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Joining of zirconia ceramics in green state using a paste of zirconia slurry

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Abstract

A new technique for the green state joining of zirconia ceramics has been developed simply by using a paste of zirconia slurry. The interlayer of the joints has the same composition as the parent green bodies and, therefore, the mechanical properties of the joint are comparable to those of the bulk materials. Using this method, large and/or complex ceramic components could be produced cost effectively, because it minimizes the machining of the sintered body and eliminates the need for special equipment. This process can be applied to the joining of various other advanced ceramics.

Keywords: A. Joining; A. Shaping; A. Sintering; D. ZrO_2

1. Introduction

As an effective way to produce large and/or complex shapes of advanced ceramics, joining of ceramic parts has always been challenging [1]. Over the many years, an extensive studies on joining advanced ceramics has been conducted, which includes the methods of joining by glass-frit bonding [2,3], active metal brazing [4], diffusion bonding [5–8], and green body joining [1]. However, difficulties in joining of the ceramic parts occur due to the fact that the joined components are sometimes required to perform at very high temperatures and/or in corrosive environments. Hence, no low-melting-temperature phases and easily corroded materials can be tolerated as joining materials in that case, which excludes the joining methods like the frit bonding and the metal brazing [1]. To avoid the presence of impurities at the joint, diffusion bonding, during which a simultaneous application of high temperature and pressure is essentially required to induce plastic deformation at the joint region and consequently to obtain the joints that show high-temperature stability and strength, has been studied in detail [9,10]. However, broad application of this method is questionable, because the cost of hot pressing is substantially high, and shapes that can be achieved are limited [1].

Zirconia is one of the important ceramic materials having excellent high temperature strength and resistance to wear and oxidation. Reliable joining technologies for these materials are therefore essentially required in order to widen their applications [11]. Green state joining has been commonly being used in the clay-based ceramic industry to produce complex parts. The plasticity induced by the alkali ions in the layered structures of the clay-based ceramics renders the green body joining of clays relatively easy [12–14]. Advanced ceramics, such as ZrO_2, do not exhibit plasticity and, hence, the green state joining of ZrO_2 has been overlooked as a method of fabricating complex shapes. However, some recent research shows that, by dispersing powders in a carrier medium, the unique behavior of clay-based ceramics can be approximated [1,12,15,16]. The work of Han [12], on joining of Al_2O_3 ceramics using a paste of Al_2O_3 slurry has indicated that green state joining is potentially a viable method.

The purpose of this work is to develop the way of joining ZrO_2 ceramics in green state and the paste of ZrO_2 slurry applied to the green state joining as an interlayer. The successful method of joining ZrO_2 ceramics in green state by pasting the ceramic slurry, that has the same composition as

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the parent ZrO_2 ceramics, on the surfaces to be bonded, and then by co-sintering the parent green bodies and the interlayer between them without applying any external pressure during this sintering process, was developed in this work.

2. Experimental

The ZrO_2 slurry used as the joining paste in this work was prepared using 3 mol% yttria containing ZrO_2 powder (KZ-3YF Type C, KCM Co., Nagoya, Japan), dioctyl phthalate (DOP) (99.0%, Samchun Pure Chemical Co., Ltd., Pyongtack, Korea) as the carrier medium, and aliphatic polyether with acidic groups (EFKA-6230, EFKA additives B.V., Heerenveen, The Netherlands) as the dispersant. ZrO_2 powder at a solid volume fraction of up to 0.48 was mixed with a carrier solution that was composed of DOP and the dispersant, and then ball milled for 6 h with zirconia balls in a polyethylene container. Before making the slurry mixture, the carrier solution was prepared by dissolving 1.0 wt% of EFKA-6230 (based on ZrO_2 powder) into the DOP. The parent green parts with dimensions of $3 \times 3 \times 1\ \mathrm{cm}^3$ were made by uniaxial die pressing and subsequent cold-isostatic pressing at 135 MPa.

Before joining, the surfaces of the green compacts to be joined were ground with SiC paper (P# 500) to flatten them and then treated with dioctyl phthalate by dipping the surface into it, to reduce the absorption of the carrier medium upon pasting. After this treatment, a paste of ZrO_2 slurry with the same composition as that of the parent green parts was applied on the to-be-joined surfaces of the parent green parts to form a sandwich assembly. Joining was conducted simply by putting two such parent parts together and rubbing them face-to-face until the joining paste was almost consolidated. After drying overnight at room temperature, the joined green parts were sintered at 1500 °C for 2 h in air. A low heating rate (2 °C/min) was applied in the temperature range of 25–600 °C in order to burn out the organic additives. To evaluate the strength of the joints, the four-point bending test was conducted for $4 \times 3 \times 40\ \mathrm{mm}^3$ bars made directly by cutting the joined bodies, where the joint interface was positioned at the center of the test bar. The microstructures of the joint region were observed by scanning electron microscopy (SEM) after the thermal etching of its polished surface at 1350 °C for 0.5 h.

3. Results and discussion

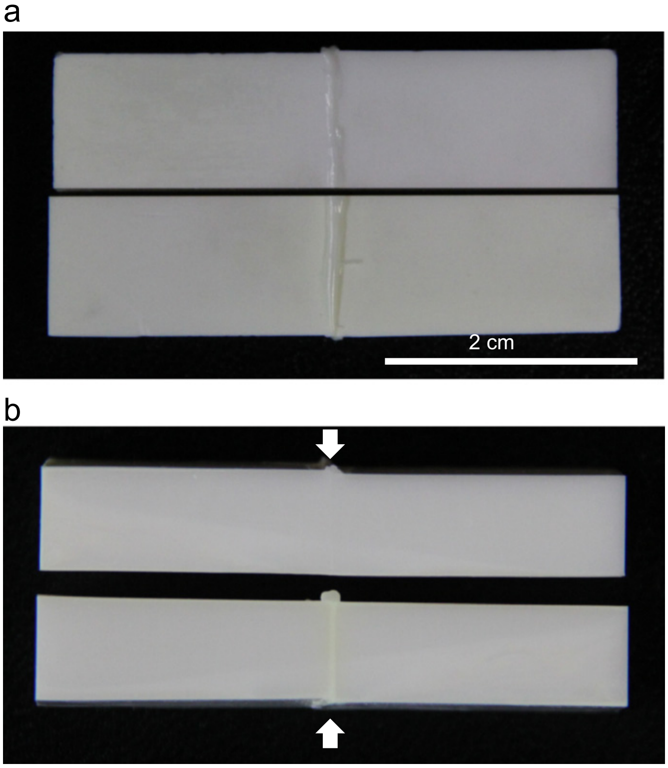

Fig. 1. Photographs showing the (a) as-sintered outer surface and (b) inner cut face of the ZrO_2 bars.

The zirconia bars sintered at 1500 °C for 2 h to join them were cut longitudinally with a diamond wheel through the center plane perpendicular to the joined faces. Fig. 1(a) and (b) show the as-sintered outer surface and inner cut face of the ZrO_2 bars, respectively. The joints are easily recognized due to the paste that was squeezed out from the joint region, as indicated by the arrows. Before the micro-structural examination of the joint, it is relatively easy to determine if a joining experiment is successful or not by observing the presence of lines due to pore arrays along the joined interface with naked eye. The microstructure of the joint region was investigated by scanning electron microscopy with specimens prepared by polishing and thermal etching at 1350 °C for 0.5 h. As shown in Fig. 2(a) and (b), the joint interface is recognizable by the presence of a pore array, as indicated by the broken lines. Pore arrays are observed more frequently in the interface region near the perimeter of the joint (Fig. 2(a)) and their occurrence tends to decrease as the distance from the perimeter increases (Fig. 2(b)), as can be noted in those figures. Fig. 2(c) and (d) show the microstructures of the joint regions near the perimeter and far from the perimeter, respectively. The microstructure is fairly homogeneous and does not contain any large pores or cracks. Furthermore, there is no clear boundary between the interlayer (paste) and matrix material. The similarity in the chemistry and microstructure between the parent and joint ceramics indicates that the sintering mechanism is the same in both areas. On the other hand, transmission electron microscopy (TEM) work on this joint region is also desirable to access the microstructure in more detail [17,18] and thus will be pursued in future studies.

The joint strength of the bar joined in this way was measured by the 4-point bending test and found to be 580.0 ± 152.9 MPa on average, which is 53% of the value of the monolith, viz. 1102.9 ± 77.0 MPa. Fig. 3 is a photograph of some fractured bars obtained after bending test, indicating that the cracks do not completely follow the joint interlayer, but propagate through the

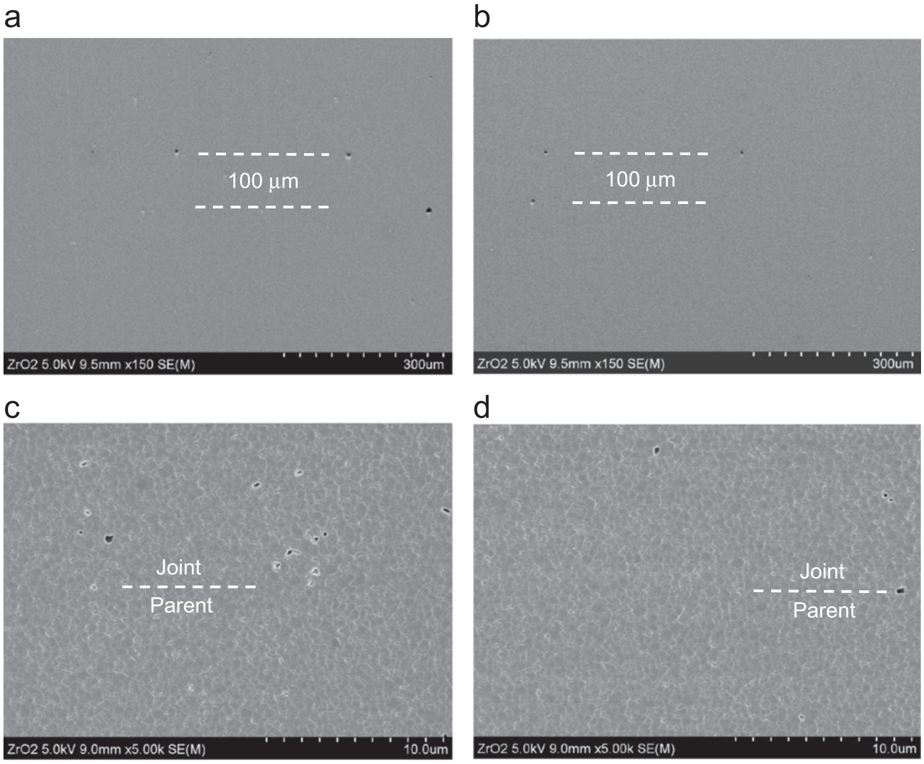

Fig. 2. SEM micrographs showing the microstructures in the joint region; low magnified micrographs of the joint regions (a) near the perimeter and (b) far from the perimeter, and high magnified micrographs of the joint regions (c) near the perimeter and (d) far from the perimeter. Note that the joined interface can be recognized by the pore array and the broken lines drawn in the micrographs.

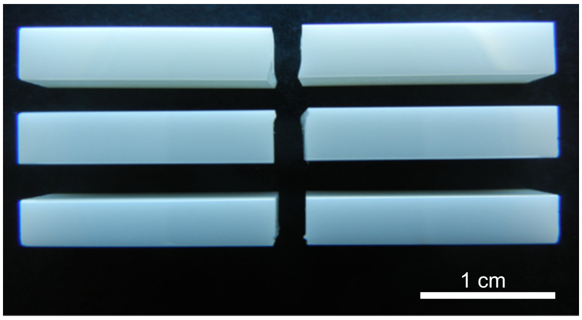

Fig. 3. A photograph showing the test bars used for measuring the 4-point bending strength (values of 738.7, 433.7, and 567.3 MPa were obtained for the specimens from top to bottom, respectively).

inside-region adjacent to the joint, although they are initiated at the joint. The pore arrays that are sometimes observed in the joint region, as mentioned above, are considered to act as weak points inducing stress concentration and ultimately bringing about crack initiation at their sites. This is why the joint strength obtained in this work is lower than the strength of the monolith.

On the other hand, due to the ceramics' properties such as high melting temperature, high hardness, low electrical conductivity, low symmetry of crystal structure, limited or inadequate slip systems for plastic deformation, and low fracture toughness, it is very difficult to shape ceramics into a variety of geometries. Although the applications of advanced ceramics are growing in the aerospace, automotive, and electronics industries, processing is one of the key issues hindering their utilization [19]. Machining operations usually required for producing high-precision ceramic products are costly and may degrade their strength, and more importantly down their productivity due to tedious machining time. Green machining is therefore preferred to reduce machining time and cost, instead of machining the final sintered ceramic parts.

In particular, considerable efforts have been focused on fabricating ceramic components with complex shapes, including ceramic parts with complicated external and/or internal geometries [20]. For example, sub-millimeter channels have been fabricated in ceramics by ultrasonic machining [21], by powder-pressing with micro-configured die faces [22], and by burning-out fugitive phases embedded within powder compacts [23,24]. Internal channels penetrating the bulk of the ceramic have been produced both by embedding fugitive phase elements and then burning-out them [23,24] and by joining subcomponents on which external channels are formed in advance before joining [22]. The external channels thus become to internal channels when the subcomponents are joined. Potentially, the ceramic components in which channels are embedded could be used to transport fuel, cooling fluids, medicine, or variety of other fluids in many diverse technological applications [20]. Miniaturized reaction systems with volumes in the sub-milliliter range and composed of microfluidic components such as micro-mixers, micro-reactors, and micro heat exchangers are used in micro process engineering for chemical and pharmaceutical reactions [25]. Ceramic micro-structured components open up new fields of application in micro process engineering, e.g., for high-temperature reactions or reactions with corrosive media, for which polymer or metal components are not suitable [25]. Often, however, the use of ceramic components suffers from their high cost and time for fabrication, in particular, in the product development phase.

In order to develop an economic and fast fabricating process for the micro-structured ceramic components by green body joining, in this process, ceramic subcomponents to be joined were prepared first by compacting ceramic powders, machined using a small bench-top CNC machine to introduce surface channels (Fig. 4(a)), pasted on their to-be-joined surfaces with ceramic slurry which is the same as the powder compacts in its chemistry, and sintered to form dense ceramics (Fig. 4(b)), and as a result, the two dense ceramics were joined together to produce internal channels (Fig. 5). Note that, in order to avoid clogging the channels with the slurry paste, the paste was applied only on one of the to-be-joined surfaces, e.g., the surface of the base green body (the right-hand side body of Fig. 4(a)) and then the other green body possessing the external channel patterns was placed on the pasted surface of the base green body.

The key factor in such successful green state joining is believed to be to keep the surfaces being joined intimately mated (in other words, in close contact) during the whole joining process, as discussed in detail in Ref. [12]. The intimate mating of the surfaces to be joined is a prerequisite for material transfer and the resultant bonding between the two surfaces. Wet clay-based materials are likely to satisfy this requirement by the plastic deformation of the parent parts. However, die-pressed green parts consisting of advanced ceramics fail to achieve the intimate mating of their surfaces, even when they are pressed at extremely high pressure, e.g. CIP (Cold Isostatic Pressing), because of their lack of plasticity. In order to overcome this problem, the simultaneous application of heat and pressure is sometimes used to achieve the intimate joining at the interface of the green bodies fabricated by tape casting, extrusion, or injection molding, in which an organic binder and plasticizer are used to endow plasticity [26]. However, this technique suffers from a limitation in terms of the available shape of the green bodies. Only flat-shaped parts can be used in practical applications, because of the need to use a high pressure hydraulic heating press.

Another approach is to use ceramic slurry to fill the gap between the surfaces to be joined to ensure their intimate mating. However, because of the capillary pressure of the parent green parts, the absorption of the liquid medium of the slurry occurs immediately upon pasting and a resultant cast layer forms at the contact interface between the green body and the slurry. The volumetric shrinkage that occurs during cast formation by liquid absorption induces a micro scale gap between the green body surface and ceramic slurry layer, thereby preventing an intimately mated interface from being obtained. Note that due to the surface tension of the ceramic slurry, the cast layer may move or shrink toward the center of the slurry layer like a continuum. This process was depicted schematically and actually observed to occur, as shown in the Ref. [12]. This is why we have not been successful in joining green ceramic parts using ceramic slurry. In order to overcome this problem, the formation of a cast layer at the moment of pasting should be avoided and a slow homogeneous consolidation process, that gives sufficient time for the particle rearrangement of the slurry layer, should be ensured.

In order to diminish the likelihood of liquid absorption, dioctyl phthalate was used in this work. Before pasting the

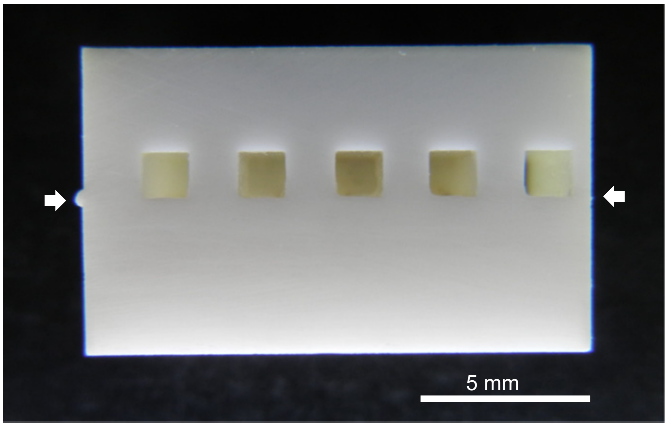

Fig. 5. A photograph showing the inner cut face of the joined ZrO_2 body of Fig. 4(b).

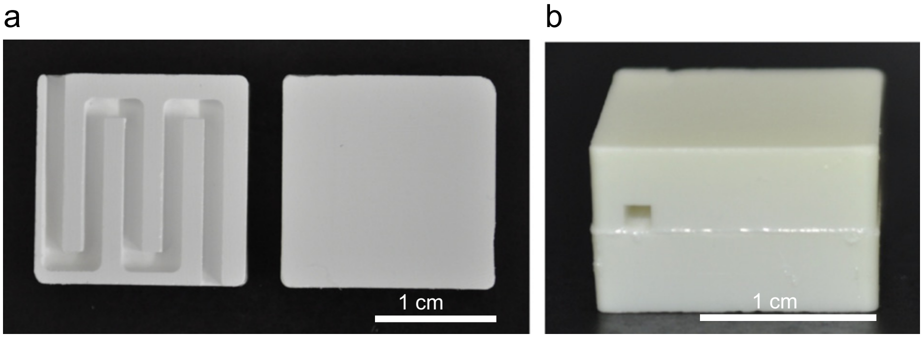

Fig. 4. Photographs showing (a) the to-be-joined external surfaces of the ZrO_2 green bodies before joining and (b) their joined body after co-sintering heat-treatment. Note that a channel pattern was formed by machining on the external surface of one of the green bodies.

slurry, the surfaces of the green parts to be joined were ground with sand paper to flatten them and coated with the dioctyl phthalate by dipping. The capillaries existing on the surfaces are filled with the phthalate solution and, in this way, the formation of a cast layer upon pasting the slurry can be avoided. It should be noted that a homogeneous intimately mated interface is obtained by this surface treatment and this is considered to be crucial in the joining technique developed in this work. The joint strength of the parts joined without the treatment after sintering is negligible and the joint could be broken at the interface even by finger pressure.

4. Conclusions

The green state joining process described herein, which consists of treating the to-be-joined surfaces to remove the capillary pressure and pasting a ceramic slurry, offers a successful way of joining zirconia ceramics and has several advantages over other joining methods. Using this method, large and/or complex ceramic components could be produced cost effectively, because it minimizes the machining of the sintered body and eliminates the need for special equipment. Furthermore, the development of an interlayer having the same composition as that of the parent green parts leads to a homogeneous microstructure and, as a consequence, mechanical properties comparable to those of the bulk material after sintering. This technique is also believed to be suitable for joining various other kinds of advanced ceramics.

Acknowledgments

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