Comparison of DMO (Lanxide) and RBAO Process

DMO

RBAO

P R O C E S S

Al ₂ O ₃ grows from molten Al pool	Mechanically mixed Al/Al ₂ O ₃ powder is first oxidized, then sintered
Shape formation takes place by "infiltration" of oxide product into porous preform	all powder metallurgical (P/M) forming techniques (e.g., iso-pressing, injection moulding, etc.) are applicable
Al ₂ O ₃ growth product must be stopped by barrier material (e.g., CaO) to confine it to preform shape	Final form and shape is determined by P/M forming technique
Green machining of preform is difficult due to low green strength (<0.5 MPa)	Green machining is easy due to high green strength (>20 MPa)
Metal dopants, such as Mg and Si, are necessary, i.e., growth cannot be initiated without Mg or Si	No dopants are required, but ZrO ₂ improves the process considerably
Processing time is about 12 hours for 1 cm ³	Processing times are shorter, especially when ZrO ₂ is present (e.g., 2 hours for 1 cm ³)
DMO process can only be applied to form Al ₂ O ₃ matrix, i.e., mullite and ZrO ₂ -toughened Al ₂ O ₃ cannot be made due to reaction with molten Al	RBAO process is not only applicable to produce Al ₂ O ₃ , but also mullite, mullite/Al ₂ O ₃ and ZrO ₂ -toughened Al ₂ O ₃ and mullite as well as some other oxides

P R O D U C T

Final Al ₂ O ₃ product always contains 10 to 30 % of residual metallic Al	Product is fully oxidized to Al ₂ O ₃ (but can be left partially unoxidized in body interior)
Al ₂ O ₃ /Al product is pore-free	RBAO contains micropores (2 to 8 %)
Shaped products containing mainly Al ₂ O ₃ (except for Al) can only be made by using Al ₂ O ₃ preform	Composition of final product is controlled by compositions of powder mixture

Al ₂ O ₃ grain size ranges between 2 and 20 μm, essentially controlled by preform microstructure	Very small Al ₂ O ₃ grain sizes (0.2-2 μm) are obtained
Not superplastic	RBAO can be shaped superplastically
Strength of Al ₂ O ₃ /Al matrix product varies between 200 and 300 MPa	Strength ranges from 400 to >700 MPa with ZrO ₂ additions
Fracture toughness is controlled by residual Al metal	Fracture toughness is comparable to conventionally sintered Al ₂ O ₃ or ZTA
Not applicable to DMO	Green product can be used as preceramic (e.g., plates, bars, etc.) shippable to final producer

M E C H A N I S M S

Liquid Al reacts with gaseous oxygen	Fine solid Al particles (at temperatures <600°C) and liquid Al (>600°C) droplets are oxidized before sintering
Oxidation of liquid Al is "dopant-disruptive"	Oxidation of Al particles is "self-disruptive"
Al ₂ O ₃ /Al growth takes place by capillary transport of liquid Al to growth front	Oxidation of Al particles takes place both by O ₂ gas and by O ²⁻ ion diffusion via Al ₂ O ₃ grain boundaries or via ZrO ₂ lattice
Al ₂ O ₃ growth occurs at T>T _m only (i.e., ~>900°C)	Oxidation occurs at T>T _m and at T<T _m (melting point of Al)
Long incubation period controlled by MgO and MgAl ₂ O ₄ formation exists	No incubation period
Si-enhanced wetting of Al ₂ O ₃ by liquid Al is required	Wettability of Al ₂ O ₃ by Al is not required

For further information please contact:

Prof. Dr. Nils Claussen
Advanced Ceramics Group
Technische Universität Hamburg-Harburg
P.O. Box 90 10 52
Denickestr. 15
D-2100 Hamburg 90
Phone: (+40) 7718-3037
FAX : (+40) 7718-2647