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Joining of alumina with a porous alumina interlayer

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Abstract

In the joining of structural ceramics, a porous interlayer is generally believed to deteriorate the mechanical properties of the joint. This paper, however, shows that a porous interlayer can sustain high adhesion strength when cavities or interfacial cracks are eliminated. The characteristic of the new slurry approach, described in this work, is that a pure alumina slurry interlayer is dried between two adjoining dense alumina plates and sintered with a negligible external pressure to form the porous interlayer. The effect of slurry concentration was studied to optimize the microstructure of interlayer. By controlling the interlayer microstructure and nature of the flaws, it was possible to fabricate high-strength bonds. The new slurry approach opens up the possibility of pure diffusion bonding which requires neither high pressure during heat treatments nor flat surfaces.

Keywords: A. Joining; B. Porosity; C. Strength; D. Al_2O_3

1. Introduction

Alumina ceramics have been used in chemical plants and semiconductor industries due to their excellent properties such as high corrosion resistance and good mechanical properties at elevated temperatures. The size of alumina components used in these industries is now required to exceed 2 m in size to improve productivity. Joining ceramics parts with a height of 1 m to form such huge assemblies is one of the best solutions to such a demand since both machining and sintering of giant green bodies are usually difficult. There are, however, four necessary conditions for the joint components and joining procedure: (1) high purity of the joint to prevent product contamination, (2) small decrease in the joint strength at high temperature, (3) no external pressure during the heat treatments since large specialized mechanical joining facilities are expensive, and (4) applicability to non-flat surfaces to reduce machining cost.

There are three major methods for ceramic-ceramic joining [1]: (1) direct ceramic-ceramic joining by solid state diffusion [2,3], (2) joining with glass or ceramic interlayer [4–8], and (3) joining with metallic interlayer. The major advantage of the first technique is the ability to not adversely affect the high temperature properties of the joint, but high pressures during the heat treatments and/or highly flat faying surfaces are necessary. In the case of joining pure alumina, neither the second or third solutions can satisfy the requirements described above because of contamination from the interlayer and the degradation of mechanical properties at elevated temperature. Consequently, none of the conventional joining techniques are sufficient for the application to huge components.

In order to maintain the strength of the joints at high temperature and avoid contamination from the interlayer, it seems inevitable to use pure alumina powders as the adhesive. However, it is expected that an alumina interlayer would be porous when sintered without external pressure because of the constrained densification between the faying surfaces. It is natural therefore to suppose that such a joint would possess poor mechanical properties since pores are generally believed to deteriorate the mechanical performance of the ceramic joint [1]. Thus, few studies have been reported regarding pure diffusion bonding without significant joining pressure [9]. However, it has been reported that pores can cause improved or unique mechanical performance when the size, shape, and

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Table 1
Characteristics of slurry, green interlayer after drying and sintered interlayer as well as shrinkage of gap ($\Delta d/d_0$) between faying surfaces due to sintering.

Material code	Volume fraction of alumina in the slurry (%)	Area fraction of cavity (%)	Relative density of green interlayer (%)	$\Delta d/d_0$ (%)	Apparent relative density of interlayer after sintering (%)[a]
ELC	31.7	16.0	43	42	74
LC	36.3	12.9	48	38	77
MC	42.2	0	49	39	80
HC	46.3	2.6	52	30	75

[a] Apparent relative density was estimated from both the relative density of the dried green interlayer and the shrinkage of gap between faying surfaces.

orientation of pores as well as grains are controlled in porous silicon nitrides [10,11]. The same could be expected for the porous interlayer as well provided the microstructures are properly optimized to exclude the strength-limiting macro defects. The flexural strengths of porous alumina reported by Lam et al. and Nanjangud et al. exceed 100 MPa when the relative density is 70% and higher [12,13]. It is expected that the porous alumina interlayer should possess enough joining strength if large flaws can be avoided.

In this study, diffusion bonding of commercial alumina was examined with a pure alumina interlayer at the joint. The interlayers were applied in the form of a slurry where the solid load was varied from 31.7 to 46.3 vol%. The joining was accomplished with a pressure of 0.03 MPa at a temperature of 1650 °C after drying the slurry in the gap of faying surfaces. Joint strength was measured at both room temperature and 1200 °C and discussed in conjunction with the microstructures of the joints.

2. Experimental procedure

A 99.6 mass% pure commercial alumina (Hi-Cera HA, Mitsui Mining & Smelting Co., Ltd.) with a density of 3.91 g/cm^3 and a room temperature bending strength of 380 MPa was used as the densified alumina bonded in this study. Alumina plates with a dimension of 20 × 16 × 5 mm were cut from the alumina sintered bodies, and the larger surfaces were ground with a 200-grit diamond wheel before joining tests. The surface roughness of ground plates, R_a was 0.39 μm with the measurement length of 3.2 mm. The starting materials for the slurry to form the joining interlayer were low soda alumina powder (0.6 μm, AL-160SG-4, Showa Denko K. K.) with less than 0.2 mass% total impurity content and distilled water. The major impurities of the alumina powder were 0.05 wt% MgO, 0.04 wt% Na_2O, 0.02 wt% SiO_2 and 0.01 wt% Fe_2O_3. A dispersant (Serna D305, Chukyo Yushi Co. Ltd.) was added to the distilled water at 5.6 mass% before mixing the alumina powder. Four types of alumina slurry with different solid concentration were prepared: extra low concentration slurry (hereafter ELC), and low, medium and high concentrations (LC, MC and HC, respectively). The solid content of each type of slurry is listed in Table 1, as well as the material code. The mixed slurry was evacuated for 2 min with a vacuum pump to eliminate bubbles and then a few drops of the slurry were spread over the 20 × 16 mm surface of the alumina plate. The other alumina piece was set on top of the alumina slurry so that the gap between faying surfaces was ~90 μm, followed by drying overnight at room temperature. The dried assemblies were heated in air at 1650 °C for 2 h with a pressure of 0.03 MPa by placing a suitable weight on top of the substrate. The pressure was selected to simulate the joining of large alumina blocks with ~1 m height without external pressure.

In order to observe the drying process of the slurry in the gap, in situ observations of the slurry were performed by employing a translucent upper plate with a thickness of ~100 μm. Fig. 1 shows a schematic diagram of the arrangement used for the direct observation. The upper alumina plate was ground with a 200-grit diamond wheel to a thickness of ~100 μm and was glued onto a slide glass to make a translucent upper part. The alumina slurry was then sandwiched between the plates with a gap of ~90 μm. The movement of the slurry during the drying process was observed directly through the translucent upper plate with an optical microscope. To calculate the densities of the green interlayer after drying, the green couples were separated and the area of interlayer without cavities and its thickness were measured to obtain the interlayer volume. The weight of the powder collected from the green interlayer was also obtained. Relative densities of the green interlayer were evaluated by using a theoretical density of 3.99 g/cm^3 for alumina. Apparent relative densities of the interlayer after sintering were estimated from both the relative densities of the dried green interlayer and the shrinkage of the gap between faying surfaces due to sintering.

The joined samples were sectioned perpendicular to the interlayer and polished with a 0.5-μm diamond slurry, followed by thermal etching before microstructural observation by

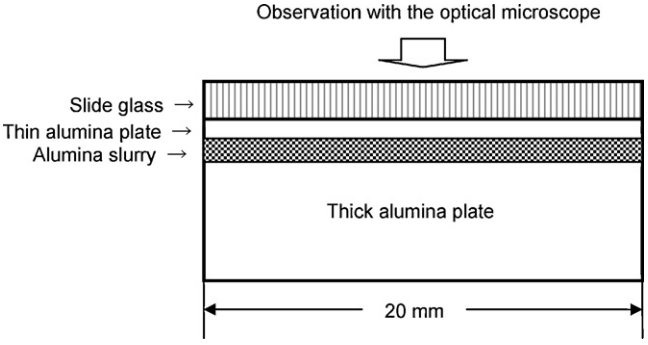

Fig. 1. Schematic illustration of the in situ observation of the slurry drying process. Formation of cavities in the interlayer during drying was detected through a thin translucent alumina plate (~100 μm) and a slide glass by optical microscopy.

scanning electron microscopy (SEM). Three to four specimens ($2 \times 3 \times 10$ mm) were prepared for strength measurements. These specimens have joints at the center of bend bars with the joints perpendicular to the longitudinal direction. The cross section of the joints was optically checked using ink-immersion method to detect large cavities. Three to four specimens without large cavities were used as test bars. Three-point bending strength was measured with a span of 8 mm and a crosshead speed of 0.5 mm/min. In addition to these small specimens, standard-size specimens were also used for MC sample which exhibited the best flexural strength. In this case, alumina blocks with a dimension of $20 \times 40 \times 13$ mm were cut from the alumina sintered bodies. Both surfaces of the 40×13 mm planes of the plates were ground with a 200-grit grinding wheel before joining tests. The joining process was the same as that for the small specimens. Test bars ($3 \times 4 \times 40$ mm) were machined from the joint sample. Four-point bending strength was measured in accordance with JIS R 1601 using an inner and outer span of 10 and 30 mm and a crosshead speed of 0.5 mm/min [14]. Five tests were repeated at room temperature. High temperature bending test was also conducted at 1200 °C in air using four JIS specimens.

3. Results and discussion

3.1. Drying and sintering behaviors of the interlayer

In-situ observation of the drying processes of the slurry in the joint gap of each sample is shown in Fig. 2. Cavities grew from the edges of the alumina plates into the center of the joints for ELC and LC samples ~25 min after the start of the drying process, whereas cavities were hardly observed for the MC and HC samples. Table 1 shows the relative densities of the green interlayers excluding the cavity region after drying of the slurry. The shrinkage of the slurry volumes after drying was estimated by dividing the solid load of the slurry by the relative density of green interlayer. The calculated decreases in the volume of slurry were ~25% for the former samples and 11–14% for the latter ones. The shrinkage of the slurry must be the origin of the cavities since the changes in thickness of the layer between the two surfaces were negligible. The area fraction of cavity should be equal to the shrinkage of slurry if the slurry was just filled only in the gap between faying surfaces. However, the area fraction of cavity for each sample was smaller than the volume change of the slurry. It is likely that small amounts of slurry protruding from the gap of the assemblies were pulled back into the gap as the water evaporated from the slurry, which prevented the growth of cavities for the latter samples. By contrast, the larger volume shrinkage of slurry for the former samples could not be compensated by this mechanism, leading to the formation of cavities.

Both changes in the thickness of the interlayer due to the sintering and the apparent relative densities of the sintered interlayer are also presented in Table 1. The shrinkage of the gap between faying surfaces was more than 37% for ELC, LC and MC samples. The maximum apparent relative density reached only 80% for MC. The change in spacing of the gap of HC was as low as 30%, leading to the second lowest apparent

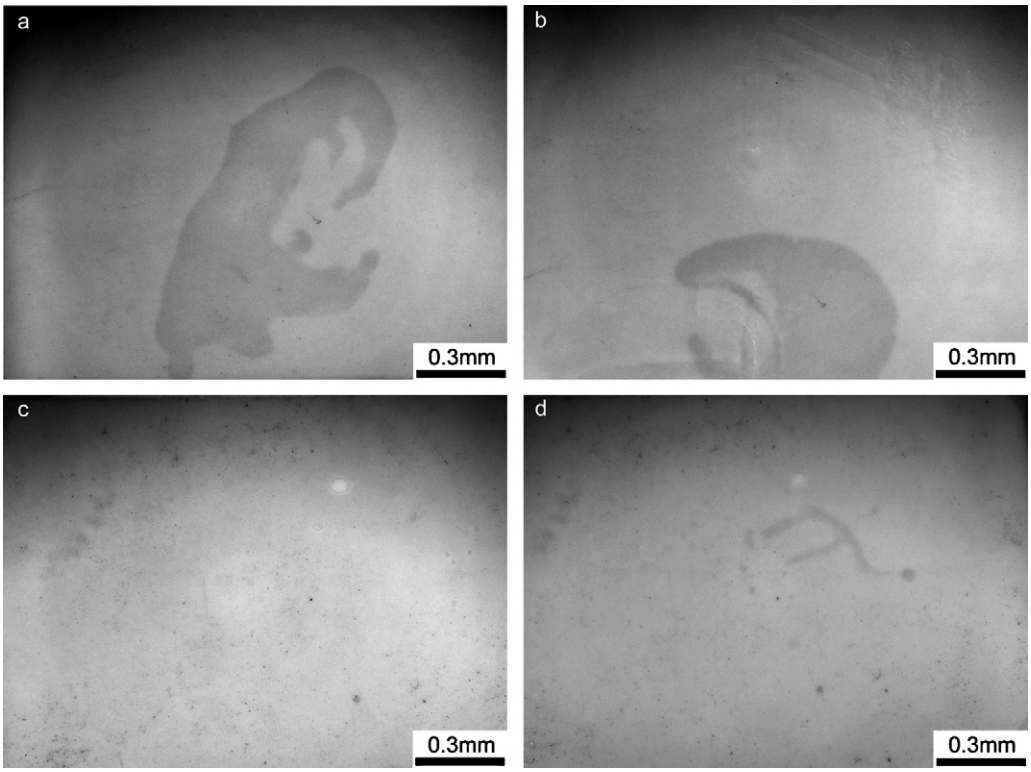

Fig. 2. Optical micrographs of the interlayers observed through a translucent thin alumina plate on the alumina slurry. The pictures were taken ~25 min after the start of drying. The solid contents of the starting alumina slurry were (a) 31.7 vol%, (b) 36.3 vol%, (c) 42.2 vol% and (d) 46.3 vol%. The dark gray areas indicate the cavities developed during the drying process of the slurry.

relative density of the sintered interlayer although the packing density of the green interlayer was the highest. The porosities of more than 20% for all these samples can be attributed to the constrained lateral shrinkage of the green interlayer sandwiched by alumina plates.

3.2. Microstructure of the alumina joints

Fig. 3 shows the microstructure of the alumina joints for ELC, LC and MC samples. The interlayer of each sample consisted of three characteristic parts: large voids, a porous area and a dense area. The heights of most voids were the same as the thickness of the interlayer. The widths of 20–60 voids measured from several SEM pictures for each sample ranged from 10 μm to ∼100 μm and the average size was in the range from 30 μm to 50 μm. Each constituent of the interlayer; voids, porous area and dense area, is enlarged further in Fig. 4 which was taken from the MC sample. The porous area contained many small pores and small grains, the sizes of both of which were around 2 μm (Fig. 4(b)). Several pores seemed to connect with each other to form pore clusters or chains with size of

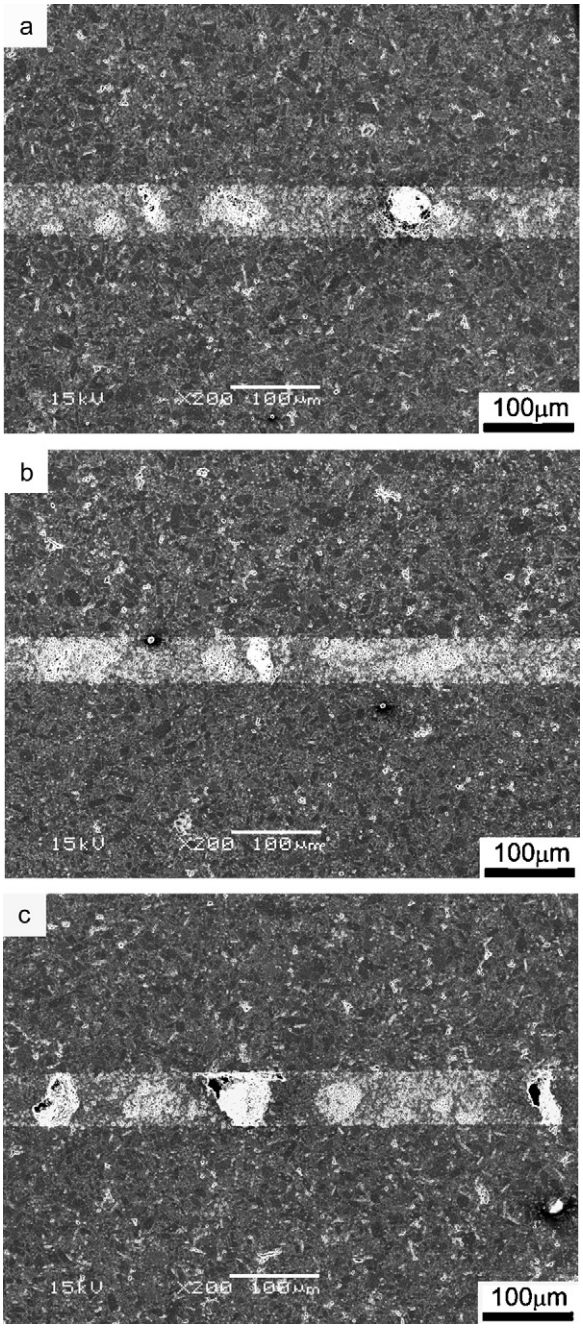

Fig. 3. SEM micrographs of the alumina joints prepared from pure alumina slurry. The interlayers consisted of large voids, a porous area and a dense area. The solid contents of the starting alumina slurry were (a) 31.7 vol%, (b) 36.3 vol% and (c) 42.2 vol%.

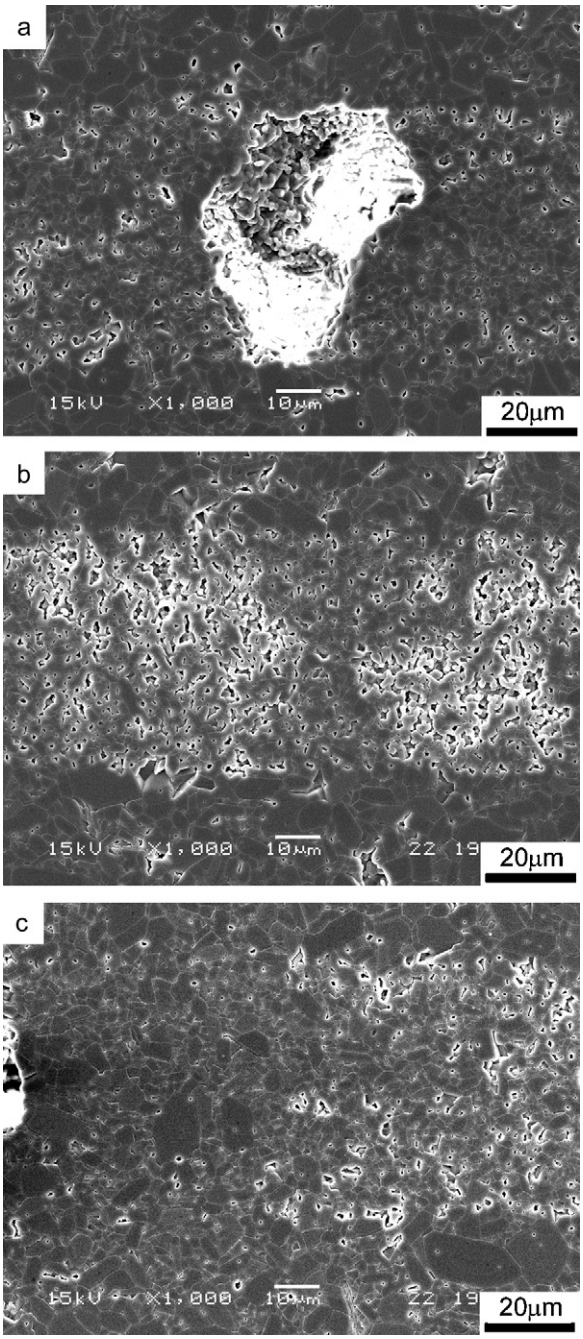

Fig. 4. Typical examples of (a) large voids, (b) a porous area and (c) a dense area in the alumina joints prepared from pure alumina slurry which solid content was 42.2 vol%.

~10 μm. The relative density of the porous area estimated roughly by the image analysis of the SEM micrograph was ~56%. By contrast, the dense area contained only a small amount of tiny pores with size of less than ~2 μm (Fig. 4(c)). The size of most grains in this area appeared to be around 2 μm, which was almost similar to that in the porous area. The area fraction of the pore in this area was measured to be ~3%, demonstrating that alumina in this area was densified almost fully. Interestingly, these dense areas were often located next to the large voids. No sharp lateral cracks on the interface between the interlayer and original alumina plates or within the interlayer were detected in both areas or in the vicinities of voids. These microstructural features were common to ELC and LC samples.

The microstructure of the joint for the HC sample with solid content of 46.3 vol% is presented in Fig. 5, where a sharp horizontal crack ran at the interface between the interlayer and the original alumina plate although other features of the microstructure were almost the same as the other samples. The interfacial cracks with sizes of more than ~300 μm were often observed in the joint. The lowest vertical shrinkage of the gap between the faying surfaces for this sample (Table 1) could be explained by the formation of these large interfacial cracks. It could be conjectured that the interfacial cracks might develop during the sintering since the dried green interlayer bonded so tightly to the faying surfaces that the assemblies could not be separated easily by hand. Further study is needed to clarify the mechanism of the occurrence of these large interfacial cracks.

3.3. Bending strength of the alumina joints

Large cavities introduced by drying, like Fig. 2a and b, were not detected during the preparation of the test specimens for LC, MC and HC samples by the ink-immersion method, while presence of large cavities was observed in some specimens for ELC samples. It was expected that the bending strength of ELC would be affected by the large cavities, and thus this sample was not included in the bending tests. After bending test, the

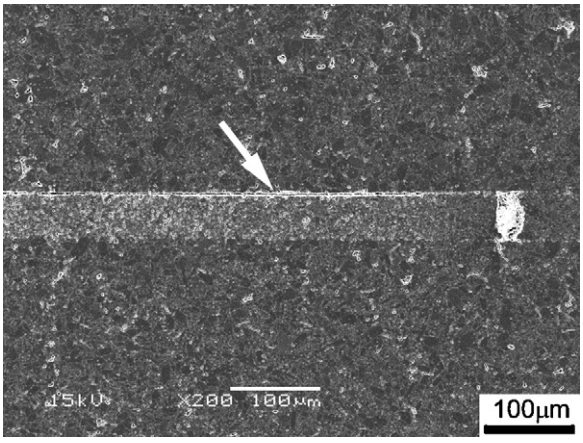

Fig. 5. SEM micrograph of the alumina joint prepared from pure alumina slurry with solid content of 46.3 vol%. The white arrow indicates an interfacial crack between the interlayer and the original alumina plate. Large voids, a porous area and a dense area were also observed in the interlayer.

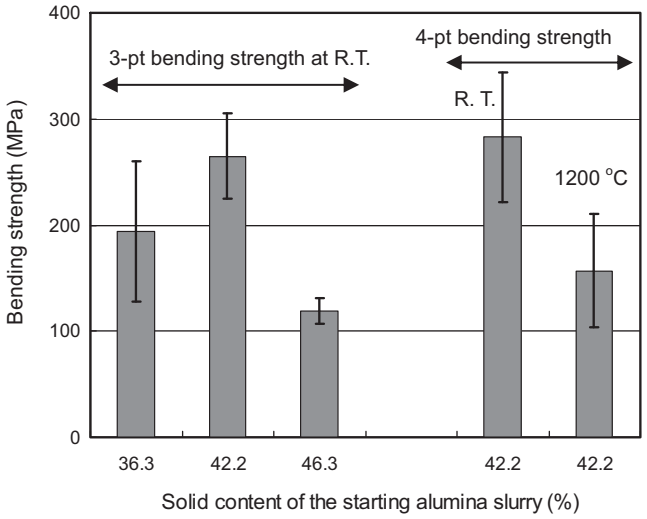

Fig. 6. Bending strength of the alumina joints prepared from pure alumina slurry with solid contents of 36.3, 42.2 and 46.3 vol%. Three point bending was carried out on 3–4 samples at room temperature while 4-point bending was carried out on five JIS-sized samples at room temperature and four at 1200 °C.

fracture surfaces were observed for all test bars. Only one test bar for the MC sample contained an internal cavity; the strength of this bar (71 MPa) was removed from the data set. Then the number of strength data for each sample was three. Three-point bending strength of the alumina joints for LC, MC and HC samples are presented in Fig. 6. An average strength of 265 MPa was attained for MC with slurry concentration of 42.2 vol%. By contrast, the average strength decreased significantly to 119 MPa as the solid content of the slurry increased to 46.3 vol% (HC sample). It was suspected that the high strength of more than 200 MPa for the MC sample may be due to the small volume of the test specimen. In order to exclude such a suspicion, four-point bending strength of JIS standard-size specimens was evaluated for MC. Large cavities introduced by drying were detected in some specimens during the preparation of the test specimens by ink-immersion method. Then only good specimens were selected for the test. Fracture surfaces showed no evidence of large cavities introduced by drying. A sufficiently high average bending strength of 283 MPa was also obtained for the sample by this method. Three out of five MC specimens broke at the interface and the fracture origins of the other samples were located out of the interface, which confirmed the high interfacial bonding strength. It is obvious that the superior joint strength of MC was attributable to the lack of interfacial cracks which deteriorated the bonding strength of HC. The reason why 2 of 5 fractures occurred away from the interlayer might be the degradation of bending strength of the original alumina plate due to coarsening of the microstructure by heat treatment at quite high temperature of 1650 °C for 2 h. The bending strength of most alumina joints with glass interlayers range from 150 to 260 MPa [4–8]. Therefore, the flexural strength obtained in this study was comparable to the best results previously reported for alumina joints with glasses. The MC sample also exhibited relatively high average strength of 157 MPa at 1200 °C, which cannot be expected for those alumina joints with glasses since

most of the softening temperatures of those glasses used in the joints were below 1100 °C [4,5,7]. It is evident that the developed alumina joint is of great advantage over those with glass interfaces when it is applied to components used in high-temperature conditions.

The mechanical strength of porous alumina has been examined by Lam et al. and Nanjangud et al. [12,13]. Lam et al. showed that the flexural strength of partially densified alumina is a function of fractional densification, $(\rho - \rho_0)/(1 - \rho_0)$, where ρ is the relative density of the porous alumina and ρ_0 is the initial relative density of the powder compact [12]. The fractional densification for the MC sample in the present work is calculated to be $(0.8 - 0.5)/(1 - 0.5) = 0.6$. The bending strength at this value of fractional densification is roughly estimated to be around 240 MPa by using their function, which is consistent with that of the MC sample. Nanjangud et al. reported that fracture strengths of samples with a relative density of 0.73 were about 110 MPa and those of samples with a relative density of 0.92 were around 260 MPa [13]. Thus, the bending strength of the joint with porous alumina in this study seems reasonable when compared with the flexural strength of porous alumina with a similar porosity.

However, our result is unusual in the field of joining since it was reported that diffusion bonding of zirconia with pure zirconia interlayer from slurry was difficult even when a large compressive pressure of 10 MPa was applied [3]. The microstructure of the joint in that work seemed to partially resemble those in the current work, but the joining was unsuccessful. Two possible reasons could be deduced for our notable results. The first is that in the current work the slurry concentration was optimized whereas in that previous work it was fixed although the thickness of the interlayer was varied. The second reason lies in the difference in the procedure, that is, the slurry was dried in the gap of faying surfaces to bond the green interlayer tightly to the adherents, while in the previous work both plates were coated with a slurry and assembled after drying.

Ozturk et al. reported that diffusion bonds of zirconia could be achieved with low applied pressure of 0.2 MPa by using electrophoretic deposition of a fine-grained particulate interlayer [9]. Low densities and shrinkage voids were not present in their sintered interlayer. While this is a useful technique for small sized samples due to the extremely low applied pressure as compared to conventional methods, the joining pressure is still inconvenient for the joining of large components. Furthermore, electrophoretic deposition on large ceramics parts would need special expensive facilities, which turn out to be impractical for the large-sized industrial applications.

Generally, both high pressure at elevated temperature and highly smooth faying surfaces are believed to be necessary for the diffusion bonding of ceramics since pores at the joints are believed to deteriorate the bonding strength [1,2]. This study, however, revealed that a porous interlayer possessed sufficient adhesion strength provided that macro defects, which seriously limit the strength, were eliminated. With this finding, pure diffusion bonding of alumina with high mechanical performance could be successfully achieved employing neither substantial applied pressure nor well polished surfaces.

However, there are some disadvantages for our technique. The method may not be applicable to the sealing components for vacuum devices since the final interlayer density was 80%. Because the constrained slurry is dried between the dense alumina plates in our approach, the time required for drying will depend on distance from the sample edge to the sample center. It is likely that much time is necessary for drying in the case of large samples. Other difficulty for joining of large samples is that large cavities may grow during drying process since the volume shrinkage of slurry will be difficult compensate by the pulling-back mechanism of slurry out of gap. Thus, the joining of large-area pieces by this method is challenging issue. It is also apparent that the original alumina substrate may be degraded by an extremely high joining temperature of 1650 °C. Consequently, our newly developed slurry approach is very attractive, and needs more studies to optimize the process parameters for practical applications.

4. Conclusion

In order to fabricate an alumina joint with pure alumina interlayer, a pure alumina slurry with dispersant was sandwiched by an alumina plate couple. The slurry was dried in the gap of faying surfaces and sintered at 1650 °C without substantial external pressure. Macro defects, which limit the strength, such as large cavities and lateral interfacial cracks were not observed in the joints when the solids loading in slurry was optimized. The microstructure of the interlayer was composed of three different regions: (a) large voids which width of less than ~100 μm, (b) a porous area with small pores (~2 μm) and (c) a dense area with small pores (<2 μm). An average of flexural strength of more than 280 MPa was attained at room temperature for the joint prepared from a slurry with solid content of 42.2 vol%, although the porosity of the interlayer was ~20%. Furthermore, a high temperature strength of more than 150 MPa was achieved at 1200 °C in air for this sample. It was revealed that high quality diffusion bonds of alumina could be made without either joining pressure or perfectly flat surfaces provided the microstructure of the porous interlayer was properly controlled.

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