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Novel structure of ceramic tape for multilayer devices

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Abstract

To reduce the content of binders surrounding ceramic powders in a ceramic tape and the residual pore after burnout to a minimum, a ceramic tape with double layers was manufactured. One layer was comprised of only organic binder, which imparted sufficient strength and strong adhesive property to the green tape. The other one was a ceramic layer with a very small amount of binder. The binder content of the slurry for ceramic layer was less than 2 wt%, which could lower the viscosity, make the slurry well dispersed and considerably increase solid loading in the slurry. This higher solid loading led to higher green tape density, higher fired density of the product. The two-layer ceramic tape showed much better qualities than a common (or conventional) green tape especially in microstructure, laminatablilty, and tape density. In the multilayer structure made of the two-layer ceramic tape, the binder layer completely disappeared after binder-burnout and no defects from the two-layer structure were observed.

Keywords: Tape casting; Binder; Glass ceramics; Substrate; Lamination

1. Introduction

Tape casting is a low-cost process for making high-quality laminated materials for which an adequate thickness control and good surface finish are required.[1] The tape casting process produces a thin layer of composite material (ceramic and organic) by coating a carrier surface with casting slurry as it passes under a doctor blade.[2] Stable slurry is composed of ceramic powder dispersed in a solvent which contains dispersant, binder, plasticizer, and other surfactants.[3] Organic additives like dispersants, plasticizers, and binders impart a variety of properties to the slurry and the green tape. Dispersants assure the stability of the suspension by keeping particles apart. The purpose of plasticizers is to make the tape flexible for handling in subsequent processing steps.[4] Binders impart a certain amount of strength and toughness to the thin tape by surrounding the powder particles, anchoring itself to their surfaces, and creating a strong three-dimensionally interconnected skeleton of resin. When designing a slip recipe, one will generally begin with selecting a suitable polymer binder system because of its central role in determining the green tape properties like strength, flexibility, laminatability, toughness, and printability.[5] But these roles of binder are limited only to pre-sintering processing procedures. Before sintering, binder should be completely removed from green tape by binder burnout. So it is necessary to minimize the binder concentration, but insufficiency of binder deteriorates the strength and laminatability of the green tape. On the other hand, an excessive binder also results in such a problem as the residual pores after binder-burnout, which prevents the green tape being densified. That is, sufficient binder concentration is good to the green process but bad to the firing process. To the extreme degree, we need a nearly binder-free ceramic tape with sufficient strength, flexibility, and laminatability. That is a kind of contradiction. The purpose of this study was to solve that inconsistency by manufacturing a binder-free ceramic layer with good process feasibility.

2. Experimental procedure

To manufacture two-layer ceramic tapes comprised of a binder layer and a ceramic layer, the binder solution and the ceramic slurry were prepared, respectively. To form a uniform binder layer, the binder solution of poly(methyl methacrylate) (PMMA, Geomyung, Ceonan, Korea) and toluene/ethanol (Samchun Pure Chemical, Songtan, Korea) mixture was coated by doctor blade method and dried on a PET carrier film (L150L, Nanya, Taipei, Taiwan). The binder layer was uniform and about 10 μm in thickness. Two glass ceramic systems, including a low-fire $CaO–Al_2O_3–SiO_2$-based glass + Al_2O_3 (CASA) and

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Table 1
Properties of the used powders

Type	Mean particle size (μm)	Specific surface area (m^2/g)	Density (g/cm^3)
$CaO–Al_2O_3–SiO_2$-based glass	3.11	2.60	2.69
$Cu_2O–Bi_2O_3$-based glass	0.98	2.67	7.56
Al_2O_3	1.50	1.80	3.98
$BaTiO_3$	0.69	2.81	6.00

a high-fire $Cu_2O–Bi_2O_3$-based glass + $BaTiO_3$ (CBBT), were used for a ceramic layer of the two-layer tape, respectively. The CASA and CBBT systems had a glass content of approximately 50 wt% and 9 wt%, respectively. Table 1 shows the mean particle size, the specific surface area, and the density of the used powders. The ceramic slurry for the ceramic layer was prepared with ceramic powder, PMMA binder, toluene/ethanol mixture, and dispersant (DisperBYK-103, BYK Chemie, Germany). After being deagglomerated and mixed by ball milling for several hours, the slurry was cast on the binder layer to form a 40-μm-thick ceramic layer using doctor blade method, too. For successful tape drying the drying zone in a casting machine was divided into four parts, which have room temperature, 50 °C, 70 °C, and 90 °C respectively. Conventional ceramic slurry in this experiment was prepared with the same materials and process as the ceramic slurry for two-layer tape, and it was cast into a 50-μm-thick ceramic tape on the PET film. The composition of the slurry for the ceramic layer was considerably different from that of conventional slurry especially in binder concentration. The standard composition of the slurry with CASA for the two-layer tape and that of conventional slurry are shown in Table 2. The lamination experiments were carried out on the two-layer tape and a conventional one. Samples were prepared by laminating 10 layers of CASA green tapes with a uniaxial pressing laminator. The pressure was varied from 1 MPa to 30 MPa, and the temperature and the time for press were fixed at 85 °C and 5 min, respectively. To evaluate the expansion rate of laminates with lamination pressure, the expansion was calculated by measuring each distance between two via patterns on laminates before and after firing. The evaluation patterns are shown in Fig. 1. The green laminates were fired at a heating rate of 1 °C/min from room temperature to 450 °C to remove binder. To remove the organic completely, the laminates were held at 450 °C for 6 h. After binder burnout, the laminates were fired at a heating rate of 5 °C/min to 890 °C with a holding time of 2 h, followed by natural cooling to room temperature. The green density of the ceramic tapes and the pressed laminates were determined from geometrical measurements using a micrometer (No. 389-511-30, Mitutoyo, Kawasaki, Japan) accurate to 0.5 μm on a carefully cut of 1 cm^2 size and the fired density of the laminates was evaluated by Archimedes' method. The ultimate tensile strength of the CASA green tapes was measured in a universal testing machine (5543Q2982, Instron, MA). Dog-bone specimens were prepared with a tensile width of 1 cm and a 4.0-cm grip. The microstructures were studied by scanning electron microscopy (220A-1SPS, Noran Instruments, Model No., UK). The capacitance of the laminates was measured with capacitance meter (Agilent, 4288A, CA) at frequency of 100 kHz at room temperature. All those properties of the two-layer tape were compared with those of a conventional ceramic tape of the same inorganic composition.

Table 2
Standard composition of the slurry with CASA for the two-layer tape and the slurry for a conventional tape

Name	Conventional (wt%)	Two-layer (wt%)
Powder	56.2	79.2
Toluene	19.4	11.5
Ethanol	12.9	7.7
Dispersant	0.3	0.4
Binder	11.2	1.2
Total	100	100

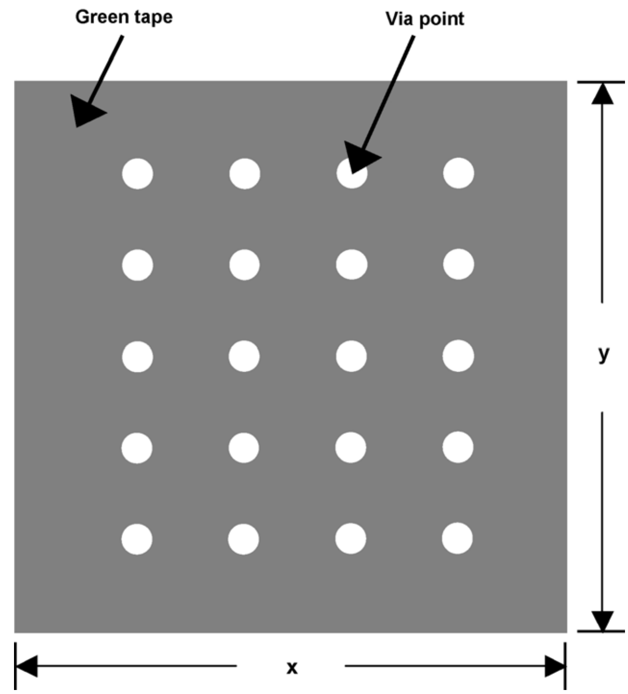

Fig. 1. Shrinkage evaluation pattern.

3. Results and discussion

Fig. 2 shows the 10-μm-thick binder layer coated on a PET carrier tape. Because the binder solution for the binder layer consisted of only binder and solvent, the flat and pure binder layer could be formed after evaporating solvent.

Fig. 3 shows the cross-sectional image of the CASA two-layer tape. The homogeneous ceramic layer was formed on the binder layer and the boundary between the two layers was clearly observed.

Fig. 4 shows the surface morphology of a conventional tape and the two-layer tape. Generally, binder can act as another powerful dispersant if it is added to well-dispersed suspension[6] and increase the bulk green density if it is added in proper content. But there are some adverse effects arising from adding binder. First, perfect deagglomeration and dispersion of

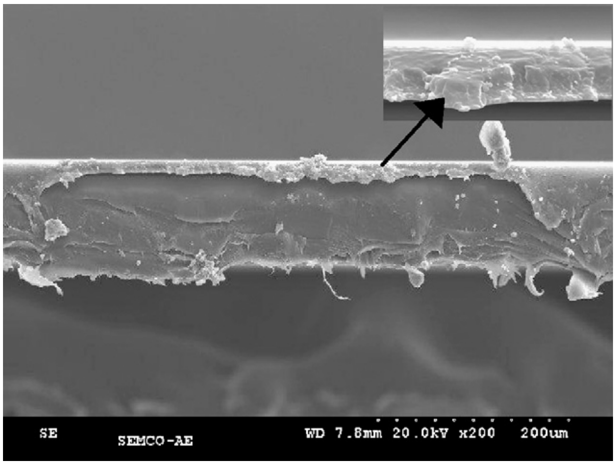

Fig. 2. Cross-sectional image of the binder layer on a PET carrier film.

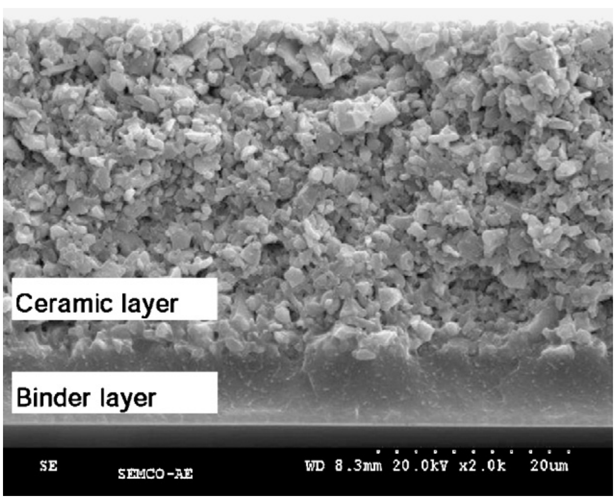

Fig. 3. Cross-sectional image of the two-layer tape.

ceramic powders cannot be always guaranteed especially in an industrial field. If the binder is added before deagglomeration and dispersion are accomplished perfectly, the binder may unhappily surround some remaining agglomerates and make them act as a single unit during the tape casting process. Then, the slurry cannot be cast into dense ceramic tapes. Second, while many ceramic formation processes keep the binder content low in order to achieve higher ceramic particle loadings and higher densities, tape casting needs more binder than the volume of pores in order to make the tape withstand handling or machining. Adding excess binder results in increasing interparticle distances and decreasing the green density. Results in Fig. 4 show that the microstructure of the conventional tape is porous and a few agglomerates are surrounded with binder. On the other hand, particles in the ceramic layer of the two-layer tape were well deagglomerated and densely packed, which is due to extremely low binder content.

Theoretically, as little as about 1 wt% of organic additive can be sufficient to completely coat a typical ceramic powder with a layer of additive which is just one molecule thick.[7] But ceramic tapes are supposed to endure some mechanical impact during punching and printing process, so the minimum content of binder in the ceramic tape should be higher than the theoretical value. In this experiment, a two-layer tape with a ceramic layer containing less than 1.5 wt% of binder was not suitable for tape processing because particles in the ceramic layer were easily separated from tape by weak impact during punching and printing of the tape. More than 1.5 wt% of binder in the ceramic layer could prevent particles from being separated from the ceramic layer and make the two-layer tape suitable for tape processing. In addition to holding particles, ceramic tapes are required to have a sufficient tensile strength to avoid deformation during multilayer process with automatic or semiautomatic handling equipment. So the mechanical strength of the two-layer tape was compared with a conventional one.

Fig. 5 shows the mechanical properties of CASA green tapes under tensile test. The two-layer tape has higher strength and better flexibility than a conventional one, which is due to the homogeneous binder layer imparting homogeneous mechanical properties to the two-layer tape.

For the two-layer tape and the conventional one the lamination experiments were carried out and resulted in different qualities of junction. According to Hellebrand, for ideal lamination individual particles at the surfaces of the tapes in contact have to move and interpenetrate within a thin, surface-near region, which can be guaranteed by the optimum ratio of binder, powder and pores in the green tape.[8] But even under optimum conditions, high temperatures above the binder's glass transition point and high pressures are needed to achieve a homogeneous body. The lamination of conventional tapes

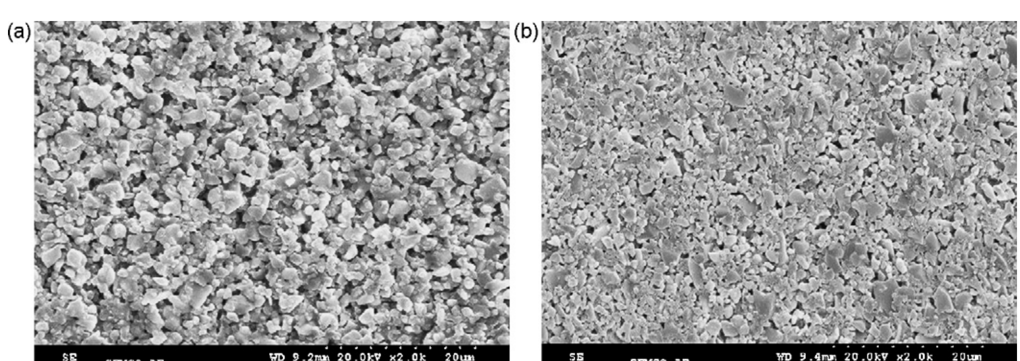

Fig. 4. Surface morphology of (a) a conventional tape and (b) the two-layer tape.

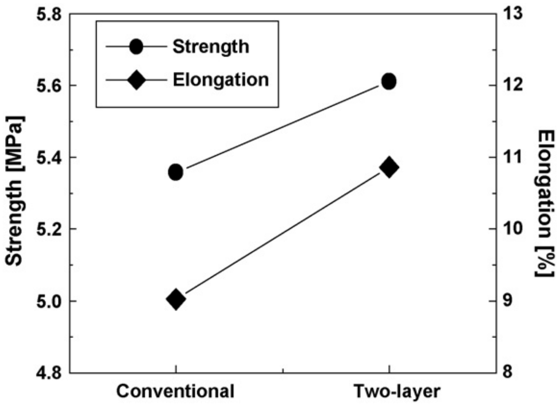

Fig. 5. Mechanical properties of ceramic tapes.

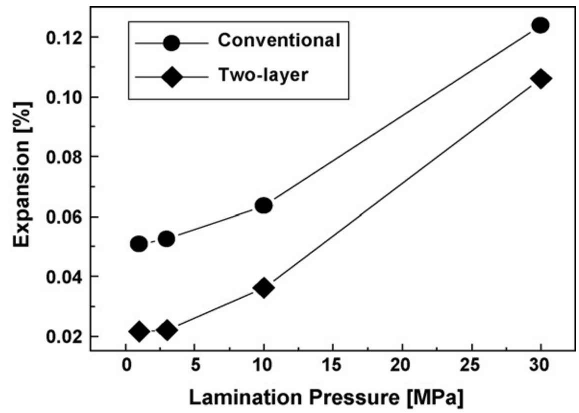

Fig. 7. Changes in expansion rate of laminate with lamination pressure.

resulted in delamination at low pressure of 10 Mpa or under and defect-free laminate was obtained at the pressure of as high as 30 MPa, as shown in Fig. 6. On the other hand, for the two-layer tapes, there was no dependency on the applied pressure during the lamination process. The two-layer tapes made a good junction of layers at the pressure of as low as 1 MPa. Because the binder layer imparts intense stickiness to the two-layer tape, very slight pressure is sufficient for good lamination and high pressure for interpenetration of the particles are unnecessary.

Fig. 7 shows changes in expansion rate of laminate by pressure. The rate of expansion increases as lamination pressure increases. We can confirm two advantages of two-layer tape over a conventional one. First, under the same pressure the expansion rate of two-layer tape is less than that of a conventional one, which is due to high packing density of the ceramic layer in the two-layer tape. Second, a conventional tape required high pressure of 30 MPa to make a good junction. But in case of two-layer tape, a slight pressure of 1 MPa was sufficient for a successful lamination, which is due to the binder layer in the two-layer tape. In other words, two-layer tape requires so low pressure for good junction that the risk of deformation during lamination is very low.

Fig. 8 shows cross-sectional images of green, baked-out, and sintered laminates using the CASA two-layer tapes, respectively. The binder layer in green laminate was completely removed after binder burnout and no defects were observed in the laminate. This means that good joining of the tapes after firing can be achieved without interpenetrating of particles during lamination process. The driving force for the joining of the tapes is the capillary force that exists during the burnout process. The binder removal is attributed to the transport of the viscous binder phase.[9] The viscous phase which occurs at the interface of the porous microstructure of the green tapes causes capillary forces, and these forces result in an approach of the ceramic layers towards each other.[10] As the ceramic particles get close enough after the removal of the binder layer between ceramic layers, the particles at the edges can rearrange and move so that the ceramic

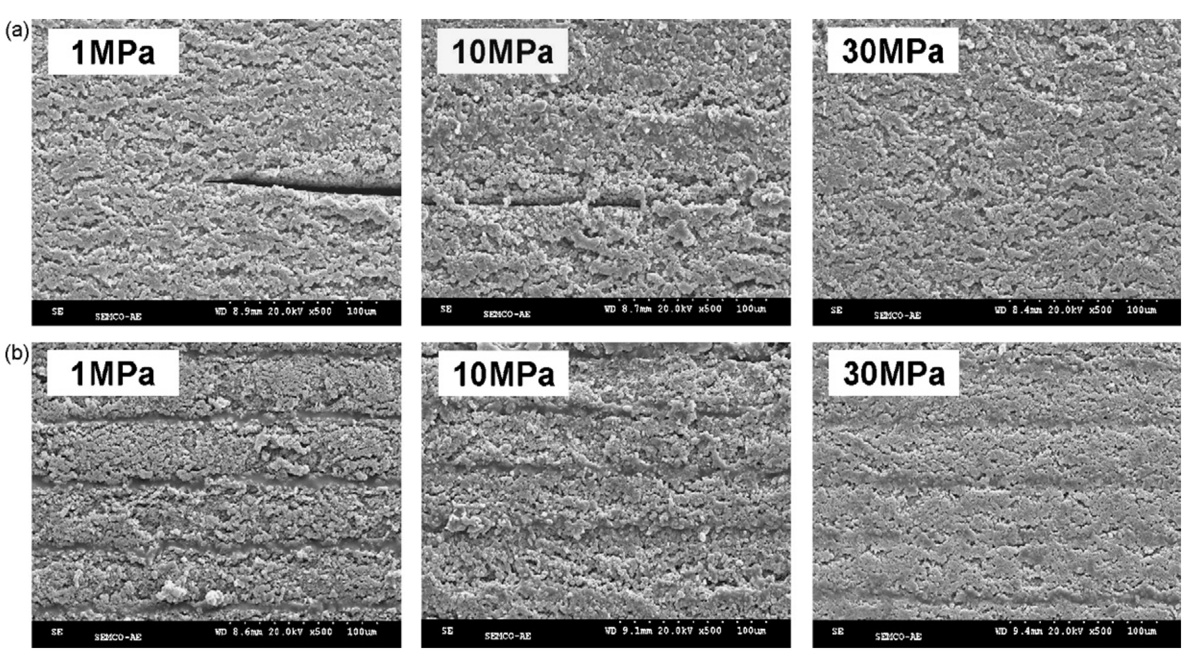

Fig. 6. Cross-section of green laminates of (a) conventional tapes and (b) two-layer tapes by lamination pressure.

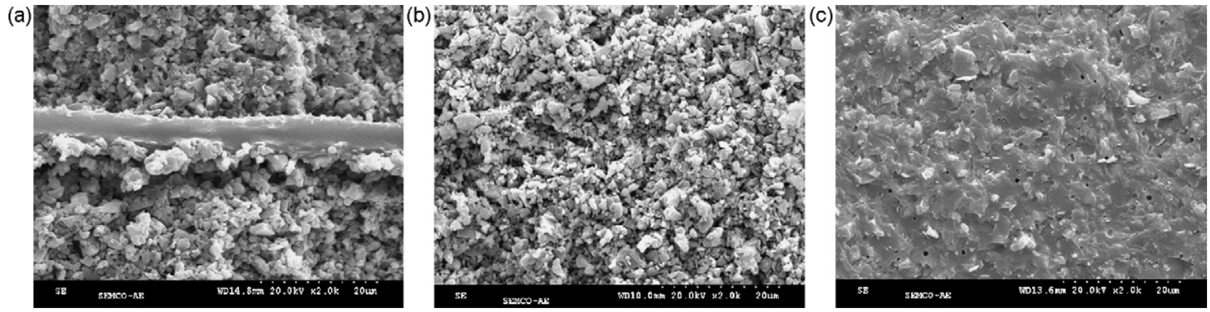

Fig. 8. Cross-section of (a) green, (b) baked-out and (c) sintered laminates using two-layer tapes.

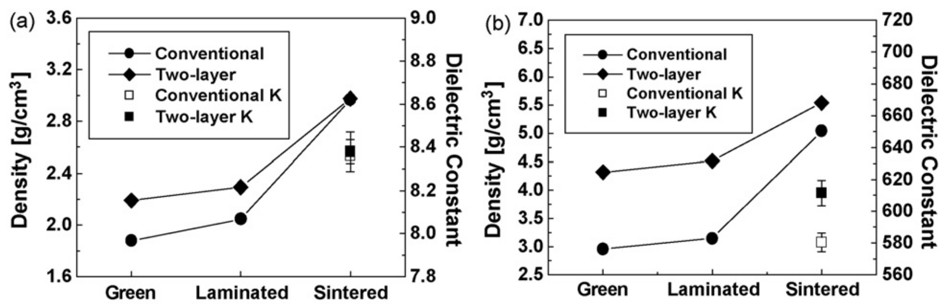

Fig. 9. Comparison of properties of the two-layer tape with a conventional one: (a) the low-fire CASA system and (b) the high-fire CBBT system.

layers interpenetrate each other and make a homogeneous junction due to the capillary force. After binder burnout the binder layer in Fig. 9(a) was completely removed, and the following sintering process made the laminate defect-free.

Fig. 9 illustrates the changes of density by processing procedure. The CASA two-layer tape shows higher density in green and laminated state, but there is no difference in sintering density between two-layer tape and a conventional one. Because this low-fire material has a sufficient driving force for sintering at the limited sintering temperature, two kinds of tapes could be equally densified regardless of the different green density. Because of the equivalent densification the dielectric constants of the two tapes were about the same. On the other hand, the high-fire CBBT tapes of Fig. 9(b) showed different behavior from the CASA tapes of Fig. 9(a). From Fig. 9(b), we could confirm that the higher density of the two-layer tape in the green state led to the higher fired density under the limited sintering condition. And the higher fired density resulted in higher dielectric constant. Because of the high packing density of the ceramic layer the two-layer tape could provide much more contact points among powders, which made the driving force for sintering much higher in the two-layer tape than in a conventional one.

4. Conclusions

By manufacturing the two-layer tape, a highly dense ceramic layer could be obtained. The binder content in the ceramic layer of the two-layer tape could be lowered from 11.2 wt% to 1.2 wt% and the powder content could be increased from 56.2 wt% to 79.2 wt% in comparison with a conventional green tape. This higher solid loading led to higher tape density, higher laminated density, and higher fired density of a multilayer product. Especially in case of the high-fire material, the high packing density of the ceramic layer can increase the driving force for sintering and improve the sintering behavior at a low temperature. Because the binder layer imparts good physical properties to the two-layer tape, tensile strength of the two-layer tape was higher than that of a conventional one in spite of extremely low binder content of the ceramic layer. In addition, the binder layer is so adhesive that the two-layer tapes could make a homogeneous junction of layers under very low external pressure in the green state. During binder burnout the binder layer in the two-layer tape could be completely removed and the ceramic layers interpenetrated each other by internal capillary pressure. As a result, no defects caused by the two-layer structure were observed in the final product.

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