The Influence of Particle Characterizations of Inner-Constraining Layer upon Constrained Sintering Shrinkage†

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Abstract

Constrained sintering of a substrate with a sandwich structure, which was the laminated inner-constraining alumina layer between the glass-alumina mixed layers, has been studied. The influence of specific surface area of the particles and porosity of inner constraining particle layer upon sintering shrinkage was investigated. Specific surface area of the alumina powder for the inner constraining particle layer could be changed by grinding and blending two different particle size powders. As for the debinded sheet used with ground alumina powder, the pore distribution was sharp, and the bending strength was proportional to the specific surface area. In the case of inner constraining particle layer used with ground alumina powder, penetration length of molten glass from glass-alumina mixed layers obeyed Kozeney-Carman’s equation. On the other hand, as for the debinded sheet with particle size blended powder, the effects of specific surface area on the bending strength and the penetration length of molten glass differed from the results of the grounded one. Sintering shrinkage in X-Y direction of the sandwich substrate was basically related to the bending strength of debinded alumina powder sheet for inner constraining particle layer in both cases.

Key words: Constrained sintering, Sandwich substrate, Inner-constraining layer, Penetration, Particle size, Pore distribution, Bending strength

1. Introduction

Recently, electronic equipment has become ever smaller, reflecting the growing demand for more compact, lower-profile electronic components and higher density electronic component packaging applications.

In the field of ceramic multi-layer substrates, a method for manufacturing LTCC (Low Temperature Co-fired Ceramics) substrates, whereby silver or copper electrode materials of relatively low electric resistance are fired together with ceramic powder, is gathering attention, and research work is underway to constrain sintering shrinkage to improve the dimensional accuracy of LTCC substrates.

Some of this research proposes methods to reduce sintering shrinkage in the X-Y direction on substrate1-6). According to these methods, a particle layer with a high melting point material, such as alumina, is laminated and fired on the surface of a formed member. Any of these methods can be used to produce an LTCC substrate with higher dimensional accuracy.

As a compound material consisting of glass and ceramic, LTCC substrates have a lower bending strength compared with conventional alumina substrates, etc.7). However, including a larger proportion of ceramic powder within the LTCC substrate composition does facilitate bending, although a higher sintering temperature is required. As a result, if electrodes are to be fired together with glass and ceramic powders, the potential amount of ceramic powder to be blended is limited8).

The authors have attempted to develop a substrate manufacturing process that is dissimilar to conventional equivalents of the non-shrinkage variety. With our substrate manufacturing process, a high melting point ceramic particle layer, which is not sintered at the normal glass material sintering temperature, is formed within the multi layer substrate in order to constrain sintering shrinkage in its horizontal direction. Namely, during the sintering process, the molten glass penetrates into the pores among the particles in the ceramic particle layer to form a low-porosity compound solid member consisting of glass and ceramic. The authors have proven that this method, combined with inhibition of LTCC substrates' sintering shrinkage, can improve the bending strength of LTCC substrates9, 10).

The authors have investigated the effects of a ceramic particle layer, which is not sintered at the normal glass material sintering temperature used in the authors' process, on the constraint of sintering shrinkage and densification of the substrate.

2. Experimental Method

2.1 Starting materials

The glass powder used for our experiment was a Si-Ca-Al-Mg-B-O based material available on the market; with a glass transition temperature of 933K, a thermal expansion coefficient of 4.4×10^{-6}/K and a specific gravity of 2.48. Low soda alumina powder was added to this glass powder at an amount of 40% by weight to prepare the glass-alumina mixture layer.

For the alumina particle layer, two alumina powder types with mean particle sizes of 0.4 and 1.5 µm respectively were used as starting materials. These powders were blended, taking their particle sizes into consideration, to provide particle-size blended powder types. At the same time, other powder types were prepared by grinding an alumina powder with a mean particle size of 1.5 µm at mass ratios of 100:0, 75:25, 50:50, 25:75 and 0:100.

The glass-alumina mixture slurries were dried and formed into 180 µm sheets, while the alumina slurries were dried and formed into 12 and 40 µm sheets.

These sheets were laminated to constitute the sandwich structure shown in Fig. 1 and then compressed into a solid member. More specifically, a 180 µm-thick glass-alumina mixture sheet was laminated on either side of a 12 or 40 µm-thick alumina sheet respectively, following which the laminates were compressed using a single-axis press.

Each compressed member was punched into pieces of specific dimensions, and each piece was then debinded by heating, with a temperature increase rate of 1K/min and a maximum temperature of 827K. Sintering was performed in air using a batch oven; the heat increase rate was 7K/min, the sintering temperature was 1153K, and the retention time was 60 min. The process chart of the experiment is shown in Fig. 2.
2.3 Method for measurement

2.3.1 Powder characteristics of alumina powder and alumina particle layer

The particle size distribution of each ground alumina powder was measured using a laser diffraction/dispersion particle size distribution analyzer (LA-700: Horiba).

As for the alumina powders having undergone particle size blending, the formed sheets were debinded by heating at 773K for 60 min, prior to the measurement of particle size distribution on these sheets using the aforementioned analyzer. The surface area of these alumina powders was measured using a BET technique (Monosorb: Yuasa Ionics).

2.3.2 Porosity and pore size distribution of alumina particle layer

The porosity and pore size distribution of the alumina particle layer were measured using a mercury porosimeter (Model 2000: Carlo Erba). The samples used were debinded sheets that were prepared by laminating 40 alumina green sheets, each one formed 40 µm-thick, compressing them together at 110 MPa and heating them at 773K for 60 min.

2.3.3 Bending strength of alumina particle layer

40 alumina green sheets, each one formed 40 µm-thick, were laminated; the green sheets were compressed together at 110 MPa and punched to provide a formed member measuring 5.0 x 3.0 x 1.5 mm. The formed member was debinded by heating at 773K for 60 min, before then being subjected to a three-point bending test with a fulcrum span of 25 mm and a cross head speed of 0.1 mm/s. The bending strength $\sigma_B$ of the formed body was determined with Eq. (1).

$$\sigma_B = \frac{3F_B L}{2Wt^2}$$

where, $F_B$ is the load at which the sample was broken, W, the width of the sample, t, the thickness of the sample, and L, the fulcrum span. A total of 10 identical samples were used for testing.

2.3.4 Penetration length of glass into alumina particle layer

A 180 µm-thick glass-alumina layer was forcibly bonded to each side of the 40 µm-thick alumina particle layer; then the resultant formed member was punched into 35 x 35 mm square samples, and the cross-section of samples analyzed for Al and Si mapping using a wave-length dispersion X-ray micro analyzer WDX (JXA-8800:JEOL). Based on the Al mapping diagram, the thickness of the alumina particle layer was measured, and then from the Si (a component of the glass) mapping diagram, the penetrating depth of glass into the alumina particle layer was measured. Hence, based on the difference between the thickness of the alumina particle layer and the penetrating depth of the glass, the glass packing depth into the alumina particle layer was determined.

2.3.5 Shrinkage percentage

A 180 µm-thick glass-alumina layer was forcibly bonded to each side of a 40 µm-thick alumina particle layer; the resultant formed member was then punched into 35 x 35 mm square samples, and the longitudinal and lateral dimensions of the compressed and sintered samples were measured. The shrinkage percentage was determined for the longitudinal, lateral and thickness directions of the samples; based on the proportion of the difference in dimensions before and after sintering.

3. Experimental Results and Discussion

3.1 Characteristics of alumina particle layer consisting of ground material

Fig. 3 provides particle size distribution curves obtained from powders that were prepared by grinding alumina powder of mean particle size 1.5 µm using a dry media agitating mill and respective grinding durations of 30, 120 and 300 min. The longer the grinding time, the smaller the proportion of large size particles. As a result, the particle size of each powder sample decreased as grinding proceeded, meaning the form of particle size distribution curves varied from a two-peak to a single-peak pattern. With a short
grinding time of 30 min, the ground powder was seen to peak at around 2.3 \( \mu \)m, with particle size distribution similar to that of a starting material, and a high volume percentage of large size particles in the ground powder. With longer grinding times (i.e. 120 and 300 min), the peak at 2.3 \( \mu \)m disappeared and the percentage of particles sized at around 0.5 \( \mu \)m increased.

**Fig. 4** summarizes the tendency of the specific surface area of ground powder that is dependent on the grinding time\(^{11}\). With a grinding time of 30 min or longer, the specific surface area increases proportional to the square root of the grinding time. However, the gradient gently increases within the time span from 0 to 30 min, meaning that the grinding speed is low. The reason for this seems to be the time lag before the aggregated starting powder material starts dispersion. **Fig. 5** illustrates the relation between the surface area and porosity with the debinded sheets; prepared using powders that were ground for 30, 120 and 300 min respectively. **Fig. 5** reveals the fact that the porosity remains unchanged, regardless of the specific surface area values. **Fig. 6** meanwhile shows the relation between the specific surface area of powder material before grinding and the bending strength of the debinded member that was heated at 773K for 60 min. **Fig. 6** shows that the bending strength of the debinded member increases proportional to the specific surface area of the powder material after grinding.

The relation between the three-point bending strength and the characteristics of the particle layer summarized here can be considered as follows: The issue of three-point bending strength can be treated as bending of a cantilever beam, the center of which is exposed to a concentrated load between both fulcrums. According to a bending strength formula derived from the Bernoulli-Euler assumption, maximum amounts of tensile and maximum compression stresses are exerted onto the outer skin of beam\(^{12}\). The compression breakage strength exceeds the tensile breakage strength and during a three-point bend-
ing test, breakage starts from the outer skin location exposed to the maximum tensile stress test. The three-point bending stress is considered to be equivalent to the tensile breakage strength.

It has been reported that the tensile breakage strength of a particle layer is affected by the interparticle adhesive force and the number of contact points [13-15]. Based on Fig. 5, since the porosity remains unchanged, regardless of the specific surface area, the coordination number of the particles seems to also remain virtually the same [16]. However, it appears that as the surface area of a powder increases, the number of particles in the unit area on the breaking face does the same. As a result, the number of contact points does likewise, which enhances the bending strength.

### 3.2 Characteristics of particle size blended alumina particle layer

Fig. 7 summarizes the relation between the blend proportions and specific surface areas resulting from samples prepared by particle size blending with alumina powders of which the mean particle sizes are 1.5 and 0.4 µm respectively. Based on Fig. 7, it is apparent that as the proportion of the large size particles increases, the resultant specific surface area linearly decreases.

Fig. 8 reveals particle size distribution curves with blend percentages of large size particles of 0% 25% 50% 75% and 100% respectively and with each sample exhibiting a two-peak particle size distribution pattern. Judging from the trend in Fig. 8, no peak shift occurred, even though the alumina powder was ground in a ball mill. This appears to result from the synthesis of particle size distribution curves of two alumina powders used for particle size blending.

Fig. 9 illustrates the relation between the proportion of large size alumina particles and the porosity of the alumina particle layer. Fig. 9 reveals that when the proportion of large size alumina particles is 25% the porosity is minimized and when the proportion of large size alumina particles exceeds 25% it increases. Fig. 10 shows the pore size distribution curves of the particle size blended powder samples. When the proportion of large size particles is 0% (A), a sharp peak is present at an R_p of 0.05 µm. When the proportion of large size particles is 25% (B), a peak occurs at R_p of 0.06 µm, meaning a slight shift in this peak. When the proportion of large size particles is 50% (C), two peaks are present on the pore size distribution curve; namely one at 0.06 µm and the other at 0.1 µm. When the proportion of large size particles is 75% (D), there is no peak at 0.06 µm while peaks are present at 0.1 and 0.20 µm. The latter peak, at 0.20 µm, is also pre-
sent when the proportion of large size particles is 100% (E). It appears that the peak at 0.22 µm shows a slight tendency to shift to the smaller particle size side.

From these findings, it seems that the pores are present in several clear-cut size groups and that small pores are present among finer particles, large pores are present among larger particles, and there is also the presence of medium-sized pores. The medium-sized pores are considered to be pores that occur following disordered arrangement of fine particles situated near the large particles within an alumina layer packed with arranged fine particles.

**Fig. 10** illustrates the relation between the proportions of large size alumina powder and the pore radii $R_{P90}$, $R_{P50}$, and $R_{P10}$, measured using a mercury porosimeter. The pore radius $R_{P50}$ increases in correlation with an increase in the proportion of large size alumina particles. The pore radius $R_{P90}$, however, remains virtually constant up to the blending proportion of large size particles of 75% and rapidly increases when the proportion of large size particles is 100%. The pore radius $R_{P10}$ increases until the proportion of large size particles reaches 50% and becomes virtually constant when the proportion of large size particles is 75% or higher.

**Fig. 11** provides the relation between the specific surface area of ground and size blended alumina particles and the bending strength of the alumina particle layer. The ○ marks in the diagram represent the results obtained from alumina particle layers made from size blended alumina particles, while the ● marks indicate the results obtained from alumina particle layers made from ground alumina particles. Though the porosity of the alumina particle layers made from size blended alumina particles exceeds...
that of the alumina particle layers made from ground alumina particles, the bending strength of the former layers is lower than that attained by the latter that are made from ground alumina particles and have a lower porosity. An alumina particle layer comprising 75% of large size particles (Point A) and one composed of particles ground for 120 min (Point B) each exhibit a specific surface area of approximately $4 \times 10^3$ m$^2$/kg. From this diagram, the bending strength of alumina particle layers comprising size blended particles can be considered to have degraded, due to the blending of particles of a smaller specific surface area. The bending strength values at Points A and B are 1.5 and 2.8 MPa respectively; with the latter twice as large as the former. Likewise, at Points C and D, each exhibiting a specific surface area of $6 \times 10^3$ m$^2$/kg, the bending strength values are 2.8 and 4.2 MPa; with the latter 1.5 times the former.

In addition, the bending strength of the alumina particle layer with 75% of large size particles (Point A) is equivalent to an alumina particle layer composed of 100% of large size particles. The possible reason is considered to be as follows: With size blended particles, the pores formed among large size particles are packed with fine particles, resulting in a higher packing density. If a smaller amount of fine particles is present, virtually all of them fill the pores among those of a larger size; hence the bending strength of the alumina particle layer is governed by the contact points between the large size particles.

Seemingly, as the proportion of small size particles increases, the inter-particle distance between the large size particles does the same; the number of contact points among the small size particles rapidly increased, as did the bending strength of the alumina particle layer.

3.3 Effect of alumina constrained layer onto substrate characteristics

3.3.1 Effect on shrinkage of substrate

Sandwich substrates, each consisting of a 12 µm alumina particle layer sandwiched between 180 µm glass layers, were prepared, where the 12 µm alumina particle layer was formed using ground or size blended particles. Fig. 13 illustrates the relation between the bending strength and shrinkage in the horizontal directions (X-Y) of these substrates. The ○ marks represent alumina particle layers made from size blended particles while the ● marks stand for those made from ground particles. As Fig. 13 reveals, the results from all starting materials can be plotted on a single curve. Although the horizontal shrinkage is extremely large when the bending strength of the alumina particle layer is 1.8 MPa or lower, conversely, when the bending strength is 1.8 MPa or higher, the shrinkage is as low as 0.5%

Glass layers on both sides of a constrained layer shrink when the substrate is fired, and a compression stress is exerted onto both faces of the constrained layer. Assume that the constrained layer is separated in its mid section. A bending moment will occur on each constrained layer toward the glass-alumina layer. When the alumina particle layer can no longer withstand this moment and fails to maintain the layer structure, the shrinkage value climbs. Therefore, it is important to increase the bending strength of the alumina particle layer in order to decrease the sintering shrinkage.

3.3.2 Effect on substrate porelessness

To be able to produce a poreless ceramic substrate, molten glass must penetrate into its alumina particle layer during the sintering process. Hence, the authors investigated the effect of the packing structure of alumina particle layer onto the distance of glass penetration. Crystallization of the glass was inspected on a glass-alumina layer, which was sintered at 1153K with a X-ray diffraction technique. As a result, no peak other than that for alumina was found. This means that crystallization of the glass did not occur.

Generally, when liquid penetrates into a particle layer, the distance of penetration can be defined with the Kozeny-Carman formula:

$$l^2 = \frac{e^3 \cdot \Delta P \cdot T}{K (1-e)^2 S^2 \cdot \eta}$$  \hspace{1cm} (2)

where, $l$ is the distance of liquid penetration into a particle layer, $\Delta P$, the difference in pressure that is a
motive force for penetration, \( T \), the time needed for penetration, and \( \eta \), the viscosity of the liquid. \( K \), meanwhile, is a constant known as the Kozeny constant. The difference in pressure \( \Delta P \) that is a motive force for penetration is considered to be a value equivalent to a capillary suction force \( P_C \) of a particle layer. When the radius of the capillary is \( r_C \), the capillary suction pressure \( P_C \) can be expressed using the following formula:

\[
P_C = 2\sigma_s \cdot \cos \theta / r_C \tag{3}
\]

where \( \sigma_s \) is the surface tension of liquid, and \( \theta \) the contact angle of wetting between the liquid and particle layers. The hydraulic radius \( r_H \) used to derive the Kozeny-Carman formula can be defined by the following formula:

\[
r_H = \left\{ e / (1 - \epsilon) \right\} \left( S_W / \rho \right) \tag{4}
\]

When \( \gamma_H \) is substituted for the capillary radius \( \gamma_C \) in Eq. (3), and \( P_C \) is substituted for \( \Delta P \), then Eq. (2) can be represented by Eq. (5).

\[
{ e^2 \over (1 - \epsilon) \cdot S_W} \tag{5}
\]

From the formula above, it can be understood that the square of distance of glass penetration \( l \) into a particle layer is proportional to \( e^2 / \left\{ (1 - \epsilon) \cdot S_W \right\} \).

**Fig. 14** shows the effect of the distance of glass penetration onto \( e^2 / \left\{ (1 - \epsilon) \cdot S_W \right\} \) when sintering was performed at 1153K for 60 min.

In **Fig. 14**, the \( \circ \) marks represent alumina particle layers made from size blended alumina particles and the \( \bullet \) marks stand for alumina particle layers made from ground alumina particles. In the case of alumina particle layers made from ground alumina particles, the square of the penetration distance varies in proportion with \( e^2 / \left\{ (1 - \epsilon) \cdot S_W \right\} \) according to the Kozeny-Carman formula. Incidentally, with alumina particle layers made from size blended alumina particles, glass readily penetrated into the alumina particle layer in comparison with those made from ground alumina particles. As the pore size distribution curves in **Fig. 10** indicate, the alumina particle layers made from size blended alumina particles, unlike those made from ground alumina, exhibit two clear-cut peaks. From Eq. (5), it also appears that glass selectively penetrated into larger sized pores. Because larger sized pores appear to govern the penetration of glass, the relation between \( R_{P10} \) and the penetration distance was plotted in **Fig. 15**. The pore size \( R_{P10} \) and distance of penetration exhibit a linear relation. For this reason, larger pore sizes are considered to greatly affect the distance of glass penetration. Additionally, the peak in the large size particles in the alumina particle layer made from particle size blended alumina particles appears to be greatly affected by the packing structure around the larger particles.

**4. Conclusion**

The authors investigated low temperature-fired substrates using a glass-alumina mixture, and more specifically, the effect of the packing structure of an alumina constrained layer on the substrate, wherein the alumina constrained layer, which is not sintered at a sintering temperature for the substrate materials, is provided in the middle of the substrate.

The results obtained from the investigation are summarized below:

1) As the bending strength of an alumina sheet to be used as a constrained layer increases after debinding, the shrinkage of the substrate in horizontal directions decreases. In addition, the relation between the bending strength and shrinkage in hori-
...cal directions of the substrate can be plotted on the same curve, regardless of whether the constrained layer is made from ground alumina or size blended alumina particles.

2) When the constrained layer is made from ground alumina particles and assuming the porosity of the particle layer remains constant, the bending strength is proportional to the specific surface area.

3) When the constrained layer is made from size blended alumina particles, the pore size distribution curves each exhibit a two-peak pattern, and the bending strength of an alumina particle layer made from size blended alumina particles was lower than that obtained from any alumina particle layer made from ground alumina particles. This fact seems to result from a decrease in the number of contact points around the large particles, which led to a loss in bending strength.

4) The distance to which the glass penetrates the alumina particle layer made from ground alumina particles conforms to the Kozeny-Carman formula. In the case of an alumina particle layer made from size blended alumina particles, glass penetrates more readily into the alumina particle layer. With an alumina particle layer consisting of size blended alumina particles, two peaks occur on the pore size distribution curve owing to the presence of large size particles, and the penetration distance is dependent on the larger pore size of the two peaks.

**Nomenclature**

- \( D_p \) : particle diameter (\( \mu m \))
- \( D_{SW} \) : specific surface area diameter (\( \mu m \))
- \( F_B \) : bending force (N)
- \( K \) : constant for Eq. (2) (–)
- \( L \) : fulcrum span (m)
- \( l \) : distance of penetration (\( \mu m \))
- \( P_C \) : capillary suction pressure (M Pa)
- \( R_p \) : pore size (\( \mu m \))
- \( r_c \) : radius of capillary (\( \mu m \))
- \( r_h \) : hydraulic radius of powder bed (\( \mu m \))
- \( S_W \) : specific surface area (m\(^2\)/kg)
- \( T \) : time of penetration (s)
- \( t \) : thickness of the substrate (m)
- \( V_L \) : proportion of large size alumina (\%)
- \( W \) : wideness of the substrate (m)
- \( \Delta P \) : difference of pressure (M Pa)
- \( \varepsilon \) : porosity (–)
- \( \eta \) : viscosity (Pa·s)
- \( \rho \) : density of particle (kg/m\(^3\))
- \( \sigma_B \) : bending strength (M Pa)
- \( \sigma_s \) : surface tension (N/m)

**References**

Author’s short biography

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