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Processing, reaction mechanisms and properties of oxidation-formed Al_2O_3 -matrix composites

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ABSTRACT

Reaction forming of non-oxides has been investigated and applied for long. Oxidation forming, however, has only recently been introduced in the form of directed molten metal oxidation (DMO) either into free space or into porous ceramics preforms. The newest technology in this respect is reaction bonding of aluminum oxide (RBAO) somewhat in analogy to RBSN. Both forming methods are outlined and compared.

INTRODUCTION

Reaction forming of ceramics as an alternative to conventional processing has been of general interest for long. Various advantages, such as low processing temperatures, low raw material costs, near-net-shape tailorability, and glass-phase-free grain boundaries are most attractive for many technical and high-performance applications. Especially the low to zero shrinkage capability makes most reaction forming techniques suitable for the fabrication of composites, e.g., CVI processing of SiC fiber composites. Most R + D activities have been emphasizing non-oxides, such as RBSN, RBSC, and CVD-SiC. Oxidation reactions have been widely studied, though not usually for the sake of producing ceramic components. Only a few years ago, directed oxidation of molten metals (DMO) has been introduced [1-4]. In this technique, an $\text{Al}_2\text{O}_3/\text{Al}$ composite is produced by oxidizing molten Al alloys. The most recently developed oxidation-forming technique is based on the reaction-bonding of Al_2O_3 (RBAO), essentially starting from a mixture of Al and Al_2O_3 powder [5-9]. This technology shows wide microstructural variability and a great application potential.

The objective of this paper is to summarize and compare results obtained in examining both DMO and RBAO technologies. In optimized modifications, zero shrinkage is achieved in both methods as indicated in Fig. 1 which compares three different ways of fabricating Al_2O_3 -based ceramics. In DMO processing, a porous ceramic preform, e.g., composed of large Al_2O_3 particles, is "infiltrated" by the $\text{Al}_2\text{O}_3/\text{Al}$ reaction product. While conventional sintering is associated with shrinkages of 15 to 20%, DMO and RBAO parts retain shape and dimensions of the preform and the green body, respectively. In the conclusion of this paper, the various characteristic differences between DMO and RBAO are outlined.

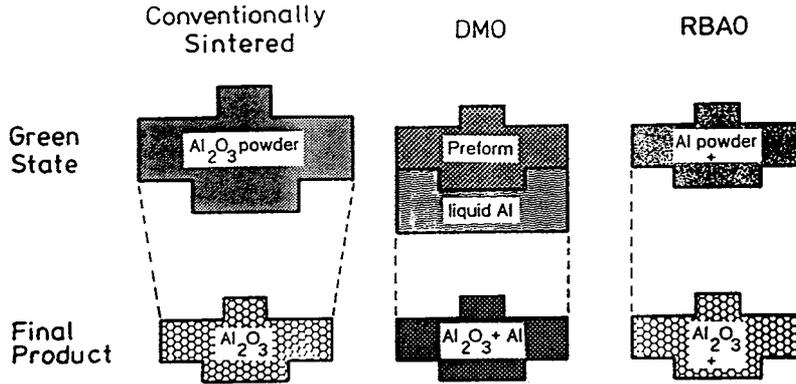


Fig.1 Comparison of different technologies for fabricating Al_2O_3 parts.

PRINCIPLES OF DIRECTED METAL OXIDATION (DMO)

The directed metal oxidation process is based on the reaction of a molten metal with an oxidizing gas; for example, the reaction of an aluminum alloy with air to form $\alpha\text{-Al}_2\text{O}_3$. In a certain critical temperature range above the melting temperature of the metal, the reaction product grows outward from the original pool surface either into free space (see Fig. 2a) or into a filler (see Fig. 2b). The reaction is sustained by the wicking of liquid metal through tortuous microscopic channels in the reaction product to reach the product-gas interface. The growth proceeds until the metal supply is consumed or until the reaction front meets a barrier material which suppresses any further reaction.

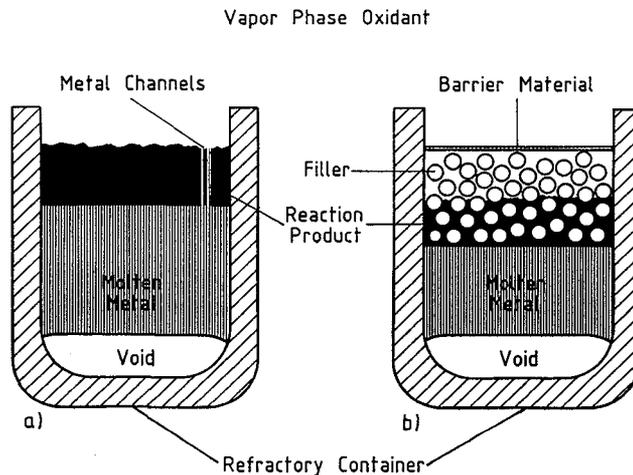


Fig.2 The directed metal oxidation process: Growth into (a) free space, and (b) a filler material. The void indicates that, in this small-scale experiment, capillary forces draw the liquid metal to the growth front against the influence of gravity [2].

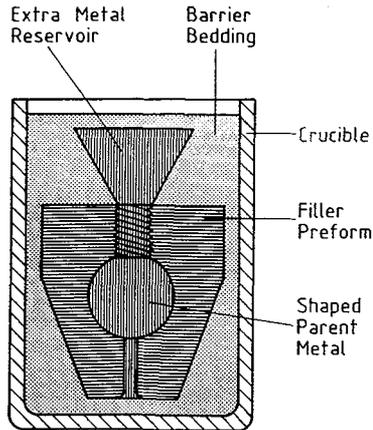
The reaction product that, in case where it "infiltrates" a porous filler, represents the matrix material is itself a ceramic-metal composite where both phases are three-dimensionally interconnected. The volume fraction of the metal may range from 0.05 to 0.3 depending on the processing conditions. Hence the mechanical properties tend to be dominated by the ceramic phase. The filler may be any material that is compatible with the reactant atmosphere and the molten metal. The filler may consist of particulates or fibers with a wide variety of possible sizes and shapes in various arrangements and volume concentrations. Some of the essential advantages of the process become apparent in the fabrication of complicated composite components; no shrinkage is involved and low temperatures are sufficient for matrix growth. Forming and shaping of the composite parts is achieved by utilizing one of two phenomena. In one method the shape and dimensions of the part can be determined by the shape of the filler preform which is coated with a barrier material preventing matrix overgrowth beyond the filler surface. Alternatively, the shape and dimensions of the original Al surface can be precisely replicated in the ceramic composite part, a method that is especially suitable for intricate internal surfaces not attainable by other techniques (Fig. 3). The nature of matrix growth has only been described for the Al_2O_3 -Al system, although some of the features of the process may also be characteristic for other ceramic-metal systems.

It is well known that oxidation of pure aluminum is usually slow due to the formation of a protective Al_2O_3 layer. In order to generate rapid and continuous growth of the oxidation product, certain dopants in the aluminum melt are necessary to initiate the growth, to prevent the formation of a protective reaction product and to improve the wettability of the growing Al_2O_3 and possibly that of the filler in respect to liquid aluminum. Alloying elements such as magnesium are suitable and active at the growth front in forming a thin MgO layer on the surface of the liquid metal.

The molten aluminum alloy is supplied to the surface by wicking through the microscopic channels of the Al_2O_3 product. The MgO layer prevents the formation of a protective Al_2O_3 layer; it also is believed to control the growth rate which is nearly independent of the thickness of the reaction product. This constant growth rate is analogous to the constant combustion rate of candles and oil lamps (which, with appropriate level markers, were utilized in ancient times as clocks). Hence, the liquid metal (liquid wax) supply is sufficiently rapid to allow the time-linear growth rates at otherwise constant process parameters. Typical growth rates are in the range of 0.5-0.8 cm per day with maximum rates of 3 cm per day.

In addition, the process may require another dopant selected from the group IVa elements, such as silicon. These elements may also enhance the wettability of Al_2O_3 with respect to liquid aluminum. Other additions to the starting aluminum alloy have been found to influence the microstructure (e.g. the fineness) of the reaction product and are useful in the tailoring of properties [4].

The critical temperature range in which growth takes place is determined by the threshold temperature for the formation of spinel (800-900°C) or for the nucleation of alumina, and by a reduced reaction rate at temperatures greater than 1400°C. A feature of the process is the reduction of less stable oxides (e.g. SiO_2) by the molten aluminum. Consequently the grain boundaries and filler matrix interfaces are free of glassy phases, SiO_2 can also be added as a dopant instead of free silicon, and the aluminum alloy phase in the



Ceramic Composite Shape Formation

Fig.3 Composite shape formation by the DMO process [2].

channel system of the matrix may become enriched in silicon. Increasing the partial pressure of the reactin gas accelerates the growth rate moderately. Certain materials, such as wollastonite, prevent or stop the reaction. These growth-inhibiting materials are, therefore, used as shape limiters.

One way of fabricating a part with precisely defined inner and outer shape is shown in Fig. 3. The filler preform, which has been placed around a machined parent metal part, is embedded in the barrier powder to prevent growth across the outer shape. The machined parent metal precisely replicates the inner shape of the final composite component.

As indicated in Fig. 2b, the reaction product grows progressively through the filler with no displacement or disturbance of the filler configuration. Composites using the Al_2O_3 matrix system uniaxially reinforced with SiC fibers have shown average strengths of 720 MPa and steady-state fracture toughnesses of $> 20 \text{ MPa m}^{1/2}$, ranking these materials among the toughest ceramics produced. In this case, the fracture toughness results from extensive debonding and pullout of the fibers from the grown ceramic matrix bridging the crack faces. But also systems with strong interfacial bonding show large toughnesses resulting from crack bridging by the ductile aluminum phase which necks down to sharp edges. Excellent mechanical properties are also obtained with platelet fillers [4].

PRINCIPLES OF REACTION-BONDED Al_2O_3 (RBAO) TECHNOLOGY

Al metal and Al_2O_3 powder, usually with 30 to 60 vol% Al, is intensively mixed in a ball mill with ZrO_2 milling media such that the Al is reduced to small ($\sim 1 \mu\text{m}$) particles with submicron Al_2O_3 and ZrO_2 dispersions. The ZrO_2 dispersion usually result from the wear of the milling balls (e.g., 3Y-TZP) while the Al_2O_3 originates both from the fines fraction of the admixed Al_2O_3 and the Al oxidation products caused by the milling process. After milling, the powder mixture is passivated such as to allow safe handling.

Any green compacting technique can be applied to form the required shapes. As shown schematically in Fig. 4, Al particles are plastically deformed which results in strong Al/Al contacts bridging the Al₂O₃ particles. Green density is, therefore, high and green strength may attain values more than an order of magnitude higher (20 - 50 MPa) than those of conventional ceramic green bodies. On heating the

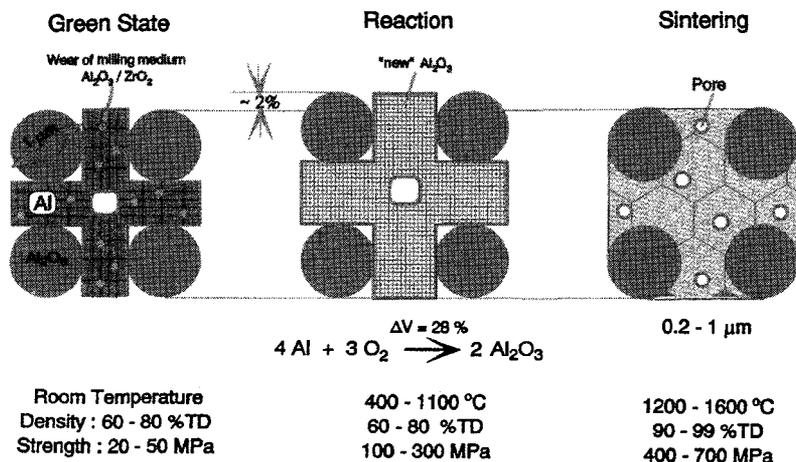


Fig.4 Schematic diagram of the RBAO process. In the green state, "old" Al₂O₃ particles are bridged by contacting Al particles containing oxide dispersions from mechanical alloying. In the reaction stage, associated with an expansion, Al transforms to nano-sized Al₂O₃ particles which sinter at temperatures > 1200 °C.

compact in an oxidizing atmosphere (usually air) to temperatures between 500 to 1100 °C, Al reacts to Al₂O₃ which is associated with a 28% volume expansion (reaction stage). In the sintering stage at temperatures >1200 °C, the body shrinks. The total dimensional changes during the complete process are small though because the expansion on reaction partially compensates for the shrinkage. Completely reaction-bonded bodies usually exhibit 3 to 8% homogeneously distributed micropores between grains of sizes <1 μm. The strength of RBAO samples is therefore higher than that of conventionally sintered Al₂O₃ bodies at a given density, e.g., >500 MPa at 94.5% TD and 20 vol% 2Y-TZP content.

The RBAO process can be modified in various ways by either metal (e.g., Zr, Cr, Si) or ceramic additives (e.g., ZrO₂, Cr₂O₃, MgO, SiC, etc.). The main purpose of ZrO₂ is to enhance the microstructural development, i.e., to promote homogeneity and to reduce grain growth. The other additives, e.g., SiC, are to further compensate for the sintering shrinkage by extended expansions during the reaction stage. The mechanisms taking place in the RBAO process have recently been analyzed [8]. It is obvious that they differ significantly from those occurring in the DMO process. Over 50% of the Al-to-Al₂O₃ reaction proceeds as solid state/gas reaction in the temperature range 520-580 °C. Above the melting point, 660 °C, further expansion takes place due to the completion of the reaction. The reaction is usually completed at 1000 to 1150 °C. Due to the extremely fine crystal size, sintering starts already at temperatures >1200 °C.

Dopants, such as Mg, Si, Zn, are not required to initiate and sustain the reaction as is the case for the DMO process. The facts that sustained oxidation at $T < 660^\circ\text{C}$ takes place and that the incubation period and the channel system associated with the growth of DMO products are lacking, are evidence for different oxidation mechanisms prevailing in either DMO or RBAO processes.

The reaction-bonding mechanisms suggested for the RBAO process, by which complete oxidation is achieved, are depicted schematically in Fig. 5. At temperatures $< 450^\circ\text{C}$, the amorphous thin passivating skin, coating the Al particles developed during milling, grows by Al^{3+} ions diffusing outward through the layer and reacting with oxygen. However, this mechanism contributes only little ($< 5\%$) to the total oxidation in this temperature range. At temperatures between 450° and 660°C , Al oxidizes directly to crystalline $\gamma\text{-Al}_2\text{O}_3$, and the preexisting amorphous phase also crystallizes to $\gamma\text{-Al}_2\text{O}_3$. Oxygen diffuses along grain boundaries in the oxide skin, which, because of its incoherent nature and the ultrafine grain size of the "new" Al_2O_3 crystals, offers an effective transport path, because of the 45% volume

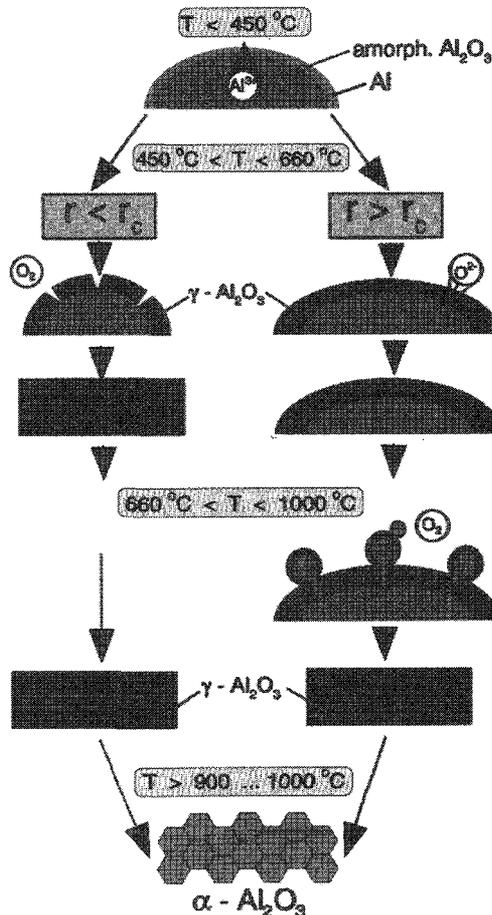


Fig.5 Model suggested for the reaction mechanisms operating in the RBAO process.

expansion associated with the $\text{Al} \rightarrow \gamma\text{-Al}_2\text{O}_3$ oxidation reaction, microcracks are formed in the oxide skin. Oxygen diffusion via microcracks is thus also possible. The volume expansion caused by the reaction, the thermal mismatch due to the large difference in thermal expansion coefficients of Al and Al_2O_3 , and the curvature-related pressure gradient across the oxide layer give rise to considerable hoop stresses in the oxide skin, which depends on the particle size of Al.

Considering particle size distributions normally encountered in milled powder systems, we may define a critical size of Al, r_c , below which the microcracks in the oxide skin are extended to macrocracks by the prevailing hoop stresses. However, the oxide skin coating larger Al particles ($>r_c$) remains stable, hence contains only microcracks. Then, in the reaction system, Al oxidation occurs either by oxygen diffusion along grain boundaries via microcracks in the large particles or, in the smaller particles, by gas diffusion via macrocracks in the oxide skin which continuously increases in thickness. Since the later process is faster than the former, the oxidation of small Al particles ($<r_c$) would dominate in the temperature regime between 450° and 520° , contributing significantly to the total reaction (e.g., $>30\%$, at $T = 520^\circ\text{C}$). The high exothermal reaction at $\sim 520^\circ\text{C}$ can then be explained by these arguments; i.e., the oxide layer of all of the small Al particles ($<r_c$) ruptures and complete oxidation takes place. At $>520^\circ$ further reaction occurs only in the remaining large Al particles ($>r_c$) by the above mechanisms. Consequently, the reaction rate slows down as seen in TG curves. Between 520° and 660°C only limited oxidation occurs.

At and above the melting temperature (660°C), oxidation of Al is again accelerated. Because of the 11.5% and 45% volume expansion associated with the melting and oxidation of Al, respectively, the pressure in the molten Al pool increases until Al permeates into the microcracks, puncturing the scale and spilling into the void space of neighboring particles. Because of bad wetting of Al_2O_3 by liquid Al, droplets form which are readily coated by an oxide skin again. This process continues until all Al is oxidized. Between 900° and 1100°C , γ - to α - Al_2O_3 phase transformation occurs.

In the sintering stage at $T > 1200^\circ\text{C}$, "old" Al_2O_3 particles are bonded by the "new" crystals and grain growth takes place in the final fully reaction-bonded body, "new" and "old" particles can no longer be distinguished as is also true for partially reacted compacts.

CONCLUSIONS

Both DMO and RBAO processes are ideally suited to fabricate ceramic-matrix composites mainly due to their low shrinkage. While DMO always contains some Al metal, which acts as toughening agent, RBAO renders a metal-free Al_2O_3 -based oxide matrix. DMO offers advantages for continuous fiber reinforcement, RBAO is rather suited for particulate dispersions. However, mullite-type modifications of RBAO [7] also represent ideal matrices for fiber composites. The RBAO process is much easier to reproduce than is DMO, however, for full density matrices, higher process temperatures are required for RBAO.

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REFERENCES

- [1] M.S. Newkirk, A.W. Urquhart, H.R. Zwicker, and E. Breval, "Formation of Lanxide Ceramic Composite Materials", *J. Mater.R.* **1**, (1986) 81 .
- [2] N. Claussen and A.W. Urquhart, "Directed Oxidation of Molten Metals", in *Encyclopedia of Mat. and Eng.* (Ed. R.W. Cahn), Supplementary Vol 2, Pergamon, Oxford, (1990) 1111 .
- [3] M. Sindel, N.A. Travitzky, and N. Claussen, "Influence of Mg-Al-Spinel on the Directed Oxidation of Molten Aluminum Alloys", *J.Am.Ceram.Soc.* **73**(1990) 2615
- [4] S. Anatolin, A.S. Nagelberg, and D.K. Creber, "Formation of Al_2O_3 /Metal Composites by the Directed Oxidation of Molten Al-Mg-Si Alloys". *J.Am.Ceram.Soc.* **75**(1992) 447
- [5] N. Claussen, Tuyen Le, and Suxing Wu, "Low-Shrinkage Reaction-Bonded Alumina", *J.Eur.Ceram.Soc.*, **5** (1989) 29-35
- [6] N. Claussen, N.A. Travitzky, and Suxing Wu, "Tailoring of Reaction-Bonded Al_2O_3 (RBAO) Ceramics", *Ceram. Eng. Sci. Proc.*, **11**, (1990) 806.
- [7] Suxing Wu and N. Claussen, "Fabrication and Properties of Low-Shrinkage Reaction-Bonded Mullite", *J.Am.Ceram.Soc.* **74**, (1991)
- [8] Suxing Wu, D. Holz, and N. Claussen, "Mechanisms and Kinetics of Reaction-Bonded Aluminum Oxide Ceramics", *J.Am.Ceram.Soc.*, **76** (1993) 970
- [9] D. Holz, Suxing Wu, and N. Claussen, "Processing of Reaction-Bonded Aluminum Oxide", *J.Am.Ceram.Soc.* **77**(1994)

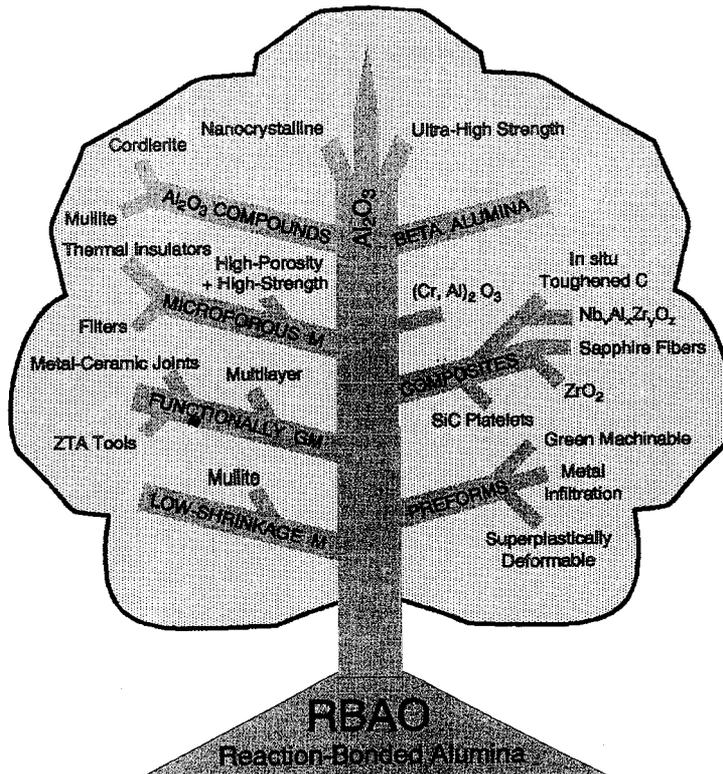


Fig.6 "Japanese tree" showing the various directions RBAO technology has taken.