Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 40 (2014) 3123–3129
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Joining partially-sintered alumina ceramics using a mixture slurry of alumina sol and suspension

Joo-Hwan Han*

School of Materials Science and Engineering, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Republic of Korea

Received 5 September 2013; received in revised form 28 September 2013; accepted 28 September 2013
Available online 7 October 2013

Abstract

The joining of advanced ceramics allows the manufacture of components with a range of complex shapes that cannot be achieved in a cost-effective manner using existing techniques, i.e. green state shaping and/or machining. A new technique for joining partially-sintered alumina ceramics was developed by simply using a mixed slurry of Al_2O_3 sol and suspension. The interlayer of the joints had the same composition as the parent bodies, and the mechanical and chemical properties of the joint were comparable to those of the bulk material. This process can be applied to the joining of a variety of advanced ceramics.

Keywords: A. Joining; Ceramics; Partially-sintered; Alumina; Machining

1. Introduction

Joining of ceramic parts, as an effective way to produce large and/or complex shapes of advanced ceramics, has always been a challenge [1,2]. The joining of advanced ceramics that have been extensively studied over many years include the methods of joining by glass-frit bonding [3,4], active metal brazing [5], diffusion bonding [6–9] and green body joining [1,2]. On the other hand, difficulties in the joining of ceramic parts occur because joined components are sometimes required to perform at very high temperatures and/or in corrosive environments. Therefore, no low-melting-temperature phases or easily corroded materials can be tolerated as joining materials, which excludes joining methods, such as frit bonding and metal brazing [1,2]. To avoid the presence of impurities at the joint, many studies have examined diffusion bonding, in which the simultaneous application of high temperatures and pressures are required to induce plastic deformation at the joint region and consequently obtain joints with high-temperature stability and strength [10,11]. However, broad applications of this method are questionable because of the substantially high cost of hot pressing and the limited shapes that can be achieved [1,2].

Alumina 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 required for increasing their applications [12]. Green state joining is commonly used in the clay-based ceramic industry to produce complex parts. The plasticity induced by alkali ions in the layered structures of the clay-based ceramics renders the green body joining of clays relatively easy [13–15]. Advanced ceramics, such as Al_2O_3, do not exhibit plasticity. Hence, the green state joining of Al_2O_3 has been overlooked as a method of fabricating complex shapes. Nevertheless, some recent research has shown that the unique behavior of clay-based ceramics can be approximated by dispersing powders in a carrier medium and pasting this slurry on joint interfaces [2,13,16,17]. Han [13] examined the joining of Al_2O_3 ceramics using an Al_2O_3 slurry paste and reported that green state joining is a potentially viable method.

Although there have been some successes in the green state joining of ceramics, this technique is limited when applying it to the joining of engineering components made of advanced ceramics. To machine green ceramic components, e.g. the principal challenge is to obtain sufficient strength for the component to withstand the stresses generated during

---

*Tel.: +82 53 810 2567; fax: +82 53 810 4628.
E-mail address: jhhan@yu.ac.kr

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.09.133

machining whilst maintaining the advantages of the easy machining of porous ceramics [18]. Partial sintering conducted before machining can provide structural integrity to allow the machining of the ceramic components with metalworking tools. The particles in the green ceramic components form particle–particle bonds (i.e. necks) between them during partial sintering. Although little or no densification occurs during this heat-treatment, the strength and elastic modulus of the partially-sintered bodies increases dramatically. As a result, the alumina bodies impart sufficient mechanical strength to withstand the stresses generated by machining [18]. Therefore, the machining of partially-sintered bodies followed by joining is preferred over machining the green ceramic parts due to the high strength and the fully densified ceramic parts due to the reduced machining time and cost.

The aim of this study was to develop a way of joining partially-sintered Al_2O_3 ceramics using Al_2O_3 sol-suspension mixture slurries as an interlayer. A method was developed for joining partially-sintered Al_2O_3 ceramics by pasting a mixture slurry on the to-be-bonded surfaces followed by co-sintering the parent partially-sintered bodies and interlayer between them without applying external pressure during sintering.

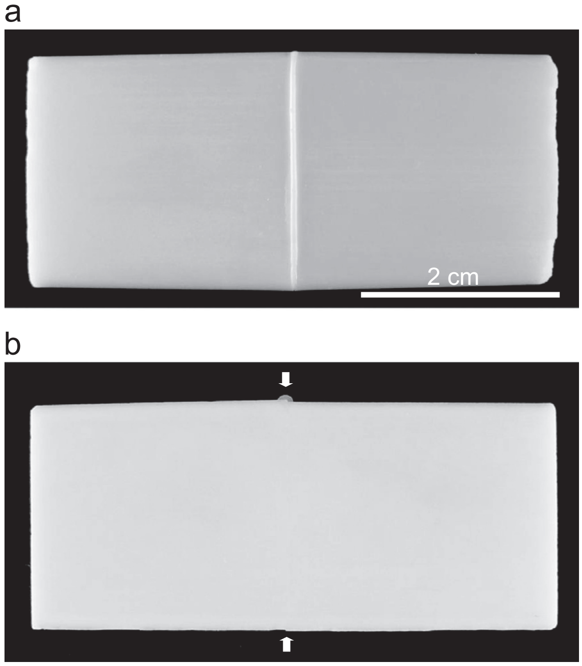

Fig. 1. Photographs showing the (a) as-sintered outer surface and (b) inner cut face of the Al_2O_3 bars.

2. Experimental

The joining paste used in this study was prepared by mixing an Al_2O_3 sol and its suspension. The alumina sol was first prepared using methyl alcohol (CH_3OH, Extra Pure Grade, Duksan Pure Chemicals, Ansan, Korea) as the solvent, $AlCl_3 \bullet 6H_2O$ (Extra Pure, Daejung Chemicals & Metals Co., Ltd., Shiheung, Korea) as the Al^{3+} source and acetyl acetone ($CH_3C(O)CH_2C(O)CH_3$, Extra Pure, Daejung Chemicals & Metals Co., Ltd., Shiheung, Korea) as the chelating agent to form the Al ion-complexes. The methyl alcohol solution, where aluminum chloride was dissolved to a concentration of $[Al^{3+}] = 1.26$ mol/l, was mixed dropwise with the other methyl alcohol solution containing 2.46 mol/l of the chelating agent. The concentrations of the aluminum chloride and acetyl acetone in the resulting sol solution were controlled to 0.62 and 1.24, respectively. The resulting sol solution was stirred for several days to develop the Al ion complexes, during which the solution changed from a colorless clear tone immediately after mixing to a yellowish tone with increasing stirring time. Ethylene glycol ($(CH_2)_2(OH)_2$, Guaranteed Reagent, Junsei Chemical Co., Ltd., Japan) was then added to the solution at a concentration of 50 wt% to prevent drying of the solution. To prepare a mixture slurry of the alumina sol and suspension, 72.2 wt% of Al_2O_3 powder (AES-11, Sumitomo Chemical Co., Ltd., Tokyo, Japan) was mixed with the sol solution and ball milled for 6 h with alumina balls in a polyethylene container. The partially-sintered alumina samples, $2.7 \times 2.7 \times 3$ cm^3 in size, were prepared by uniaxial die pressing, cold-isostatic pressing (CIP) at 135 MPa and pre-sintering at 1150 °C for 0.5 h, and used as the parent parts for joining.

Before joining, the surfaces of the partially-sintered green compacts to be joined were treated by dipping the surface into molten wax to reduce the absorption of the carrier medium when pasting the Al_2O_3 sol-suspension mixture slurry. The capillary pressure exerted by the porous surfaces of the green bodies deprives the mixture slurry of its carrier liquid, thereby hindering the rearrangement of particles in the joint region, which is believed to be essential for joining, due to the rapid consolidation of the paste. After this treatment, the to-be-joined surfaces were ground to a smooth surface with SiC paper (P #500). A paste of the Al_2O_3 sol-suspension mixture slurry was then applied to the to-be-joined surfaces of the parent partially-sintered green parts to form a sandwich assembly. Joining was performed simply by placing two 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 1650 °C for 2 h in air. A low heating rate (1 °C/min) and holding (at 160 °C for 1 h, 350 °C for 1.5 h and 600 °C for 1 h) was applied at temperatures ranging from 25 to 600 °C to burn out the organic additives.

To evaluate the strength of the joints, the joined bodies were cut into $4 \times 3 \times 40$ mm^3 bars, where the joint interface was positioned at the center of the test bar, and their outer surfaces were then polished using diamond pastes with decreasing sizes to 6 μm. The flexural strength of the joint was measured by three-point bending with a 20 mm span on an universal testing machine (Autograph 500, Shimadzu Co., Kyoto, Japan) at a displacement rate of 0.5 mm/min. Six test bars were tested to obtain the mean bond strength of the joints. The microstructures of the joint region were observed by scanning electron microscopy (SEM, S-4200, Hitachi High-technologies Co., Ltd., Tokyo, Japan) after thermal etching of its polished surface at 1550 °C for 0.5 h.

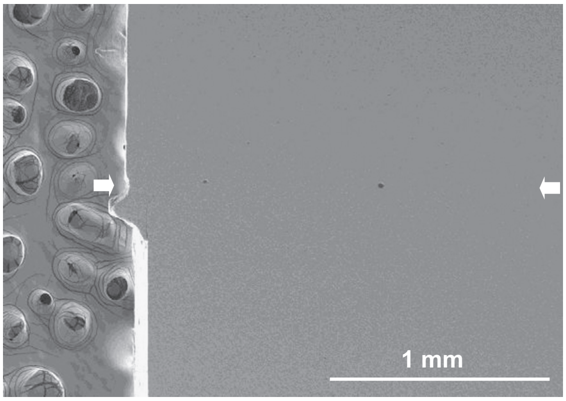

Fig. 2. SEM image showing the microstructure in the joint region; note that the joined interface is recognized by both the paste squeezed out and the pore array indicated by the arrows.

3. Results and discussion

The alumina bars, which had been sintered at 1650 °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) shows the as-sintered outer surface and inner cut face of the Al_2O_3 bars, respectively. The joints could be recognized easily by the paste that has been squeezed out from the joint region, as indicated by the arrows. Without the aid of the paste, however, it is not possible to find the joint on the inner cut face, even upon close examination. Before the microstructural examination of the joint, it was relatively easy to determine if the joining experiment was successful by observing the presence of lines along the joined interface by the naked eye.

The microstructure of the joint region was examined by SEM with specimens prepared by polishing and thermal etching at 1550 °C for 0.5 h. As shown in Fig. 2, the joint interface was recognizable by the presence of a pore array and the paste that had been squeezed out, as indicated by the arrow. Pore arrays were observed more frequently in the interface region around the perimeter of the joint, and their occurrence tended to decrease with increasing distance from the perimeter. Fig. 3 shows the microstructures of the joint region of the specimens joined using the Al_2O_3 slurry mixed (a) and (b) with and (c) and (d) without its sol solution. As shown in Fig. 3(a) and (b), successful joining was obtained when the Al_2O_3 sol and suspension mixture slurry was used as an interlayer. In Fig. 3(a) and (b), the joint region (interlayer) between the parent bodies indicated by the two broken lines showed a similar microstructure to that of parents. Hence, there was no clear boundary between the interlayer and parent bodies. The microstructure was fairly homogeneous and did not contain any large pores or cracks. The similarity in chemistry and microstructure between the parent and joint ceramics suggests that the sintering mechanism was the same in both areas. However, the microstructure of the joint region showed a slightly different grain size from those of the parents. As shown in Fig. 3(b), the grains in the interlayer region were significantly smaller than those in the parent bodies. This was quite different from the results (Fig. 3(d)) obtained for the specimens joined using the Al_2O_3 slurry without the sol solution, where the grains in the interlayer region were similar to those of the parent microstructures.

The mean joint strength of the bar joined using the mixture slurry of the Al_2O_3 sol and suspension, which was measured using a 3-point bending test, was 248.3 ± 24.0 MPa, which is 68% of the value of the monolith (365.0 ± 3.0 MPa). In contrast, the mean joint strength of the bar joined using the Al_2O_3 slurry without its sol was 105.7 ± 29.8 MPa. The pore arrays, which are sometimes observed in the joint region, act as weak points inducing a stress concentration and ultimately causing crack initiation at their sites. Therefore, the joint strength obtained in this study was slightly lower than the strength of the monolith. In order to understand why the sol-suspension mixture was better than the suspension pasted as an interlayer when joining partially-sintered green parts, it is important to consider the particle rearrangement processes that occur during ceramic processing, such as pasting, drying and heat-treating, which might induce a loss of boundary contact between the green parts and interlayer.

Green state joining is basically composed of sintering processes that occurs simultaneously both at the to-be-joined, mating surfaces (interlayer) of green parts and within the green parts themselves. Therefore, the prerequisite for joining is to keep the particles on the mating surfaces in contact with each other during the entire sintering process to provide the pathways for material transport. No neck formation and resulting shrinkage in the inter-particle distance occurs once two particles are not in contact but distant from each other. During the ceramic process, e.g. pasting a ceramic slurry, the net forces exerted on each particle develop as a result of various interactions between particles, and act as the driving force for their rearrangement. This driving force is consumed with the evolving rearrangement, and eventually decreases to zero at the completion of the rearrangement where local force equilibrium is established between particles. On the other hand, the force equilibrium will be broken and a new rearrangement process will begin again when a disturbance affecting the force balance, such as solvent drying, binder burning-out, sintering etc., occurs. Typical examples of particle rearrangement are those frequently observed in ceramic processing, such as warping, cracking and distortion occurring during solvent drying, binder burning-out and sintering.

When two ceramic green parts are assembled into contact with a ceramic slurry pasted between them, as depicted in Fig. 4(a), the net force exerted on particles, e.g. '**A**' in the interface region, is determined by the vector sum of the forces acting on the particle. The van der Waals forces and electrostatic and/or steric forces can arise from the interactions between the particle of concern and its surrounding particles. These forces, however, can be neglected once a dispersion of the slurry is achieved because their vectors are normally small in magnitude and mutually almost compensating. Therefore, the forces that should be considered in a particle rearrangement are those due to the negative curvatures formed on the necks between the particles, and the force due to the surface tension of the liquid continuum (in the case that the liquid on the necks

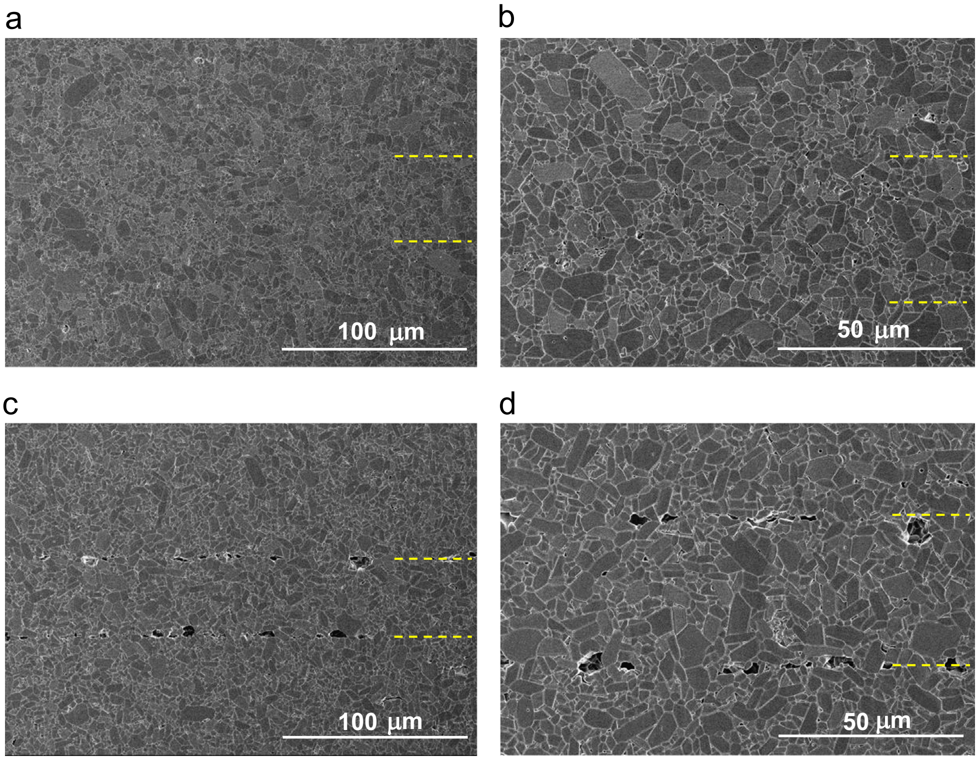

Fig. 3. SEM images showing the joint region of the joined specimens; (a) low and (b) high magnified images of the specimen joined using the Al_2O_3 slurry with its sol, and (c) low and (d) high magnified images of the specimen joined using the Al_2O_3 slurry without its sol.

is connected continuously). When its distribution is disturbed, the liquid tends to shrink toward its center of curvature, together with the particles. The presence of this surface tension causes particle '**A**' to move toward the center of curvature of the liquid when the liquid is absorbed by the green part upon pasting, as indicated by the arrow in Fig. 4(b). This means that a microscale gap develops at the to-be-joined interface (i.e. a loss of boundary contact develops). Consequently, the joining in this region fails, as proven in Ref. [13]. To prevent the formation of microscale gaps (the loss of boundary contact), liquid absorption by the green parts should be minimized by pre-wetting the green part with a liquid or by plugging its surface capillaries with non-permeable materials before pasting, as adopted in the present study.

In addition to liquid absorption, uneven and rapid drying of the solvent from the paste also gives rise to changes in the spatial distribution of the liquid continuum. The resulting net forces developed by its surface tension induce particle rearrangement, resulting in a microscale gap between the green part and paste, which is analogous to what occurs when the liquid of the paste is absorbed by the porous surface of the green part. To overcome this problem, a slow homogeneous consolidation process, which allows sufficient time for the particles of the slurry layer to adjust and fill into the gaps by viscous flow, should be used. In this respect, alcohol used as a solvent to prepare the paste is undesirable because of its higher volatility, particularly in the case of a paste with a high solid loading (>45 vol%), as was used in the present work. Ethylene glycol is much more suitable because of its negligible volatility at room temperature, and was used to reduce the drying rate of the solvent in this study.

Although the microscale gap formation due to liquid absorption and drying can be avoided at the early joining process (pasting and drying stages) by reducing the surface porosity of the green parts and by using non-volatile solvents, it can also occur during heat-treatment for binder burning-out and/or densification (sintering). Because the liquid continuum is removed by the consolidation process via liquid absorption and drying, the forces exerted on the particles in this circumstance are endowed with organic materials (binder, plasticizer, dispersant, remnant solvent, etc.) or inorganic materials formed as a result of sintering on the necks between the particles. The forces exerted on the particles, e.g. '**B**' shown in Fig. 4(c) are created by the negative curvature of the materials on their surrounding necks. Therefore, their adhesion to others is naturally dependent on the surrounding environment, such as the inter-particle distances and particle coordination.

The removal of organic materials on the necks and/or the neck-growth that occur during heat-treatment cause the collapse of the local force balance that has been maintained, and triggers a new particle rearrangement with a concomitant decrease in inter-particle distance. Because the particle rearrangement is a collective and cooperative process with other particles, the resulting microscale gaps (losses of contact) are most likely to develop at the region where inter-particle adhesion is smaller than the forces driving the particle rearrangement. The particles on the interface of two different

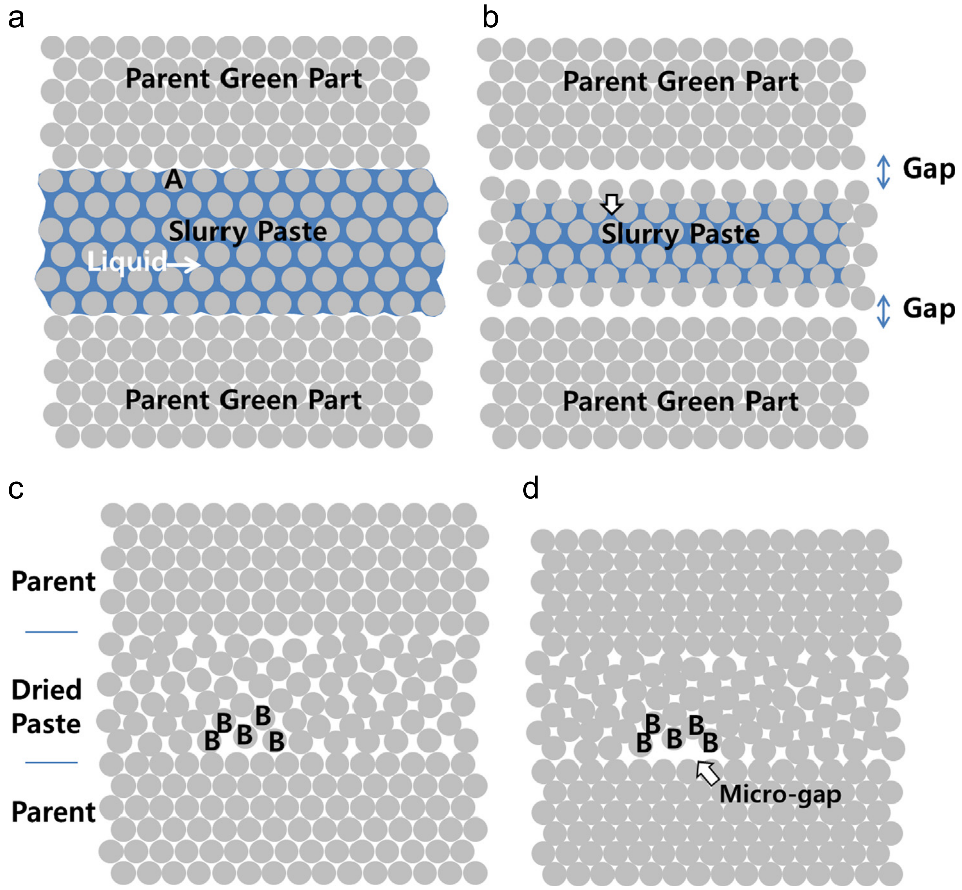

Fig. 4. Schematic diagram depicting the process during which a gap between the parent green part and slurry paste develops by liquid absorption upon pasting; (a) before absorption and (b) after absorption, and by particle rearrangement upon heat-treating; (c) before and (d) after rearrangement. (Note that the organic or inorganic materials on the necks between particles are not drawn for clarity.)

adjoined layers generally possess fewer coordinating particles and greater inter-particle distances due to the differential shrinkage between the two different layers that occurs during heat-treatment, which leads to smaller inter-particle adhesion than the forces exerted on the particles upon rearrangement. The particles marked by '**B**' in the joining paste are forced to move away from the interface as a result of the net forces created by the curvature variation of the materials on their necks during the heat-treatment. Consequently, a loss of boundary contact (Fig. 4(d)) and thus, failure to maintain the intimacy can result.

In contrast to the successful joining observed when using the sol-suspension mixture slurry, the joining of partially-sintered green parts using only the Al_2O_3 slurry without its sol solution was unsuccessful, as shown in Fig. 3(c) and (d). Many un-joined gaps at the joint were observed, and the joint strength was smaller (~100 MPa). Linear shrinkage of ~1% was measured during partial sintering (1150 °C for 0.5 h), showing that small, hard, rigid necks were formed between the particles. As expected, the rigid necks between the particles formed in the partially-sintered parts are rather strong. Therefore, they do not allow the particles to rearrange to comply with the movement of particles in the paste upon heat-treating, which results in microscale gaps at the joint region. Therefore, joining with the partially-sintered parts fails. On the other hand, stronger adhesion between the particles of the paste and those of the partially-sintered part was provided by the mixture slurry of the Al_2O_3 sol and suspension pasted between the assembled partially-sintered green parts upon heat-treatment. With the exception of applying the mixture slurry, they were again joined using the same process by joining the green parts with an Al_2O_3 suspension slurry. As shown in Fig. 3(a) and (b), the microstructure and joint strength were improved significantly by the greater adhesion between the paste and green parts, which is believed to be endowed with the sol solution, by providing the formation of strong necks between the particles on the interface between the green parts and interlayer (paste). Note that the particles pasted on the to-be-joined surfaces of the green parts are expected to form strong necks with the aid of the alumina sol before the green body is sintered. The alumina sol prepared by mixing the alcohol solution containing Al^{3+} with acetyl acetone, which is identical to that of this study, was reported [19] to be composed of Al chelates and transform to γ-Al_2O_3 above 600 °C and to α-Al_2O_3 above 1200 °C during heat-treatment. Therefore, the alumina sol, which precipitated on the necks of the particles both on the interface between the green part and interlayer and within the interlayer itself, allows small, hard, rigid necks to form between particles through the above-mentioned phase transformation at

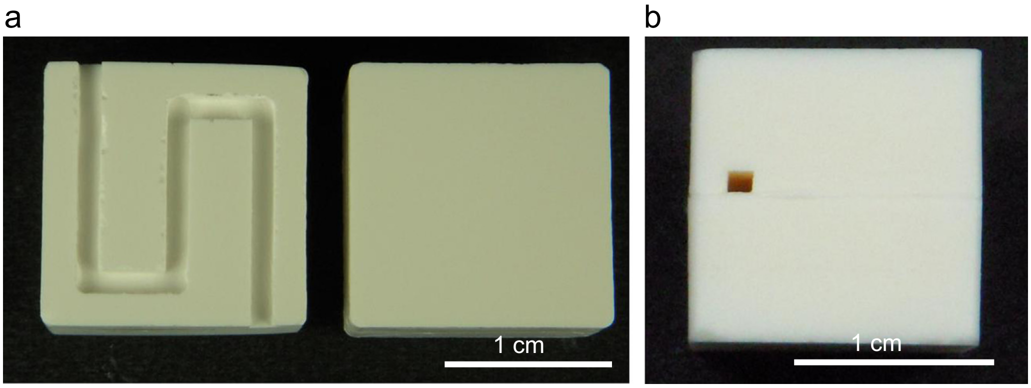

Fig. 5. Photographs showing (a) the to-be-joined external surfaces of the partially-sintered Al_2O_3 green bodies before joining and (b) their joined body after co-sintering heat-treatment. Note that a channel pattern was formed by machining on the external surface of one of the green bodies.

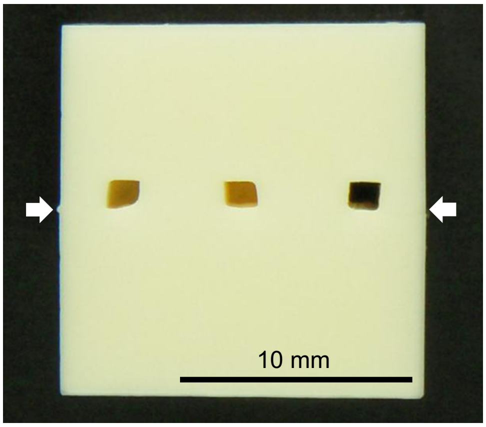

Fig. 6. A photograph showing the inner cut face of the joined Al_2O_3 body of Fig. 5(b).

temperatures below the sintering temperature, resulting in an adhesion strength sufficient to maintain the close contact during sintering. As discussed above, it is extremely important to maintain the to-be-joined interface in close contact during the entire joining process and control the process variables to ensure this intimacy.

In order to show that the joining process developed in this study is an economic and fast fabricating process for the micro-structured ceramic components, partially-sintered alumina subcomponents to be joined were prepared first by compacting alumina powders followed by pre-sintering at 1150 °C, machined using a small bench-top CNC machine to introduce surface channels (Fig. 5(a)), pasted on their to-be-joined surfaces with the Al_2O_3 sol-suspension mixture slurry, and sintered to form dense ceramics (Fig. 5(b)), and as a result, the two dense ceramics were joined together to produce internal channels (Fig. 6).

4. Conclusions

The joining process of partially-sintered green parts, which consists of treating the to-be-joined surfaces with a molten wax to remove the capillary pressure and pasting a mixture slurry of Al_2O_3 sol and suspension, offers a better way of joining partially-sintered alumina ceramics than other joining methods. Using this method, large and complex ceramic components can 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 with the same composition as the parent green parts leads to a homogeneous microstructure, and as a consequence, similar mechanical and chemical properties to those of the bulk material after sintering. This technique is also believed to be suitable for joining other types of advanced ceramics.

Acknowledgments

This study was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2012R1 A1A4A01001363).

References

[1] Joo-Hwan Han, Joining of zirconia ceramics in green state using a paste of zirconia slurry, Ceramics International 39 (2013) 239–243.

[2] Jing Zheng, Mufit Akinc, Green state joining of SiC without applied pressure, Journal of the American Ceramic Society 84 (2001) 2479–2483.

[3] M.G. Faga, et al., Alumina/alumina and alumina/alumina–zirconia joints through glass interlayers, microstructure, mechanical properties and residual stresses, Advanced Engineering Materials 7 (2005) 535–540.

[4] S. Fujitsu, et al., Joining of single-crystal sapphire to alumina using silicate glasses, Journal of the Ceramic Society of Japan 111 (2003) 448–451.

[5] M.C.A. Nono, J.J. Barroso, P.J. Castro, Mechanical behavior and microstructural analysis of alumina-titanium brazed interfaces, Materials Science and Engineering A 435–436 (2006) 602–605.

[6] M.G. Nicholas, Diffusion bonding, in: M.G. Nicholas (Ed.), Joining Process: Introduction to Brazing and Diffusion Bonding, Kluwer Academic Publishers, Dordrecht, Netherlands, 1998, pp. 78–91.

[7] F. Gutierrez-Mora, et al., Influence of internal stresses in superplastic joining of ZTA, Acta Materialia 50 (2002) 3475–3486.

[8] Carl H. Bates, et al., Joining of non-oxide ceramics for high-temperature applications, American Ceramic Society Bulletin 69 (1990) 350–356.

[9] S. Dahms, et al., Diffusion joining of silicon nitride ceramics, Estonian Journal of Engineering 15 (2009) 301–308.

[10] J. Ye, A. Dominguez-Rodriguez, Joining of Y-TZP parts, Scripta Metallurgica et Materialia 33 (1995) 441–445.

[11] Jules L. Routbort, Dileep Singh, Kenneth C. Goretta, Felipe Gutierrez-Mora, Joining of advanced materials by plastic deformation, United States Patent Application Publication, US 2007/0187464 A1, August 16, 2007.

[12] Hai Gao, Jiachen Liu, Haiyan Du, Mingzheng Liu, Weirong Huo, Lijuan Wang, Effects of adhesive composition on bond strength of green joined $CePO_4$–ZrO_2 ceramics, Scripta Materialia 49 (2003) 515–520.

[13] Joo-Hwan Han, Joining alumina ceramics in green state using a paste of ceramic slurry, Journal of Materials Processing Technology 211 (2011) 1191–1196.

[14] J. Zheng, et al., Green state joining of silicon carbide using polycarbosilane, Journal of the American Ceramic Society 83 (2000) 1687–1692.

[15] Liwu Wang, Fritz Aldinger, Joining of advanced ceramics in green state, Materials Letters 54 (2002) 93–97.

[16] Hai Gao, et al., Effects of interlayer composition on joining of 25% $CePO_4$/ZrO_2–ZrO_2 ceramics on green state, Ceramics International 30 (2004) 823–827.

[17] Jing Zheng, et al., X-ray tomography study on green state joining of silicon carbide using polymer precursors, Journal of the American Ceramic Society 84 (2001) 1961–1967.

[18] Eldon D. Case, et al., Machining and ceramic/ceramic joining to form internal mesoscale channels, International Journal of Applied Ceramic Technology 1 (2004) 95–103.

[19] Qiang Fu, et al., Preparation of alumina films from a new sol–gel route, Thin Solid Films 348 (1999) 99–102.