

Effect of stress on the densification of a low-temperature cofired ceramic (LTCC) system under constrained sintering

Jui-Chuan Chang¹, Jau-Ho Jean¹ and Yao-Yi Hung²

¹Department of Materials Science and Engineering, National Tsing Hua University

²ACX Corp. (www.acxc.com.tw)

Hsinchu, Taiwan, ROC

The effect of stress on the densification behavior of a low-temperature cofired borosilicate glass (BSG)+alumina system during constrained sintering of a multilayer BSG+alumina/alumina laminate has been investigated. Poorer densification and larger porous bulk viscosity are observed for the BSG+alumina densified under pressure-less constrained sintering in comparison to free sintering. This is caused by the in-plane tensile stress and anisotropic development generated in the transverse directions of the laminate during constrained sintering. The applied uniaxial stress required in the thickness direction to densify BSG+alumina under constrained sintering at 700-800°C varies in the range of 50-400 kPa, in agreement with those calculated theoretically.

Introduction

Several constrained sintering techniques, such as sinter forging [1-3], using non-shrinking green tapes [4-6], using rigid substrates [7-13] or self-constrained sintering [14], are reported. The technique using non-shrinking green tapes is commonly used due to its ease and flexibility in green line and cofiring processes. In this approach, alumina green tapes are used as constraining layers [4-6], and a sandwich structure of alumina/borosilicate glass (BSG)+alumina/alumina is fabricated. Since the sintering temperature required for alumina tape is much higher than that of BSG+alumina, the lateral shrinkages of the laminate are eliminated by the non-shrinking alumina tapes during cofiring. This generates an in-plane tensile stress in the transverse directions of the laminate, which reduces the total driving force of densification [5]. For the technique of sinter forging, the applied stress required in the thickness direction to fully constrain the BSG+alumina system, i.e., zero strain or strain rate in the lateral directions, is in the range of 20-250 kPa [2] at 700-900 °C. The required uniaxial stress increases with temperature initially, reaches a maximum at 725-800 °C, and then decreases with increasing temperature.

To have better understanding of mechanical response and densification behavior of the low-fire BSG+alumina system under constrained sintering, a combination of the above two techniques, i.e., pressure-assisted constrained

sintering, is used. One of most important advantages to conduct pressure-assisted constrained sintering is that no shrinkage in the transverse directions of multilayer laminate takes place, which simplifies the analysis of mechanical response of densifying compacts at elevated temperatures. The low-fire BSG+alumina system, which can be densified at 700-900 °C, is also chosen to investigate the effect of uniaxial stress on densification during constrained sintering of multilayer BSG+alumina/alumina laminates. The alumina green tape acts as a constraining layer, and multilayer BSG+alumina/alumina laminate is used to minimize the effect of free sintering, which causes significant error in measuring uniaxial strain during constrained sintering. The uniaxial stress required to densify BSG+alumina under pressure-assisted constrained sintering is determined, and compared with that calculated using the viscous analogy for the constitutive equations of a porous sintering compact [15-18].

Experimental Procedure

A commercially available borosilicate glass (BSG) powder, which had a softening point of 680-700 °C, was used. Alumina powder with a median size of 2.0 µm was used to cast constraining layer. A BSG+alumina system of 50-80 vol% BSG and 20-50 vol% Al₂O₃ was prepared. Slurry with a commercial nonaqueous organic vehicle (B73305, Ferro, CA) containing binder, plasticizer and solvents was used to cast

green tapes. The slurry was cast on Mylar carrier (DuPont, Delaware) using a bench-type tape caster. Tape drying was carried out isothermally at 60 °C. Green tapes on the carrier film were stored in a dry box with a controlled temperature and relative humidity at 25 °C and 50%, respectively. Both pure alumina and BSG+alumina green tapes were uniform and had a thickness of about 30 μm . For symmetric laminates, the BSG+alumina and alumina green tapes were stacked in an alternating sequence to total 61 layers, with both of the surface layers being alumina. The lamination condition used in this study was 18 MPa at 80 °C for 5 min. The relative green density of the pressed laminate was measured dimensionally, and the value was 57-58% of the theoretical density of the fired substrate. To measure the theoretical density of the fired laminate, it was ground to fine powders and the density was measured by He pycnometer (Marvlen, USA). The laminates were sectioned to have a size of 3.65x2.85x1.78 mm³, and binder removal was conducted at a heating rate of 2 °C/min from room temperature to 450 °C. To remove the organic completely, the laminates were held at 450 °C for 2h. After binder burnout, the samples were fired at a heating rate of 70 °C/min to 700-800 °C. For pressure-assisted constrained sintering, a uniaxial constant or cyclic loading was applied after binder burnout using a loading thermal mechanical analyzer (TMA, Seiko, Chiba, Japan). The linear shrinkage in the thickness direction of the multilayer laminate was measured isothermally. Microstructure of the densified multilayer BSG+alumina laminates was examined by SEM.

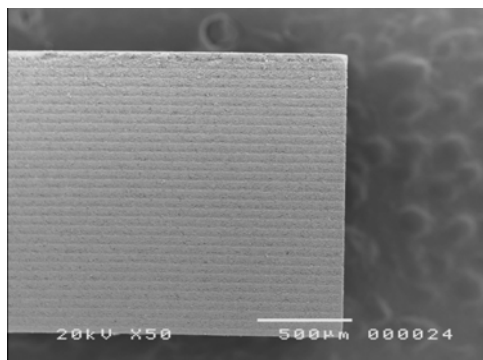


Fig. 1 SEM micrographs for multilayer Al₂O₃/BSG+alumina structure fired at 800°C for 30 min.

Results

To minimize non-uniform deformation at the edge of the laminate, a multilayer structure, which is formed by laminating an alternating sequence of BSG+alumina and alumina layers (Fig. 1), is used. A flat surface at the edge of the

multilayer laminate is observed because the thickness of BSG+alumina layer is only 30 μm that is easily constrained by the alternating alumina layers. Therefore, data obtained from the experiments using multilayer BSG+alumina/alumina laminates are discussed below.

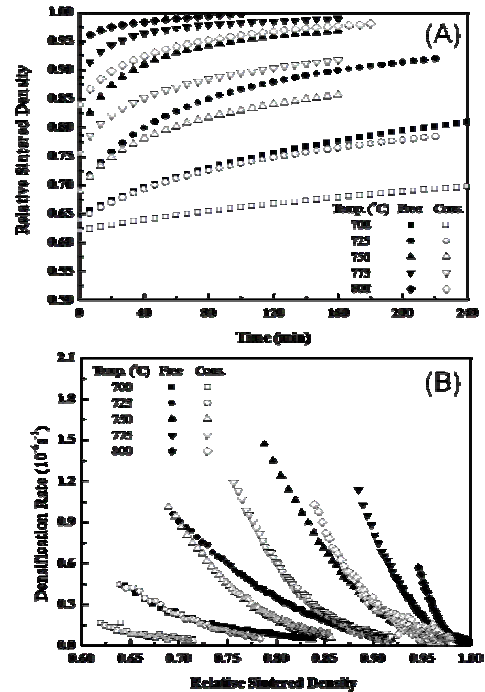


Fig. 2 (A) Densification and (B) densification rate of BSG+alumina under free and pressure-less constrained sintering at different temperatures.

Figure 2 shows typical densification results of free and constrained sintering of BSG+alumina at different temperatures. At a given temperature, the densification results measured under constrained sintering exhibit reduced densification (Fig. 2(A)) and much slower densification kinetics (Fig. 2(B)) than those obtained under free sintering. To densify BSG+alumina layer under constrained sintering, a constant uniaxial pressure in the thickness direction is applied, and the densification results are shown in Fig. 3. As expected, both densification (Fig. 3(A)) and densification rate (Fig. 3(B)) of the constrained BSG+alumina layer increase with increasing uniaxial pressure. Results in Fig. 3(B) further show that to have the same densification rate as that of free sintering, the required uniaxial pressure varies with densification, e.g., 100 kPa for a relative sintered density of 0.63, 200 kPa for 0.67 and 300 kPa for 0.79 at 700 °C. Similar experiments are also conducted at different temperatures, and the data are summarized in Fig. 4 where the uniaxial stress required varies in the range of 50-400 kPa

at 700-800°C. Moreover, it in general follows the same trend, i.e., increasing with increasing densification initially, reaching a maximum and then decreasing with increasing densification. Note that these uniaxial stress values in Fig. 4 are also consistent with those determined previously by sinter forging, i.e., 0-300 kPa [2].

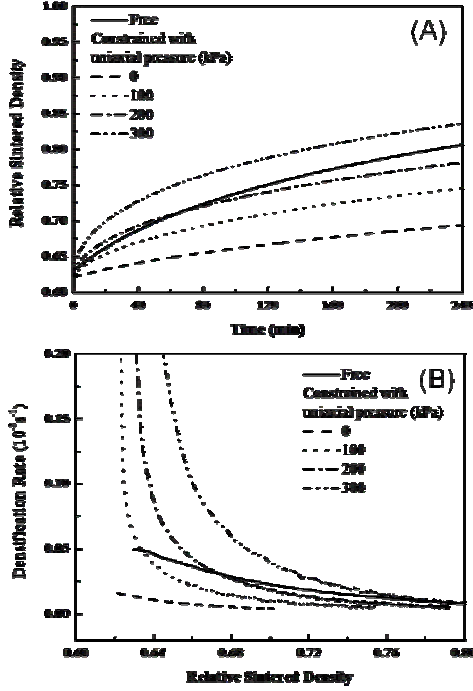


Fig. 3 Effect of uniaxial applied pressure on (A) densification and (B) densification rate of BSG+alumina under constrained sintering at 700°C.

Discussion

Since the densification behavior of a porous ceramic-filled glass composite under free and constrained sintering is primarily viscous [2,3,5,11-18], the constitutive equations to describe the deformation behavior during sintering are [15-18]

$$\dot{\epsilon}_x^{f\sigma} = \dot{\epsilon}_y^{f\sigma} = \dot{\epsilon}_x^f + \frac{1}{E_x^p} \left[\sigma_x - \nu_{xy}^p \sigma_y - \frac{E_x^p}{E_z^p} \nu_{zx}^p \sigma_z \right] \quad (1)$$

$$\dot{\epsilon}_z^{f\sigma} = \dot{\epsilon}_z^f + \frac{1}{E_z^p} \left[\sigma_z - \nu_{xz}^p \frac{E_z^p}{E_x^p} (\sigma_x + \sigma_y) \right] \quad (2)$$

where $\dot{\epsilon}_i^{f\sigma}$ and $\dot{\epsilon}_i^f$ are the strain rate under a uniaxial stress (σ_i) and free strain rate in the i direction, σ_i is the uniaxial stress and E_i^p is the porous uniaxial viscosity in the i direction, and ν_{ij}^p is the viscous Poisson's ratio in the ij plane. The above equations assume a transversely isotropic body with the X-Y plane being the isotropic plane. Using the boundary conditions of $\dot{\epsilon}_x^{c\sigma} = \dot{\epsilon}_y^{c\sigma} = 0$ for constrained sintering, the constitutive laws in eqs. (1) and (2) become

$$0 = \dot{\epsilon}_x^{c\sigma} = \dot{\epsilon}_y^{c\sigma} = \dot{\epsilon}_x^f + \frac{1}{E_x^p} \left[\sigma_x - \nu_{xy}^p \sigma_y - \frac{E_x^p}{E_z^p} \nu_{zx}^p \sigma_z \right] \quad (3)$$

$$\dot{\epsilon}_z^{c\sigma} = \dot{\epsilon}_z^f + \frac{1}{E_z^p} \left[\sigma_z - \nu_{xz}^p \frac{E_z^p}{E_x^p} (\sigma_x + \sigma_y) \right] \quad (4)$$

where $\dot{\epsilon}_i^{c\sigma}$ is the constrained strain rate under a uniaxial stress of σ_i in the i direction. The in-plane tensile stress generated in the X-Y directions ($\sigma_x^{c\sigma_z, \sigma_z \neq 0}$), and the strain rate in the Z direction ($\dot{\epsilon}_z^{c\sigma_z, \sigma_z \neq 0}$) of BSG+alumina under pressure-assisted constrained sintering ($\sigma_z \neq 0$) can then be expressed as follows

$$\sigma_x^{c\sigma_z, \sigma_z \neq 0} = \sigma_y^{c\sigma_z, \sigma_z \neq 0} = \frac{-\left(E_x^p \dot{\epsilon}_x^f - \frac{E_x^p}{E_z^p} \nu_{zx}^p \sigma_z\right)}{1 - \nu_{xy}^p} \quad (5)$$

$$\dot{\epsilon}_z^{c\sigma_z, \sigma_z \neq 0} = \dot{\epsilon}_z^{c\sigma_z, \sigma_z = 0} + \left[\frac{(1 - \nu_{xy}^p - 2\nu_{xz}^p \nu_{zx}^p)}{(1 - \nu_{xy}^p)} \right] \frac{\sigma_z}{E_z^p} \quad (6)$$

where $\sigma_x^{c\sigma_z, \sigma_z = 0}$ and $\dot{\epsilon}_z^{c\sigma_z, \sigma_z = 0}$ are the in-plane tensile stress generated in the X-Y directions and the strain rate in the Z direction under pressure-less constrained sintering ($\sigma_z = 0$).

Since the uniaxial stress applied in the Z direction (σ_z) is negative (compressive stress), it will reduce the in-plane tensile stress ($\sigma_x^{c\sigma_z, \sigma_z \neq 0}$) generated, but increase the strain rate in the Z direction ($\dot{\epsilon}_z^{c\sigma_z, \sigma_z \neq 0}$) under pressure-assisted constrained sintering. Since the densification rates of the laminate under pressure-assisted ($\dot{\rho}_z^{c\sigma_z, \sigma_z \neq 0}$) and pressure-less ($\dot{\rho}_z^{c\sigma_z, \sigma_z = 0}$) constrained sintering are equal to those of linear strain rates in the thickness direction ($\dot{\epsilon}_z^{c\sigma_z, \sigma_z \neq 0}$

and $\dot{\epsilon}_z^{c\sigma_z, \sigma_z = 0}$), the $\frac{(1 - \nu_{xy}^p) E_z^p}{(1 - \nu_{xy}^p - 2\nu_{xz}^p \nu_{zx}^p)}$ in eq. (6)

represents the constrained porous bulk viscosity (K^{CP}). The K^{CP} is the constrained densification modulus of the laminate, when the densification rate in the X and Y directions is constrained to be zero. The laminate becomes more difficult to be densified with increasing K^{CP} . The constrained porous bulk viscosity (K^{CP}) of BSG+alumina was determined by cyclic loading TMA [2,3,20,21] using multilayer BSG+alumina /alumina laminates, as given in Fig. 5. The constrained porous bulk viscosity (K^{CP}) increases with increasing density at a given temperature due to increased mechanical strength, but decreases with increasing temperature at a given density due to softening.

For comparison, the porous bulk viscosity under free sintering (K^f) is calculated by

$$K^f = \frac{E_z^p}{3(1 - 2\nu_{xz}^p)} \quad [15-18], \text{ as shown in Fig. 5.}$$

Note that the viscous Poisson's ratio (ν_{xz}^p) is related to the relative sintered density (ρ) by an analytical approximation of $\nu_{xz}^p = 0.5[\rho/(3-2\rho)]^{0.5}$ [19], where the relative sintered density (ρ) measured at different temperatures can be obtained in Fig. 2(A). The porous uniaxial viscosity of BSG+alumina in the Z direction under free sintering (E_Z^p), i.e., $\sigma_x = \sigma_y = 0$ and $E_Z^p = \sigma_z / (\dot{\epsilon}_z^f - \dot{\epsilon}_z^f)$ in eq. (2), is determined by cyclic loading TMA. Results in Fig. 5 show that at a given sintered density and temperature, the constrained porous bulk viscosity (K^{CP}) is always 3-10 times larger than that obtained under free sintering (K^{FP}). The above difference is believed to be due to the presence of the in-plane tensile stress in the X-Y directions (eqs. (5)) and anisotropic development generated during constrained sintering. The in-plane tensile stress represents an apparent counter stress that would eliminate the same strain rate in the X-Y directions resulted from a hydrostatic compressive sintering potentials. It reduces densification rate during constrained sintering, thus resulting in a larger porous bulk viscosity. Another experimental result to support the above argument is that the same densification controlling mechanism, i.e., viscous flow of BSG, is operative during free and constrained sintering. This is evidenced by the analysis of activation energy for the shrinkage of BSG+alumina under free and pressure-less constrained sintering [22,23].

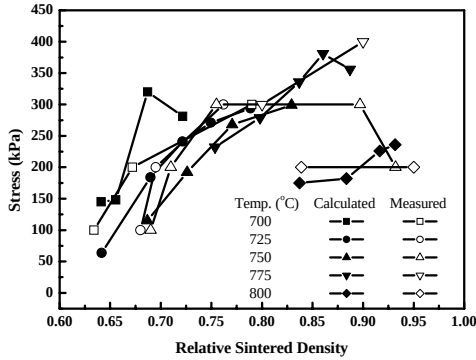


Fig. 4. Calculated and measured uniaxial stress required (σ_z^{c-req}) for the BSG+alumina to have the same densification rate under constrained and free sintering as a function of relative sintered density at different temperatures.

It has been reported [18,24,25] that the densification of LTCC under constrained sintering exhibits anisotropic characteristics, which changes the theoretical viscous Poisson's ratio to a range of -1 to +1 from 0 to 0.5 [16] for an isotropic material. This phenomenon becomes more significant for pressure-assisted constrained sintering, where the Poisson's effect is basically

restrained from occurring. The anisotropic development also increases the ratio of bulk modulus under constrained and free sintering (K^{CP} / K^{FP}) from a range of 1 to 3

$$\left(\frac{K^{CP}}{K^{FP}} = \frac{3(1-\nu^p)}{(1+\nu^p)} \right) \text{ for isotropic densification to a}$$

$$\text{range of 0 to } \infty \left(\frac{K^{CP}}{K^{FP}} = \frac{3(1-\nu_{XY}^p)(1-2\nu_{XZ}^p)}{(1-\nu_{XY}^p-2\nu_{XZ}^p\nu_{ZX}^p)} \right)$$

for anisotropic densification. This explains the ratio of K^{CP} / K^{FP} at a given density and temperature, obtained from the experimental results in Fig. 5, varies in the range of 3-10, which is much larger than that for an isotropic material, i.e., 1-3.

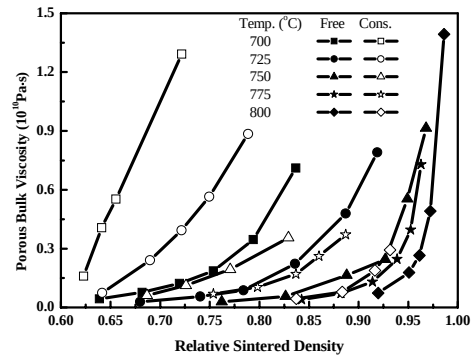


Fig. 5 Porous bulk viscosity of BSG+alumina as a function of relative sintered density obtained under constrained (K^{CP}) and free sintering (K^{FP}) at different temperatures.

The required uniaxial stress (σ_z^{c-req}) to densify BSG+alumina is calculated when the densification rate under pressure-assisted constrained sintering ($-\dot{\rho}_z^{c\sigma_z, \sigma_z \neq 0} = \dot{\epsilon}_z^{c\sigma_z, \sigma_z \neq 0}$) is the same as that obtained under free sintering ($-\dot{\rho}^f = \dot{\epsilon}_z^f + \dot{\epsilon}_x^f$) at a given sintered density. Incorporating the above relations into eq. (6), the uniaxial stress required (σ_z^{c-req}) to densify BSG+alumina is

$$\sigma_z^{c-req} = K^{CP}(\dot{\rho}^f - \dot{\epsilon}_z^{c\sigma_z, \sigma_z=0}) \quad (7)$$

where the porous bulk viscosity under constrained sintering (K^{CP}) can be obtained in Fig. 5, the densification rate under free sintering ($\dot{\rho}^f$) and the pressure-less constrained densification rate ($\dot{\epsilon}_z^{c\sigma_z, \sigma_z=0}$) are obtained by TMA in Fig. 2(B). Results of the calculated uniaxial stress required (σ_z^{c-req}) as a function of temperature are also given in Fig. 4, along with those measured. Both results exhibit significant agreement, which indicates the validity of the measured porous bulk viscosity under constrained sintering shown in Fig. 5, and using the viscous analogy for the constitutive relationships to describe the densification

behavior of a porous sintering compact under constrained sintering.

Conclusions

Compared with free sintering, the densification of BSG+alumina becomes reduced and slowed down under constrained sintering. This is caused by the presence of in-plane tensile stress generated in the transverse directions of BSG+alumina under constrained sintering, which reduces the amount of sintering potential available for constrained densification. Another factor contributing to the above phenomenon is that the porous bulk viscosity of BSG+alumina under constrained sintering is 3-10 times larger than that obtained under free sintering at a given density and temperature. This is resulted from the anisotropic characteristics developed during constrained sintering. To enhance constrained densification of BSG+alumina in the temperature range required for free sintering, a uniaxial stress applied in the thickness direction is needed. To have the same densification rate between free and constrained sintering of BSG+alumina, the required uniaxial stress varies in the range of 50-400 kPa at 700-800°C. The above data are in agreement with those calculated using the viscous analogy for the constitutive relationships of a porous sintering compact.

References

- [1] W. A. Vitrio and R. L. Brown, US patent No. 4,656,552, 1987.
- [2] C. C. Huang and J. H. Jean, *J. Am. Ceram. Soc.*, 87 [8] 1454-58 (2004).
- [3] C. D. Lei and J. H. Jean, *J. Am. Ceram. Soc.*, 88 [3] 599-603 (2005).
- [4] K. R. Mikeska and D.T. Schaefer, US patent 5,454,741, 1994.
- [5] S.Y. Tzeng and J. H. Jean, *J. Am. Ceram. Soc.*, 85 [2] 335-40 (2002).
- [6] Y.C. Lin and J.H. Jean, *J. Am. Ceram. Soc.*, 85 [1] 150-54 (2002).
- [7] B. Geller, B. Thaler, A. Fathy, M. J. Liberatore, H. D. Chen, G. Ayers, V. Pendrick and Y. Narayan, *J. Microwave*, 42 [7] 64-72 (1999).
- [8] J. W. Choe, J. N. Calata, and G. Q. Lu, *J. Mater. Res.*, 10 [4] 986-94 (1995).
- [9] T. J. Garino and H.K. Bowen, *J. Am. Ceram. Soc.*, 70 [11] C315-17 (1987).
- [10] T. J. Garino and H.K. Bowen, *J. Am. Ceram. Soc.*, 73 [2] 251-57 (1990).
- [11] G. W. Scherer and T. Garino, *J. Am. Ceram. Soc.*, 68 [4] 216-20 (1985).
- [12] R. K. Bordia and R. Raj, *J. Am. Ceram. Soc.*, 68 [6] 287-92 (1985).
- [13] R. K. Bordia and A. Jagota, *J. Am. Ceram. Soc.*, 76 [10] 2475-85 (1993).
- [14] J. C. Chang and J. H. Jean, *J. Am. Ceram. Soc.*, 89 [3] 829-35 (2006).
- [15] R. K. Bordia and G.W. Scherer, *Acta. Metall.*, 36 [9] 2393-97 (1988).
- [16] R. K. Bordia and G.W. Scherer, *Acta. Metall.*, 36 [9] 2399-2409 (1988).
- [17] R. K. Bordia and G.W. Scherer, *Acta. Metall.*, 36 [9] 2411-16 (1988).
- [18] R. K. Bordia, R. ZuO, O. Guillon, S. M. Salamone and J. Rodel, *Acta Mater.*, 54 [1] 111-118 (2006).
- [19] K. R. Venkatachari and R. Raj, *J. Am. Ceram. Soc.*, 69 [6] 499-506 (1986).
- [20] P. Z. Cai, G. L. Messing and D. L. Green, *J. Am. Ceram. Soc.*, 80 [2] 445-52 (1997).
- [21] A. Mohanram, G. L. Messing and D. J. Green, *J. Am. Ceram. Soc.*, 87[2] 192-196 (2004).
- [22] J. Frenkel, *J. Phys. (USSR)*, 9 [5] 385-91 (1945).
- [23] I. B. Culter, *J. Am. Ceram. Soc.*, 52 [1] 14-17 (1968).
- [24] J. B. Ollagnier, O. Guillon and J. Rodel, *J. Am. Ceram. Soc.*, 90 [12] 3846-51 (2007).
- [25] J. B. Ollagnier, O. Guillon and J. Rodel, *Int. J. Appl. Ceram. Tec.*, 3 [6] 437-41 (2006).