Cyclic CIP of Reaction Bonded Aluminum Oxide (RBAO)

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反応焼結アルミナ (RBAO) のサイクリック CIP 成形

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Reaction bonded aluminum oxide (RBAO) is a promising oxide ceramic for engineering components due to its interesting characteristics, such as high green strength, low-to-zero shrinkage, and advanced mechanical properties. In the present work, the effect of Cyclic CIP on compaction of RBAO precursors and on properties of reaction sintered RBAO bodies was investigated. RBAO compacts were made by Cyclic CIP at 20 and 1000 cycles. A small number of cycles leads to RBAO compacts with homogeneous microstructure, however, further cycling results in degradation of the microstructure. After sintering, strength values of up to 690 MPa were obtained for samples with 20 cycles. This is more than 20% above the standard material made by ordinary CIP. This shows that Cyclic CIP can be applied as a successful compaction technique to improve the mechanical properties of metal/ceramic powder mixtures like RBAO precursor powders.

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1. Introduction

Engineering ceramics are expected for applications in diverse technologies including not only aerospace or nuclear fusion reactor power plants but also automobiles and wear resistant parts in daily life. However, expensive synthetic raw materials are required along with high temperature sintering, grinding, and polishing leading to high total costs which severely restrict engineering ceramics applications. Engineering ceramics produced via reaction forming exhibit various advantages when compared to conventionally manufactured ceramics. Low-cost raw materials, (near)-net-shape capability, and grain boundaries free of glass-phase are attractive attributes for many technical and high-performance applications.

Reaction bonding of aluminum oxide (RBAO) was developed by the Advanced Ceramics Group of Technische Universität Hamburg-Harburg as a new oxidation forming technique.¹⁾⁻³⁾ In this process, Al_2O_3/Al powder compacts are heat-treated in air so that the metal is oxidized to small "new" Al_2O_3 crystallites which sinter and thereby bond the larger "older" Al_2O_3 particles. Monolithic Al_2O_3 ceramics with low shrinkage have already been fabricated. The shrinkage on sintering is partially compensated due to the volume expansion of 28% associated with the reaction of Al to Al_2O_3 . However, in the pure RBAO system, in which only Al and Al_2O_3 are present, up to 15% linear shrinkage still remains when the final density exceeds 97%TD. In order to further reduce the shrinkage and even to achieve net-shape forming, the RBAO process can be modified in various ways by incorporating other metal or ceramic additives that exhibit a larger volume expansion on oxidation. For example, Zr is associated with a volume expansion on oxidation of 49%, Ti 76%, Cr 102%, Nb 174% and, when forming mullite from the addition of SiC via SiO_2 , the change is 132%. A more simple but very promising possibility to reduce the shrinkage on sintering is an advanced compaction technology in order to enhance the green density of the samples, e.g., by applying Cyclic CIP.

Cyclic CIP was developed by Matsuo et al. of Tokyo Institute of Technology.⁴⁾⁻⁶⁾ The method was designed for incorporating vibration forming into ordinary cold isostatic pressing. It has been demonstrated as an effective technique for fabrication of dense and homogeneous compacts under low pressures. A relative bulk density of conventional Al_2O_3 compacts was increased up to 74% by Cyclic CIP at 10000 cycles under a maximum pressure of 100 MPa and a minimum pressure of 0 MPa.⁵⁾ In case of conventional SiC, strength reliability of the sintered compacts was also improved by Cyclic CIP.⁶⁾ Although a large number of studies have been made on conventional Al_2O_3 and SiC powders, little is known about the effect of Cyclic CIP on compaction of advanced ceramic powders like RBAO precursors which include ductile metallic components.

In this study, the effect of Cyclic CIP on compaction of RBAO was investigated. RBAO compacts were made by Cyclic CIP at 20 and 1000 cycles. Green compacts were characterized by mercury porosimetry and strength measurements. After reaction bonding and sintering, strength and fracture toughness of RBAO were evaluated to study the effect of Cyclic CIP on RBAO.

2. Principle and technology of RBAO

The RBAO process starts with powder mixtures of Al (usually 30-60 vol%), Al_2O_3 , and ZrO_2 (0-20 vol%) which are intensively milled in an attrition mill so that the metallic Al (20-200 μm) is reduced to small particles (<1 μm) with Al_2O_3 dispersions. Spray drying in a closed cycle allows recycling of the milling liquid.

Any powder metallurgical forming technique, e.g., uniaxial pressing, isopressing, slip and tape casting, extrusion, low pressure injection molding, and green machining can be applied to compact and shape the green bodies. As shown in Fig. 1, Al particles are plastically deformed during compaction which results in strong Al/Al contacts bridging the ceramic particles. Therefore, green density is high and green strength attains values more than an order of magnitude

Cyclic CIP and Reaction Bonding of RBAO

Fig. 1. Schematic of the RBAO process including Cyclic CIP.

higher compared with conventional ceramic green bodies. Values of about 15 MPa are typical for ordinary green bodies, whereas up to 50 MPa can be obtained with high compaction pressures but without organic binders. Together with its good formability, RBAO compacts enable easy green machining^(7,8) or incorporation of second phases such as particles or fibers.^(9,10)

The RBAO heat treatment (Fig. 2) consists of two steps: reaction (300–1000°C) and densification (>1200°C). During reaction in an oxidizing atmosphere (usually air) the metallic Al oxidizes to Al_2O_3 . This oxidation exhibits a volume expansion of 28%. During sintering the level of shrinkage is higher than the level of volume expansion.

3. Experimental

The raw materials were milled in a continuous attrition mill (Draiswerke, Mannheim, FRG) for 2h at 3500 rpm in ethanol. ZrO_2 balls with a diameter of 1 mm were used as milling media. The composition of the powder mixture is listed in Table 1.

After milling, the RBAO powder mixture was spray dried (Closed cycle spray dryer, Niro, Copenhagen, DK). The particle size distribution of the milled and dried powder was analyzed by laser diffraction (Malvern Mastersizer S, Malvern, GB). Both primary particle size and granule size of spray dried powders were measured.

Disc shaped specimens with a diameter of 30 mm and thickness of 3 mm were prepared by uniaxial pressing at 20 MPa for 120 s. Samples were cold isostatically pressed in two different ways: (a) one cycle at a maximum pressure of 200 MPa for 120 s for standard compaction and (b) 20 and 1000 cycles at a maximum pressure of 200 MPa and a bias pressure of 0 MPa with a frequency of 1 Hz for Cyclic CIP. The influence of these process parameters in Cyclic CIP on the characteristics of compacts is described in detail elsewhere.^{(4)–(6)} Pore volume and pore size distribution of the green bodies were analyzed by mercury porosimetry (Poresizer 9320, Micromeritics, Norcross, USA). The specimens were reaction bonded and sintered in a standard box furnace (Nabertherm, Lilienthal, FRG) in air for 2h at 1550°C. The complete heating cycle is shown in Fig. 2.

The density of green bodies and sintered specimens was

Table 1. Powder Composition and Origin of Raw Materials

Contents	Material	Type and Source	Particle Size d_{50} [μm]
35 vol-%	Al	AS081, Eckart-Werke, Fürth, FRG	< 45
45 vol-%	Al_2O_3	CL 3000, Alcoa GmbH, Ludwigshafen, FRG	2.5
20 vol-%	m- ZrO_2	SF-Extra, ICI Z-Tech, Bow, N.H., USA	1
2 mol-%	Y_2O_3	Grade C, H.C.Starck GmbH, Goslar, FRG	0.31

Heating Cycle for RBAO Specimens

Fig. 2. Heating cycle for oxidation and sintering of RBAO bodies.

measured geometrically and by Archimedes method, respectively. The strength of both green bodies and sintered specimens was tested in a conventional testing machine (Zwick 1478) with a punch-on-3-balls arrangement (P3B).⁽¹¹⁾ Tests were carried out without grinding or polishing the samples in order to include the influence of surface quality on strength data.

Polished samples were used to determine fracture toughness by indentation-crack-length method using Vickers indentations with a load of 5 kg.

4. Results and discussion

The experimental results are summarized in Table 2. The analysis of particle size shows a distribution in the range of 0.6 to 10 μm with a median diameter of 0.89 μm for the primary particles. During spray drying, these particles form granules with a median diameter of 125 μm , ranging

Table 2. Summary of Experimental Results

Number of Cycles		1	20	1000
Green Density	[%TD]	53.1	58.7	60.33
Green Strength	[MPa]	16	13	14
Pore Volume	[ml/g]	0.92	0.20	0.72
Median Pore Diameter	[μm]	0.017	0.007	0.041
Sintered Density	[%TD]	98.4	99.9	100.0
Sintered Strength ^{a)}	[MPa]	560.0	687.5	563.6
Standard Deviation	[MPa]	43.1	81.0	167.7
Fracture Toughness	[MPa $\text{m}^{1/2}$]	3.26	4.16	3.70
Standard Deviation	[MPa $\text{m}^{1/2}$]	0.33	0.39	0.23

^{a)} Average of 10 specimens

Fig. 3. SEM micrograph of spray dried RBAO granules.

from 10 to 400 μm . Figure 3 shows a scanning electron microscope (SEM) micrograph of these granules.

The green density shows a significant increase with Cyclic CIP. From 53.1%TD for the standard material, the density was increased to 58.7% and 60.3%TD at 20 and 1000 cycles, respectively. The median pore size and pore volume of the green bodies decreased dramatically from 1 to 20 cycles, corresponding to the green density. It should be noted that, at this stage of the compaction process, the remaining pores are extremely fine and therefore may not be detected by Hg-porosimetry. Additionally, the use of high pressures in Hg-porosimetry systems can lead to closure of fine surface pores due to plastic deformation of Al particles.

Further cycling, however, causes an increase in both values (see Fig. 4). This increase of pore volume and diameter is caused by agglomeration of defects and pores at high cycle numbers. These pores can now be detected with accuracy. Therefore, the trend of the data is clear, although the absolute values may be questionable.

In spite of the significant increase in green density by Cyclic CIP, green strength remains unaffected (Table 2). This indicates that the strength of RBAO green bodies is dependent essentially on the strength of the metallic aluminum network and is less affected by green density of the specimens.

Corresponding to the green density, the sintered density of RBAO samples increases from 98.4 to 100%TD at higher cycle numbers (Fig. 5). However, bending strength of the sintered bodies cannot be related directly to this beneficial effect of cyclic compaction. As shown in Fig. 5, a low number of cycles leads to an increase in strength of more than 20% to 687 MPa which can be explained by homogeneous compaction at a low number of cycles, already indicated by density and Hg-porosimetry measurements of green bodies. The following decrease in strength to values close to the

Fig. 4. Pore volume and median pore diameter in RBAO green bodies, measured by Hg-porosimetry.

Fig. 5. Density and strength data of sintered RBAO specimens.

standard material is due to degradation of microstructure with formation of larger pores or agglomerates by further cycling.

Microscopic investigations of polished green bodies show the formation of defects. As illustrated in Fig. 6, a low number of cycles leads to a very homogeneous microstructure with small pores which are well distributed. By further cycling, the microstructure becomes inhomogeneous with areas of higher porosity and areas with increased density. Pores which were well distributed formerly coagulate forming large pores which lead to strength limiting defects in the sintered material. Furthermore, crack formation in the green body and fatigue of the metallic network has to be taken into account. The damaged areas in the green compact can grow during reaction bonding due to internal stresses induced by the volume increase combined with the oxidation of the metal phase.

K_{IC} values seem to be affected by cyclic compaction in the same manner as the strength data, but values are within the standard deviation. Therefore, a final statement on the effect of Cyclic CIP on fracture toughness is not possible yet.

Fig. 6. Microstructure of RBAO green bodies after Cyclic CIP. a) 20 cycles, b) 1000 cycles.

5. Conclusions

(1) Cyclic CIP can be applied as a successful compaction technique for metal/ceramic powder mixtures like RBAO precursor powders.

(2) Green density is enhanced by Cyclic CIP. A small number of cycles leads to green bodies with homogeneous microstructure. A high number of cycles results in degradation of microstructure with formation of larger pores and agglomerates.

(3) The density of sintered specimens reflects the development of green density with cycling. Cyclic CIP improves the mechanical properties of RBAO materials. Strength values of 690 MPa in punch-on-three-balls testing are more than 20% above those of conventional isopressed samples.

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