Ceramics International 30 (2004) 1945–1948

CERAMICS
INTERNATIONAL

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Joining advanced ceramics by plastic flow

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Received 8 December 2003; received in revised form 17 December 2003; accepted 22 December 2003

Abstract

Al_2O_3/Y_2O_3-stabilized ZrO_2 (YSZ) and $La_{0.85}Sr_{0.15}MnO_3$ ceramics were joined by plastic deformation at 1200–1350 °C. Pieces were joined directly to each other or with an interlayer. For some of the Al_2O_3/YSZ specimens, the interlayer was applied by spraying of powders entrained in an organic vehicle. All final joints were as dense as the host ceramics and generally featured finer grain sizes. When dissimilar compositions were joined, thermal residual stresses were generated. Choice of composition could tailor these stresses and produce joints that were as strong as the surrounding ceramics. Strength of the Al_2O_3/YSZ joints and the electrical resistivity of a joint in $La_{0.85}Sr_{0.15}MnO_3$ were as good as those of the host ceramics.

Keywords: A. Joining; B. Microstructure-final; C. Electrical properties; C. Mechanical properties

1. Introduction

Advanced ceramic components fabricated by economical means are required in many applications. Options for forming complex parts from simpler ones are restricted for ceramics. Unlike metals, which can be readily machined, or joined by mechanical fasteners, solidified molten zones, or glue, service for ceramics often demands high strength and thermal stability throughout the part. Discontinuities or softer filler materials are unacceptable. For electroceramics, adequate electrical properties are also required of any joint.

For ceramic parts that are assembled from simpler ones, joining can be accomplished by diffusional bonding [1] or plastic forming [2–10]. Plastic forming minimizes retained porosity, requires minimal surface preparation, and occurs at lower temperatures than does conventional diffusional bonding [7–10]. Plastic deformation during joining takes place by grain-boundary sliding [7–10]. At elevated temperature, the grains of adjoining polycrystalline samples slide and rotate under load to form a tight bond [7–10]. This technique can be applied in the solid state or in the presence of liquid phase. Total strains are <0.1, often <0.02, allowing for good overall control of dimensions.

Substantial advances have been made over the past few years in joining ceramics by plastic flow. This paper summarizes efforts to: (1) join structural ceramics based on Al_2O_3 and Y_2O_3-stabilized ZrO_2 (YSZ); (2) apply a sprayed interlayer to join Al_2O_3/YSZ ceramics, and (3) join the electroceramic $La_{0.85}Sr_{0.15}MnO_3$ (LSM). The LSM was joined to itself so that the electrical resistivity across the joint could be compared with that of the monolithic ceramic.

2. Experimental details

Al_2O_3/YSZ compacts were made from commercial powders: Al_2O_3 with 0.25 wt.% MgO from Malakoff Industries, Malakoff, TX, USA and 3-mol% Y_2O_3-stabilized ZrO_2 from Tosoh Ceramics, Bound Brook, NJ, USA. The average particle sizes were ≈0.5 μm for the Al_2O_3 and 0.1–0.2 μm for the Y-TZP. Particulate composites of various volume fractions were fabricated. Powders were initially ball-milled in a polyethylene jar containing ZrO_2 grinding media and isopropyl alcohol. They were then dried, cold-pressed into pellets, placed into ZrO_2 crucibles, and fired in air for 3 h at various temperatures. Specimens were >99% dense. Further details can be found in refs. [7–9].

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doi:10.1016/j.ceramint.2003.12.188

The LSM specimens were between 89 and 93% dense and were fabricated at Pacific Northwest National Laboratory [11,12]. The grains were equiaxed and ≈6 μm in average size, and most of the porosity was contained at the triple junctions [10]. Further details can be found in refs. [10–12].

LSM specimens were joined directly. Al_2O_3/YSZ specimens of various composition were either joined directly or with an interlayer separating them. The interlayer formulation was applied by spraying [9]. It consisted of powder, azeotropic solvent (xylene/butanol), binder (Rohm & Haas AT-51; Philadelphia, PA, USA), plasticizer (Monsanto S-160; Fayetteville, NC, USA), and dispersant (Solsperse S-9000; Avecia, Manchester, UK). (The AT-51 binder is a thermosetting acrylic polymer; the S-160 plasticizer is a butyl benzyl phthalate.)

The Al_2O_3/YSZ powders within the joint were one of two kinds. The first was mixed from the same powders that were used in the bulk pieces to be joined. The second powder was a 50-vol.% Al_2O_3/50-vol.% ZrO_2 mixture, but the Al_2O_3 was γ-phase and the ZrO_2 was unstabilized; i.e. no Y_2O_3 was present. These Al_2O_3 and ZrO_2 powders, purchased from Nanophase Technologies, Inc. (Burr Ridge, IL, USA), were ≤20 nm in diameter. After spraying, the organics were burned out by heating in air to 600 °C. Mating pieces, each with surfaces covered by porous Al_2O_3/ZrO_2, were then ready to be joined.

All specimens were joined in an Instron Model 1125 Universal Tester (Canton, MA, USA) that was fitted with a high-temperature furnace [13]. The Al_2O_3/YSZ specimens were compressed in Ar and the LSM specimens were compressed in air. Thin pieces of Pt foil prevented reaction between the push rods and the LSM. Average initial strain rates ($\dot{\varepsilon}$) were 1×10^{-5} to $5 \times 10^{-4}\ s^{-1}$. Total strains for the Al_2O_3/YSZ were 0.01–0.05 and total strains for the LSM were ≈0.1. A typical load/displacement curve is shown in Fig. 1; the specimen was deformed ≈9.4%.

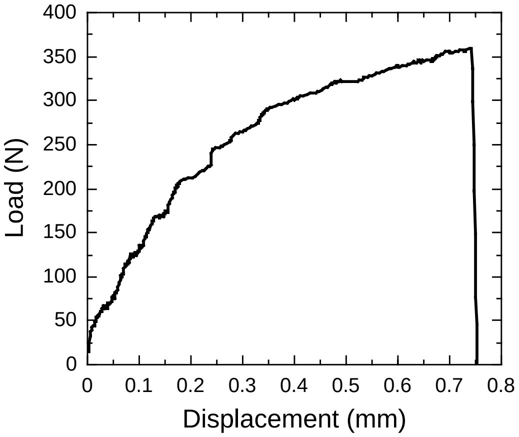

Fig. 1. Load/displacement curve for two pieces of dense 60-vol.% Al_2O_3/40-vol.% ZrO_2, joined with an interlayer of initially porous 50-vol.% Al_2O_3/50-vol.% ZrO_2; 1350 °C, strain rate $\approx 1 \times 10^{-5}\ s^{-1}$, ≈9% strain.

Joined samples were examined by scanning electron microscopy (SEM) in a Hitachi S-4700-II microscope (Tokyo, Japan), and either mechanical properties (hardness, fracture toughness, flexural strength, residual stresses) or electrical resistivity were measured. Resistivity measurements were performed at room temperature with a HP 4263B LCR meter (Hewlett-Packard, Palo Alto, CA, USA). Contacts were made with Pt mesh and wires [10].

3. Results and discussion

Dense pieces are used in most plastic joining of ceramics [2,6]. Monolithic YSZ has proved easy to densify [14] and join [2], but Al_2O_3/YSZ particulate composites have advantages of lower costs, higher hardness, lower creep rates [15], and tailored properties. For an industrial process, the advantages of applying the joint compound by a simple technique such as spraying are clear. Need to insert a dense compact between pieces to be joined will limit the shapes that can be joined. Not only did the sprayed interlayers work well, joints were formed between Al_2O_3/YSZ particulate composites of various composition. Joining was accomplished by compressing at 1350 °C; Al_2O_3-to-YSZ volume-fraction ratios ranged from 40/60 to 80/20 [7–9].

All of the joints within Al_2O_3/YSZ specimens were free of porosity. For joints made with a sprayed interlayer, substantial densification was required during compression. Because of low processing temperatures and relatively short times at temperature (≤2 h), the grains within the joints exhibited minimal growth (Figs. 2 and 3). Even the grain sizes of the nanophase Al_2O_3 and YSZ remained nearly unchanged during processing at 1200 °C. Dense, fine-grained microstructures for ceramics correspond to high strength. Thus, for a given composition, the hardness and strength of the joint material should exceed those of the host ceramics.

Varying the Al_2O_3-to-YSZ ratios allows for tailoring of residual stresses [7] because of differences in

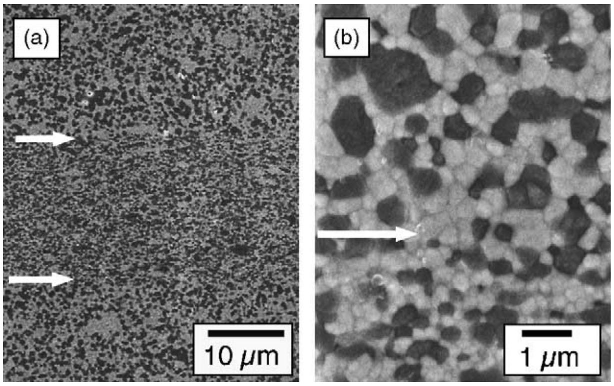

Fig. 2. SEM photomicrographs of (a) dense 50-vol.% Al_2O_3/50-vol.% YSZ joint between 40-vol.% Al_2O_3/60-vol.% YSZ compacts (Al_2O_3 is dark phase) and (b) interface between joint layer (bottom) and one compact (top), in which minimal grain growth in joint and high density are apparent; arrows mark approximate location of interface.

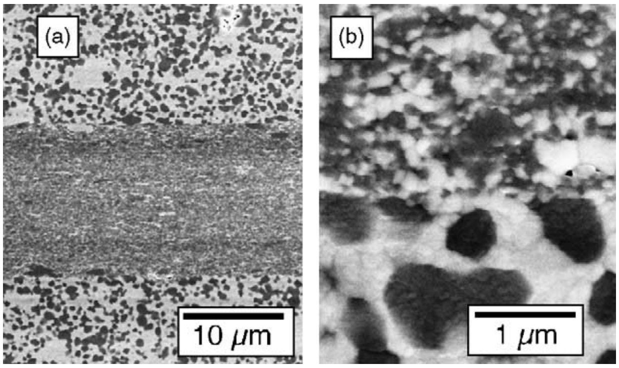

Fig. 3. SEM photomicrographs of (a) dense 50-vol.% Al_2O_3/50-vol.% ZrO_2 joint made from nanophase powders between 40-vol.% Al_2O_3/60-vol.% YSZ compacts (Al_2O_3 is dark phase) and (b) interface between joint layer (top) and one compact (bottom), in which minimal grain growth in joint and high density are apparent.

thermal-expansion coefficient between Al_2O_3 and YSZ. One can, for example, engineer compressive stresses into a joint. Such a stress state could be favorable, especially if the joint exists near a stress concentrator. Flexural experiments on several Al_2O_3/YSZ composites revealed that fracture did indeed occur at the region of maximum tensile residual stress, and not at the joint (Fig. 4). Full details of these studies have yet to be published.

For YSZ and Al_2O_3/YSZ composites, plastic joining has proved to be effective. Joints with better microstructures (fully dense with smaller grain size) than those of the host ceramics, and excellent properties, have been obtained. Wide ranges of compositions have been joined, including whisker-reinforced composites [8]. Residual stresses have been tailored and superior fracture strength confirmed [7]. The potential industrial process of spraying, which requires minimal surface preparation, has been demonstrated.

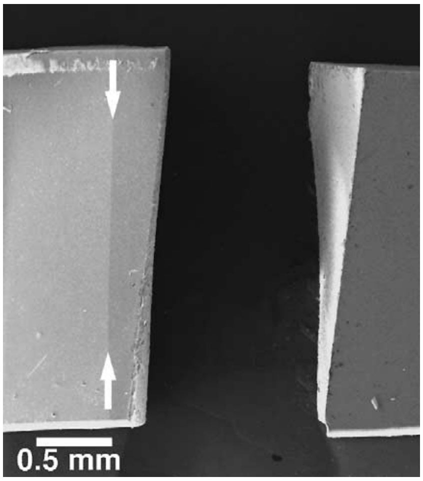

Fig. 4. SEM photomicrograph of Al_2O_3/YSZ specimen tested in four-point flexure; fracture occurred away from the joint because of compressive residual stresses at the joint.

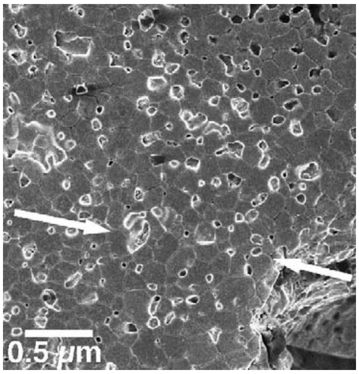

Fig. 5. SEM photomicrograph of joint formed between two pieces of LSM at 1250 °C, with $\varepsilon = 5 \times 10^{-5}\,s^{-1}$; arrows indicate the original interface, which is now indistinguishable from surrounding material.

Table 1
Electrical resistivity results for joined LSM; error bars reflect uncertainties associated with dimensions and electrical contacts

LSM sample	Maximum stress (MPa)	Resistivity (Ω cm)
Bulk	Not applicable	80 ± 10
Two pieces pressed together	Not applicable	5100 ± 100
Joined at 1250 °C	1.6	75 ± 10
Joined at 1150 °C	5.0	68 ± 10

Despite being a monolithic ceramic that exhibits only limited plastic deformation by grain-boundary sliding [11,12], LSM was also successfully joined by plastic deformation. (For strains more than several percent, cavitation between grains accompanies the grain-boundary sliding [10–12].) For example, at 1250 °C and a maximum stress of only ≈1.6 MPa, a nearly perfect joint was formed within 30 min (Fig. 5). Electrical properties are also highly sensitive to flaws or impurities that could be introduced during joining. Electrical resistivity data revealed that for the processing conditions listed the resistivities of the joints were identical to that of the host LSM ceramic (Table 1).

Joining of electronic ceramics may be of importance in devices such as fuel cells [15]. Joints formed by plastic deformation have generally been produced by compressing simple parts together. However, hydrostatic stress states should also be effective and proper engineering should allow for joining of a wider range of configurations. Powder spraying has been shown to accommodate parts that are not smooth and not completely flat. Given the current status and likely advances, the range of application for plastic joining of advanced ceramics should expand significantly.

4. Summary

YSZ, Al_2O_3/YSZ, and LSM ceramics, of different or identical compositions, have been joined by plastic deformation at 1200–1350 °C. Pieces have been joined directly or with insertion of an interlayer. All final joints were as dense as the host ceramics and generally featured finer grain sizes. When dissimilar compositions are joined, thermal residual stresses are generated. Choice of composition can tailor these stresses. Mechanical properties of the structural-ceramic joints and the electrical resistivities of the LSM joints were as good as those of the host ceramic.

Acknowledgements

We thank our colleagues T.A. Cruse and T. Tran for experimental assistance. This work was supported by the Office of Heavy Vehicle Systems of the US Department of Energy, under Contract W-31-109-Eng-38.

References

[1] R.W. Messler Jr., Joining of Advanced Materials, Butterworth-Heinemann, Boston, 1993.

[2] F. Gutierrez-Mora, A. Dominguez-Rodriguez, J.L. Routbort, R. Chaim, F. Guiberteau, Joining of yttria–tetragonal stabilized zirconia polycrystals using nanocrystals, Scripta Mater. 41 (1999) 455–460.

[3] R.J. Hellmig, H. Ferkel, Using alumina nanopowder as cement in bonding alumina ceramics, Phys. Status Solidi (a) 175 (1999) 549–553.

[4] P.A. Walls, M. Ueki, Joining SiAlON ceramics using composite β-SiAlON-glass adhesives, J. Am. Ceram. Soc. 75 (1992) 2491–2497.

[5] R.-J. Xie, M. Mitomo, G.-D. Zhan, L.-P. Huang, X.-R. Fu, Diffusion bonding of silicon nitride using a superplastic β-SiAlON interlayer, J. Am. Ceram. Soc. 84 (2001) 471–473.

[6] R. Chaim, G.B. Ravi, Joining of alumina ceramics using nanocrystalline tape cast interlayer, J. Mater. Res. 15 (2000) 1724–1728.

[7] F. Gutierrez-Mora, K.C. Goretta, S. Majumdar, J.L. Routbort, M. Grimdisch, A. Dominquez-Rodriguez, Influence of internal stresses on superplastic joining of zirconia-toughened alumina, Acta Mater. 50 (2002) 3475–3486.

[8] N. Chen, F. Gutierrez-Mora, R.E. Koritala, K.C. Goretta, J.L. Routbort, J. Pan, Joining particulate and whisker ceramic composites by plastic flow, Compos. Struct. 57 (2002) 135–139.

[9] K.C. Goretta, F. Gutierrez-Mora, J.J. Picciolo, J.L. Routbort, Joining alumina/zirconia ceramics, Mater. Sci. Eng. A341 (2003) 158–162.

[10] F. Gutierrez-Mora, J.L. Routbort, Electrical characterization of a joined electroceramic, $La_{0.85}Sr_{0.05}MnO_3$, J. Am. Ceram. Soc. 85 (2002) 2370–2372.

[11] J. Wolfenstine, K.C. Goretta, R.E. Cook, J.L. Routbort, Use of diffusional creep to investigate mass transport in $(La, Sr)MnO_3$, Solid State Ionics 92 (1996) 75–83.

[12] R.E. Cook, K.C. Goretta, J. Wolfenstine, P. Nash, J.L. Routbort, High-temperature deformation and defect chemistry of $(La_{1-x}Sr_x)_{1-y}MnO_3$, Acta Mater. 47 (1999) 2969–2980.

[13] J.L. Routbort, The stoichiometry dependence of the deformation of $Co_{1-\delta}O$, Acta Metall. 30 (1982) 663–671.

[14] R.C. Laberty, Dense yttria stabilized zirconia: sintering and microstructure, Ceram. Int. 29 (2) (2002) 151–158.

[15] F. Gutierrez-Mora, J.M. Ralph, J.L. Routbort, High-temperature mechanical properties of anode-supported bilayers, Solid State Ionics 149 (2002) 177–184.