

## Sintering Distortion of Barrier Ribs Formed via Capillary Molding Route

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### Abstract

In this study, sintering behavior of closed-cell type barrier ribs formed via capillary molding route was examined. Sintering of the molded barrier ribs revealed asymmetric shrinkage, leading to distortion of the cells. The effects of the parameters such as solid loading in the paste, presintering temperature, and morphology of the barrier ribs on the sintering shrinkage of the barrier ribs were investigated.

### 1. Introduction

Recently, PDP has been considered as a prime candidate for large-area information display. The processing costs, luminance efficiency,<sup>1</sup> and resolution of PDP must be improved more to expand the wide-spread use in wall-hanging TV. For that purpose, a new processing route for closed-cell type barrier ribs needs to be developed. Currently, barrier ribs of PDP are being produced using powder blasting process.<sup>2</sup> This process has merits of low cost, expandability to large area device, and high processing speed. This process, however, has difficulties in producing barrier ribs of closed-cell type, such as SDR, DeITA, and honeycomb.

The authors have demonstrated the possibility of using capillary molding route in producing the closed-cell type barrier ribs<sup>3</sup>. In this process, a soft working mold is placed on the top of paste coated on the glass substrate and let the capillary pressure developed between the mold and paste to fill the cavities of the mold (Fig. 1)<sup>4</sup>. The mold is released after the paste is thermally cured. This process can reduce the processing steps and loss of the materials. In addition, the dimension of the ribs produced can be refined and controlled more precisely than those produced by the powder blasting process.

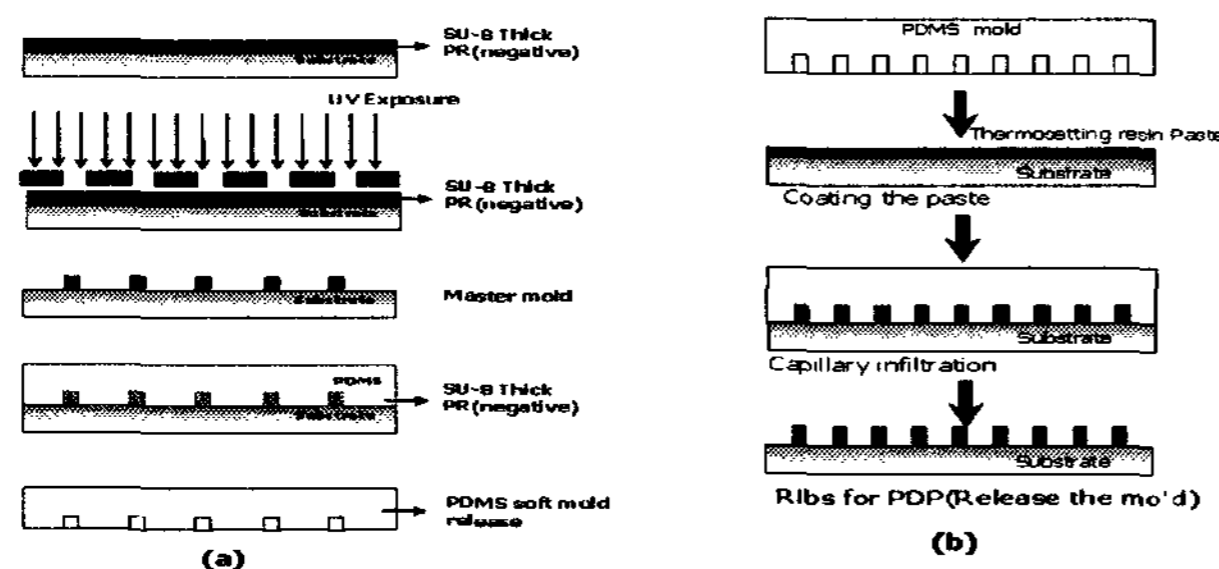


Figure 1.(a) master mold preparation and (b) capillary molding process

Sintering of the closed-cell type barrier ribs<sup>5</sup> produced by the capillary molding process, however, revealed asymmetric shrinkages of the ribs, resulting in the distortion of the sintered ribs. In this study, therefore, the effect of parameters such as solid loading in the paste, presintering temperature, and asymmetric design of the barriers ribs on the sintering shrinkage of the barrier ribs were investigated.

### 2. Experimental procedures

Master molds for the capillary molding process were prepared using a photoresist resin (SU-8 2075, Micro-Chem, USA). A resin film of 200 $\mu$ m thick was formed on a silicon wafer by spin coating. The film was patterned after the barrier ribs in cells of stripe, DeITA, and SDR arrangements using a conventional UV lithography process. The pattern was used as a master mold. Subsequently, polydimethylsiloxane (PDMS, Dow Corning, USA) mixed with a curing agent (Sylgard 184, Dow Corning, USA), was cast on the top of the master mold and cured in a vacuum oven at 120 $^{\circ}$ C for 30 minutes. The PDMS mold was used as the working mold for capillary molding process. The processing step of the mold preparation is schematically illustrated in Fig. 1(a). For the paste to fill-up the mold cavity, a thermally curable paste was used. The paste consisted of epoxy resin of biphenol A type (YH-300, Kukdo-Chem, Korea), amine type hardener (BF3-monoethylamine, Aldrich, USA), dispersant (Byk111, BYK Chem. Germany), and ceramic powders (glass frit and alumina powders).

The paste prepared was printed on a glass plate (PD-200, Asahi Glass Co., Japan) and the thickness of the layer was  $\sim$ 40 $\mu$ m. Subsequently, the PDMS mold was placed on the top of the paste and kept in a drying oven at 120 $^{\circ}$ C for 1 hour for curing of the paste. After the sample is taken out of the oven, the mold was removed from the sample. A schematic illustration of the capillary molding process is shown in Fig. 1(b). After the molding process, the sample was heated at a rate of 5 $^{\circ}$ C/min to prefiring temperatures and kept for 1 hour. The prefiring temperature was varied from 450 $^{\circ}$ C to 520 $^{\circ}$ C. After the prefiring stage, the sample was heated at the same rate to 570 $^{\circ}$ C for sintering. The holding time at the sintering temperature was 30 minutes. The sintering was conducted in air atmosphere.

### 3. Results

#### 3.1. Mechanism of sintering distortion of SDR type barrier ribs during sintering

Figure 2 shows the morphology of SDR type barrier ribs in (a) cured and (b) sintered states. As shown in the figure, the morphology of the ribs was severely distorted such that the rectangular cells were change to octagonal type cells after the sintering.

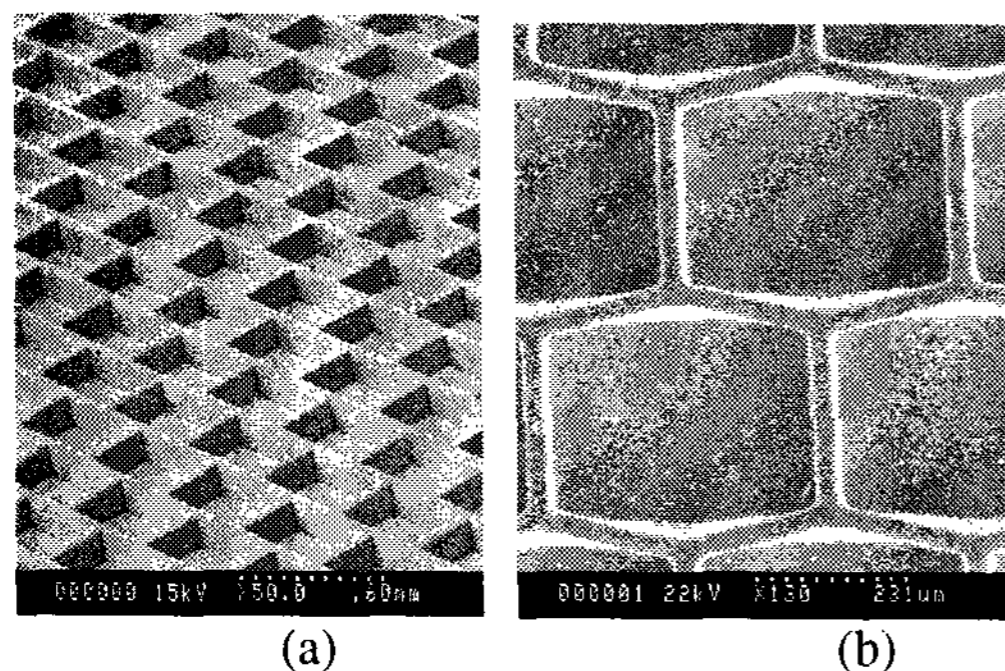


Figure 3. SEM micrographs of SDR Type in (a) cured and (b) sintered states.

This distortion is believed mainly due to an anisotropic shrinkage of the barrier ribs during sintering. As illustrated in schematic diagram (Fig. 4), the shrinkage from crossing ribs during sintering should pull the horizontal ribs together, resulting in the distortion. Similar phenomenon was observed with DelTA type cells. In this case, the ribs were observed to be twisted as the meander shape tends to straighten to minimize the surface free energy of the ribs.

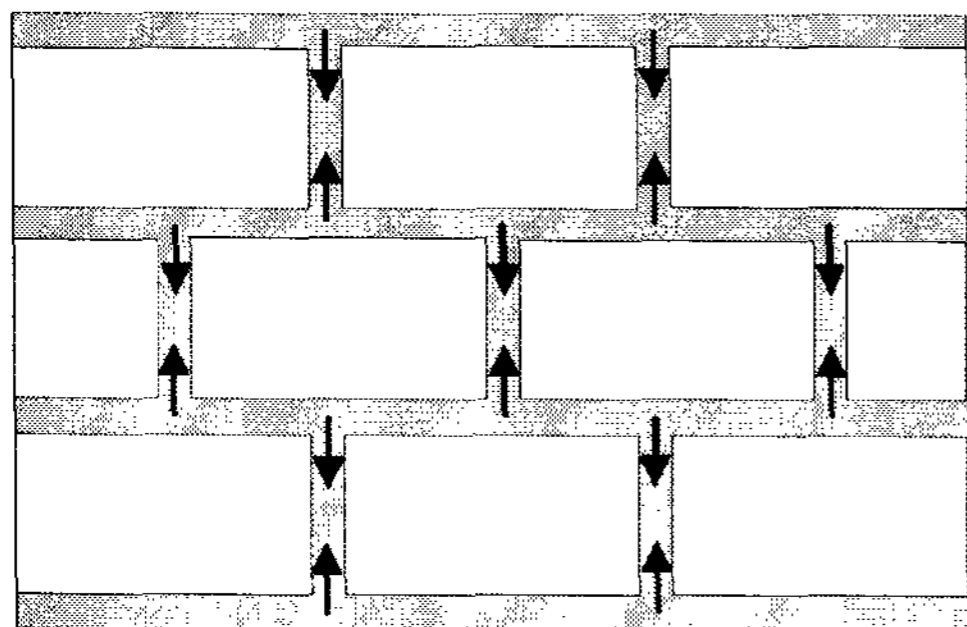


Figure 4. Schematic illustration of sintering stress on SDR type barrier ribs.

Figure 5 shows the microstructure of the barrier ribs in a cured state. In the cured state, the ceramic powders are separated from each other by the binder polymers. Upon sintering process, the binder are evaporated and powders are aggregated each other to form fully dense barrier ribs. The distortion of the ribs, therefore, may be caused either by evaporation of the organic components during the prefiring step

or by the densification of the powders during the sintering steps.

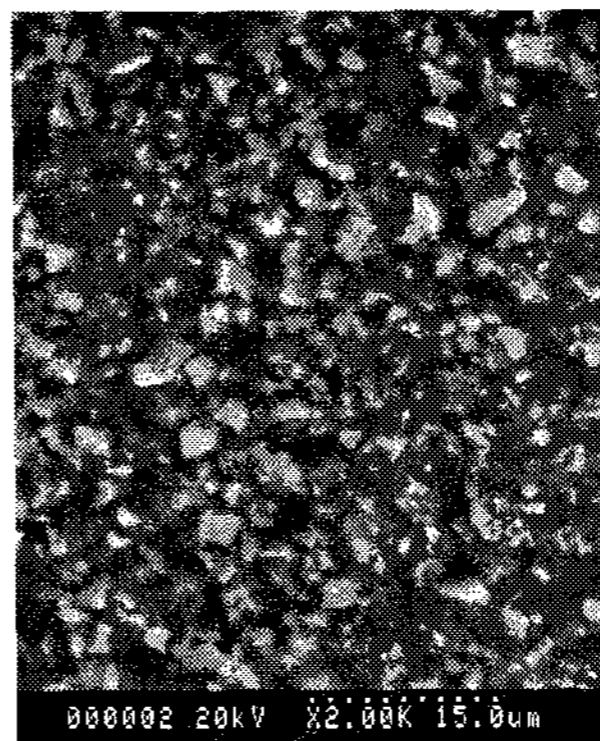


Fig.5. SEM micrograph of barrier ribs in cured state.

In order to examine the effect of the shrinkage occurring during the binder evaporation, the ratio of maximum cell width at its center ( $d_2$ ) to crossing rib length ( $d_1$ ) of SDR type cell was measured as a function of prefiring temperature. The value of a cell should increase with the distortion. As shown in the Fig. 6, the ratio was 1.38 with the cells prefired at 400°C. This means that the width of the cell at the center is larger than that at the barrier ribs by 38%. As the prefiring temperature is increased to 520°C, the ratio was slightly increased to 1.42. In other words, the distortion was not affected significantly with the prefiring temperature. This indicates that a significant fraction of the distortion occurred during the densification of the powders.

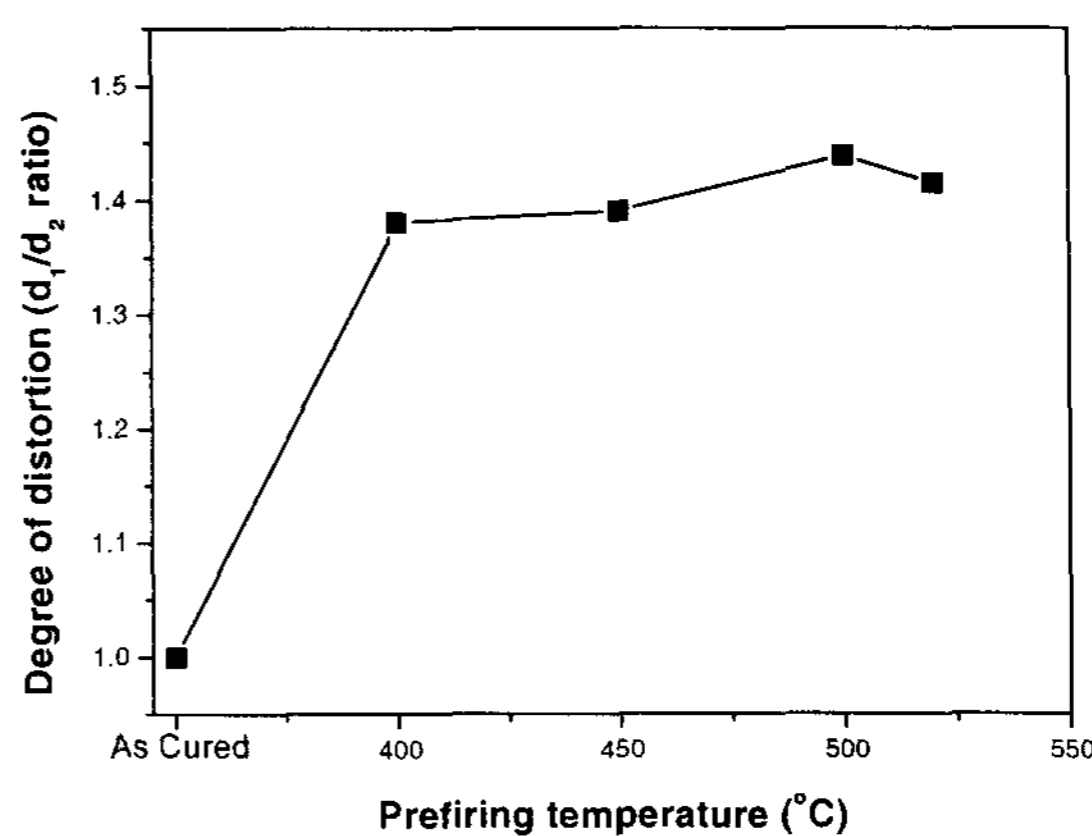


Fig. 6. Effect of prefiring temperature on the degree of sintering distortion on the SDR type barrier ribs.

Figure 7 shows the effect of powder content in the paste on the distortion of SDR type cells. The powder content in the paste was changed from 54 to 60 wt.%. The content could not be increased over 60 wt.% due to increased viscosity of paste with the powder content. As noted from the figure, the

distortion became less with the increase in the solid loading, suggesting that the shrinkage associated with densification is the main cause of the distortion.

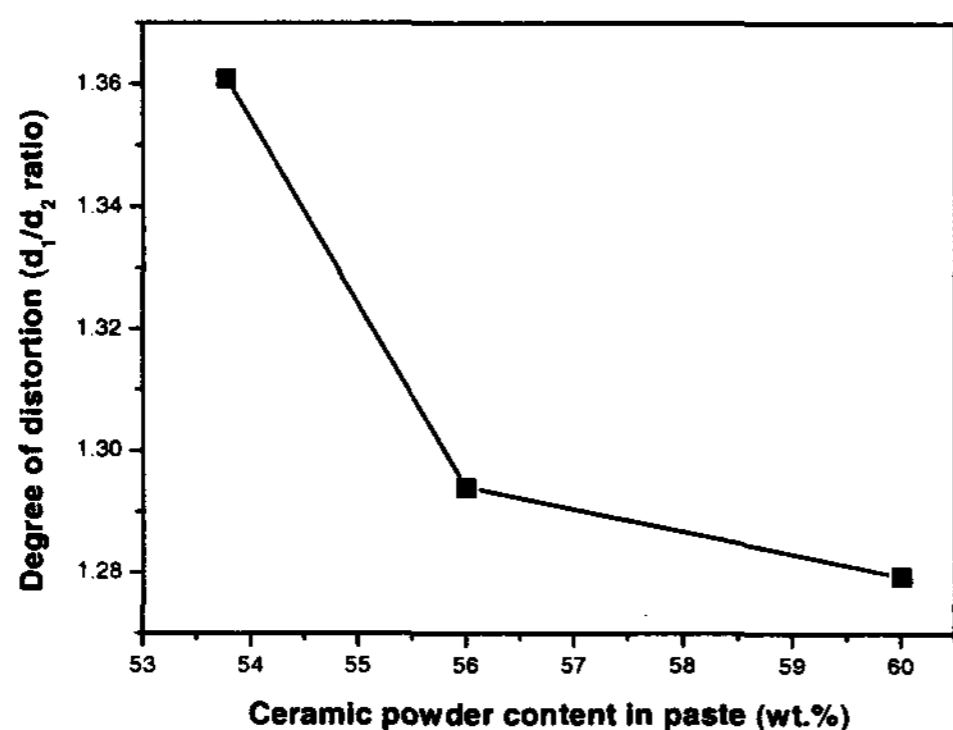


Fig. 7. Effect of solid loading in paste on the sintering distortion of barrier ribs of SDR type.

One of the ways to reduce sintering distortion is to reduce sintering distortion is to increase alumina content in the barrier ribs. Fig. 8 shows the barrier ribs of SDR type containing 30 wt.% of alumina. As shown in the figure, the distortion of the barrier ribs was minimized. The addition of alumina should have retarded the viscous sintering of barrier ribs and reduced the distortion of the ribs. The observation of the microstructure of the ribs, however, revealed that a significant amount of pores remaining in the ribs. The pores should degrade the mechanical properties of the barrier ribs and out-gassing from the ribs during operation of the PDP.

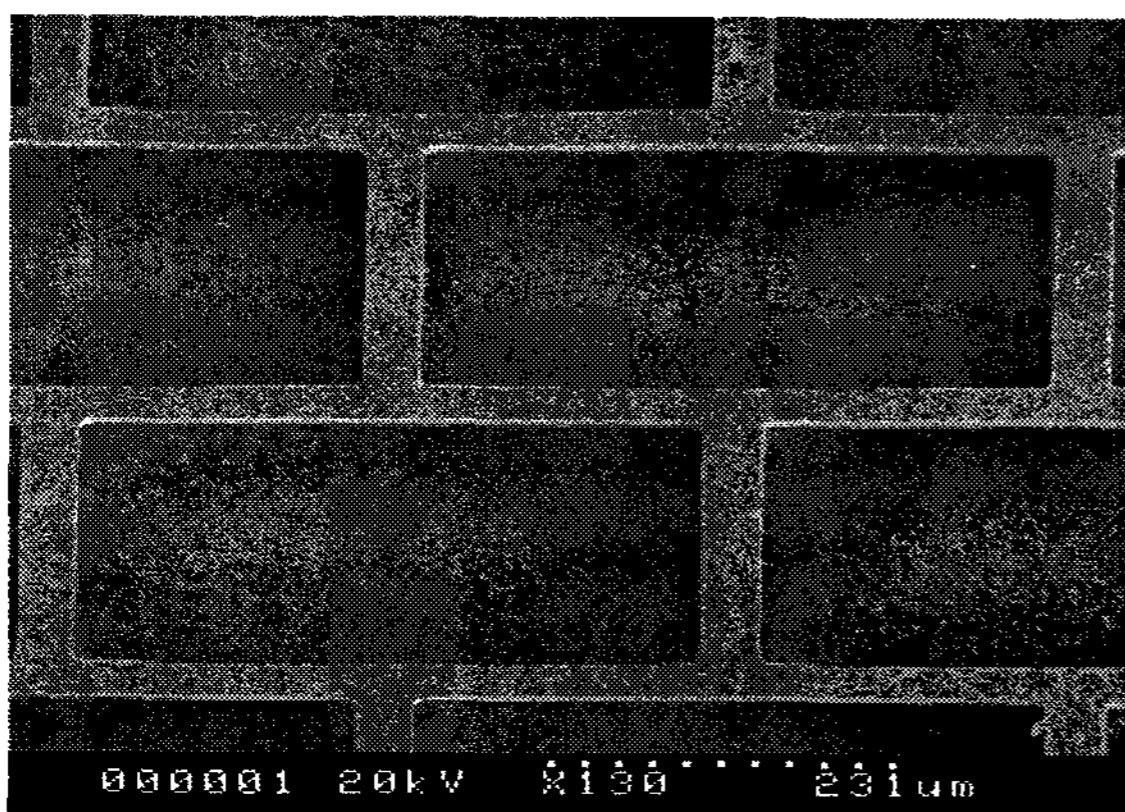


Fig. 7. Morphology of SDR type barrier ribs containing 30% alumina.

The distortion of barrier ribs of asymmetrical shrinkage poses a significant limitation for the processing of the cells such a SDR and DeITA via the sintering route. As the barrier ribs in green state should include a significant fraction of pores between powders, the distortion of the ribs may occur due to the asymmetrical shrinkage occurring during densification process. In other words, symmetrical cells such as honeycomb and waffle type cells might be more suitable for the processing of barrier rib via sintering route as the distortion associated with densification can be minimized.

#### 4. Conclusions

The distortion of barrier ribs of closed-cell type during sintering was found to occur during densification stage of sintering step. The results indicated that the degree of distortion might be minimized by employing barrier ribs of symmetrical geometry.

#### 4. Acknowledgements

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#### 5. References

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