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Bonding Strength of Conductive Inner-Electrode Layers in Piezoelectric Multilayer Ceramics

Yiping Wang† and Ying Yang
State Key Laboratory of Mechanics and Control of Mechanical Structures, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

Bingjin Zheng, Jing Chen, Jinyi Yao, and Yun Sheng
College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China and State Key Laboratory of Mechanics and Control of Mechanical Structures, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

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Multilayer ceramics in which piezoelectric layers of 0.90 $Pb(Zr_{0.48}Ti_{0.52})O_3$ -0.05 $Pb(Mn_{1/3}Sb_{2/3})O_3$ -0.05 $Pb(Zn_{1/3}Nb_{2/3})O_3$ (0.90PZT-0.05PMS-0.05PZN) stack alternately with silver electrode layers were prepared by an advanced low-temperature co-fired ceramic (LTCC) method. The electrical properties and bonding strength of the multilayers were associated with the interface morphologies between the piezoelectric and silver-electrode layers. Usually, the inner silver electrodes are fabricated by sintering silver paste in multi-layer stacks. To improve the interface bonding strength, piezoelectric powders of 0.90PZT-0.05PMS-0.05PZN with an average particle size of 23 μm were added to silver paste to form a gradient interface. SEM observation indicated clear interfaces in multilayer ceramics without powder addition. With the increase of piezoelectric powder addition in the silver paste, gradient interfaces were successfully obtained. The multilayer ceramics with gradient interfaces present greater bonding strength as well as excellent piezoelectric properties for 30~40 wt% of added powder. On the other hand, over addition greatly increased the resistance of the inner silver electrodes, leading to a piezoelectric behavior like that of bulk ceramics in multilayers.

Keywords: Piezoelectric, Multilayer ceramics, LTCC, Bonding strength

1. INTRODUCTION

On account of the excellent electromechanical properties of lead zirconate titanate [$Pb(Zr,Ti)O_3$, PZT] and other lead-based relaxor materials, they have been widely used for piezoelectric actuators, sensors, and transducers [1-3]. Meanwhile, with the ongoing developments of integrated circuit technique, high capacity, miniaturization, and low applied voltage have become the development trend of the future for transducers [4]. Generally, monolayer piezoelectric needs high applied voltage (above 200 V) [5], which cannot work when a low driving voltage and high integrations in certain sensors and transducers are required. The multilayer ceramic technique has emerged at the right moment to solve these problems, in which piezoelectric layers and inner-electrode layers stack alternately to build a parallel structure in electricity and a series in machinery.

The advanced tape-casting technique and low-temperature co-fired technique have been used as technical support for multilayer piezoelectric capacitors and multilayer piezoelectric transformers [6]. However, preparation of all these components requires piezoelectric layers to be co-fired with inner-electrode layers. Ideal inner-electrode layers should adhere strongly to and combine perfectly with the piezoelectric layers, which have excellent physical and chemical stability and good electrical conductivity. Previous experiments and studies have shown that co-firing mismatching components will introduce many interface defects, such as delaminations and cracks

† Author to whom all correspondence should be addressed:
E-mail: yipingwang@nuaa.edu.cn

at the interface [7-9]. These defects have greatly affected the reliability of the multilayer actuator. In order to overcome these drawbacks, a new interface mechanism is absolutely indispensable.

In this study, a gradient interface is formed to improve the interface bonding strength. The quaternary composition of 0.90 Pb $(Zr_{0.48}Ti_{0.52})$ O_3-$Pb(Mn_{1/3}Sb_{2/3})O_3$ -0.05$Pb(Zn_{1/3}Nb_{2/3})O_3$(0.90PZT-0.05PMS-0.05PZN) was chosen as the piezoelectric layer because of its excellent properties for actuator applications [10-12]. The corresponding PZT-PMS-PZN ceramic powder was added to the silver paste to increase the interface bonding strength. The research investigated the interface bonding strength of the multilayer ceramics as a function of the ceramic powder additions, by means of tensile strength measurement, a resistivity test, and microstructure observations of the multilayer stacks. The results could benefit other low-temperature co-firing systems.

2. EXPERIMENTAL PROCEDURE

The quaternary piezoelectric ceramic system 0.90PZT-0.05PMS-0.05PZN was prepared by a conventional solid-state reaction process. PbO, ZrO_2, TiO_2, MnO_2, Sb_2O_3, ZnO, and Nb_2O_5 with analytical purity were used as the starting materials. Piezoelectric ceramic sheets were fabricated by tape-casting the slurry containing sieved piezoelectric powders, solvent, dispersant, organic binders, and plasticizer. In order to obtain a uniform powder size, the ceramic powders were sieved to ensure that the diameters were less than 48 μm.

ESL903-A silver paste was used as the inner-electrode layer. To form a gradient interface, PZT-PMS-PZN powder in different amounts was incorporated into this silver paste. The screen-printing technique has been generally used to print the inner electrode. To ensure that the unique silver paste passes easily through the screen mesh (with mesh number of 200), the powdered 0.90PZT-0.05PMS -0.05PZN added to the silver paste was sieved to ensure that the particle diameters were less than 23 μm (with mesh number of 600). The doping amounts were 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, and 60 wt%. Rheological processing is needed for the doped silver paste [13]. As the inner-electrode layer in multilayer structures, the printed silver-paste layer should be thin enough. Diluted silver paste is more suitable for printing a thinner electrode layer. The dedicated diluter, including 6 wt% ethyl cellulose and 94 wt% terpineol, was used to dilute the silver paste to obtain the appropriate viscosity. The casted tapes were warm-pressed to stack up to the desired layers at 50℃, and then the multilayer stacks were heated to 550℃ with PZT-PMS-PZN packing power at a slow heating rate of 15℃/h for burning out organic binders. The samples were sintered at 850℃ for 4 h in a sealed alumina crucible.

To investigate the properties of the sintered multilayer actuator, external electrodes were prepared by applying a thin silver paste on both lateral sides of the actuator to connect to the inner electrodes, followed by heat treatment at 650~700℃ for 10 min to provide robust electrodes [14]. At last, the samples were poled under an electric field of 4 kV/mm at 120℃ for 20~30 min in the silicon oil bath. Figure 1 shows the process flow of the multilayer ceramic preparation.

The resistivity of the inner electrode was measured by Resistivity Measuring Instruments with Four-Probe Array Method (KunDe KDY-1, China). The electrical properties of the samples were measured by a Precision Impedance Analyzer (Agilent 4294A, USA). The shear bond strength of the multilayer ceramics was monitored by a Universal Tensile Testing Machine (Great Wall WDW-5000N, China). The interlayer morphology of the multilayer ceramics was observed by a field emission scanning electron microscope (Hitachi SU8010, Japan).

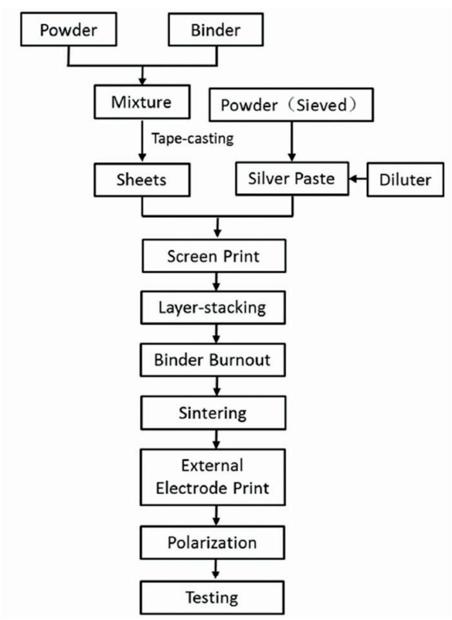

Fig. 1. Process flow of multilayer ceramic preparation.

3. RESULTS AND DISCUSSIONS

The square resistance of the inner-electrode layer, which was doped with 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, and 60 wt% PZT-PMS-PZN powder, is shown in Fig. 2. The square resistance of the initial ESL903-A silver paste was 2 mΩ/Sq. The square resistance of the inner electrode increased with the adding of ceramic powder. With less than 40 wt% of added powder, the resistance increased slowly. But the square resistance rose sharply, up to 1,500 mΩ/Sq, when the added content reached 60 wt%. The resistance increased rapidly occurred the silver layer became discontinuous when large amounts of the insulating piezoelectric powder were added.

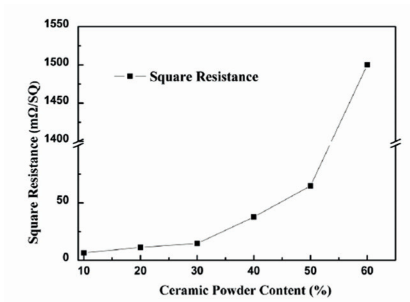

Fig. 2. Square resistance of the electrodes with different piezoelectric powder additions.

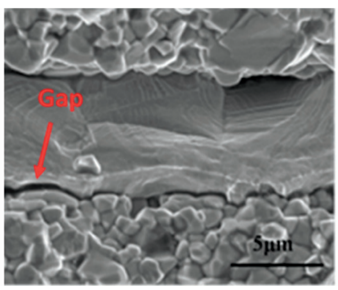

Fig. 3. Interface morphology of PZT-PMS-PZN multilayer ceramic.

Figure 3 shows the interface between the piezoelectric layer and the silver inner-electrode layer of the multilayer ceramic sintered at 850℃ for 4 h, in which the initial silver paste had no ceramic powder added. It can be seen that the piezoelectric ceramic layer presents dense morphology even at a low sintering temperature of 850℃. The inner silver electrode has a uniform thickness of 5 μm. But an obvious gap is found on the interface, which may easily induce failure of the multilayer actuator during its use.

Figure 4(a)~(f) exhibits the SEM morphologies of the multilayer ceramics in which the inner silver electrode has 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, and 60 wt% PZT-PMS-PZN powder added, respectively. As shown in Fig. 3, the interface disappears gradually as the ceramic powder is added. As the added content of the ceramic powder reaches 40 wt%, the micromorphology of the multilayer ceramic becomes like that of bulk ceramics. The ceramic is fully dense without large holes and cracks, indicating that the multilayer ceramic is well sintered at 850℃. No obvious interface is observed in the multilayer structure. The interface zone marked by the red arrows in the image was confirmed by an EDX scan of the Ag component, which is shown in Fig. 5. The ordinate shows the relative content of silver, and the abscissa shows the scan position. The relative content of silver decreases with the adding of ceramic powder. The peak essentially disappears when the added content reaches 60 wt%. At this time, the role of the inner electrode has disappeared.

Figure 6 shows the tensile strength of the multilayer ceramic in which the inner silver layer was doped with PZT-PMS-PZN ceramic powder. The prepared samples included 5 active PZT-PMS-PZN layers and 4 inner-electrode layers, and the dimension was 17.0 mm×7.8 mm×0.7 mm. The stretching speed was about 0.05 mm / s. The results show that the shear bond strength of the multilayers increased with the adding of ceramic powder, although more slowly for small amounts. At 30 wt% added, the shear bond strength was about 300 N. With larger amounts of added ceramic powder, the shear bond strength of the ceramic multilayers increased rapidly and then slowed gradually for an addition of 60 wt%, where a shear bond strength up to 680 N was obtained. The bond strength of the ceramic multilayers increased because of the improved interface structures, as shown in Fig. 4.

The overall shape of the prepared multilayer actuator for piezoelectric measurement was 7.9 mm×6.9 mm×0.3 mm; it consisted of 3 active PZT-PMS-PZN layers and 4 conducting Ag layers. The measured piezoelectric constant (d_{33}) was approximately 900 pC/N, and the static capacitance was about 14 nF for these multilayer samples with ceramic powder additions of less than 40 wt%, as shown in Fig. 7. These high d_{33} values present a typical piezoelectric behavior in

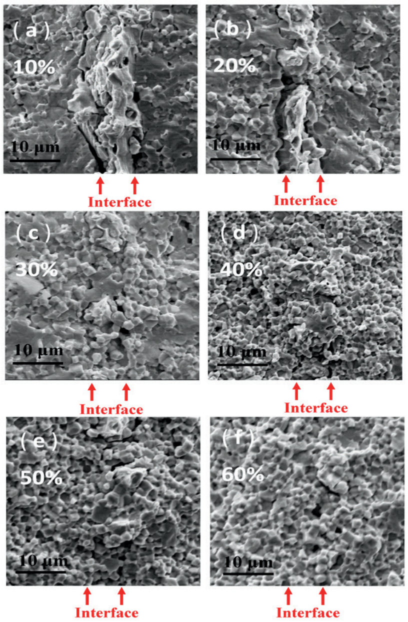

Fig. 4. SEM morphologies of the multilayer ceramics, where the inner silver electrodes have (a) 10 wt%, (b) 20 wt%, (c) 30 wt% , (d) 40 wt%, (e) 50 wt%, and (f) 60 wt% ceramic powder additions.

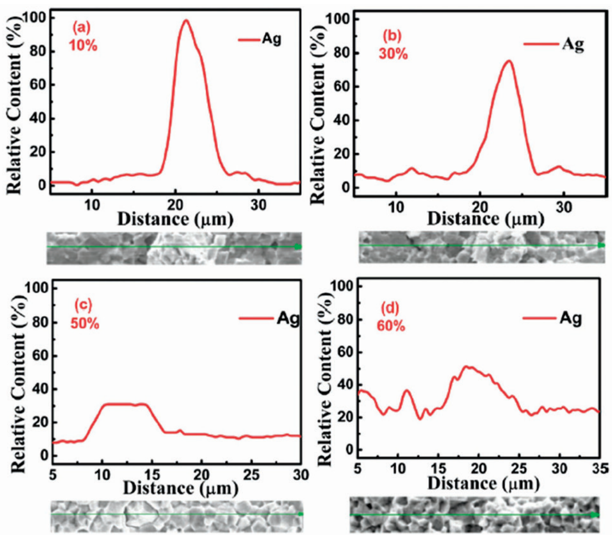

Fig. 5. The EDX of the multilayer ceramics, where the inner silver electrodes have (a) 10 wt%, (b) 30 wt%, (c) 50 wt%, and (d) 60 wt% of ceramic powder added.

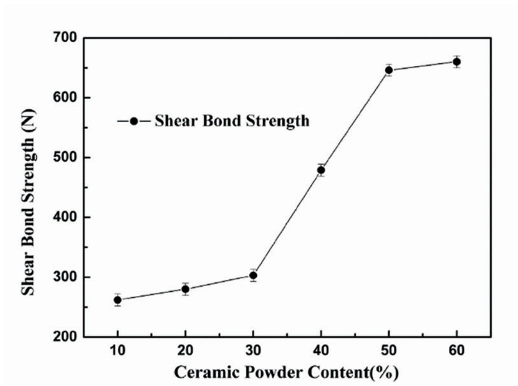

Fig. 6. Shear bond strength of the multilayer samples with doped inner electrodes by different ceramic powder contents.

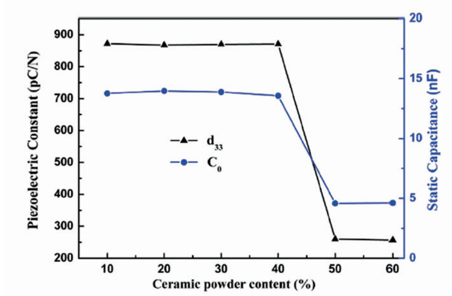

Fig. 7. Piezoelectric constants and static capacitances of the piezoelectric multilayers with doped inner electrodes by different ceramic powder contents.

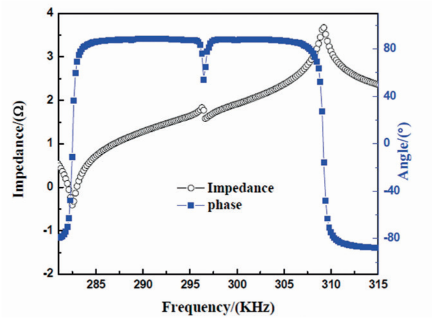

Fig. 8. Impedance of the first-order resonance frequency of the multilayer with doped inner electrodes with 30 wt% added ceramic powder.

multilayer ceramics, which are nearly 3 (the number of piezoelectric layers) times the d_{33} value of the piezoelectric monolayer. It was also verified that all the piezoelectric layers were fully polarized in the multilayer structures when their inner-electrode layers incorporated less than 40 wt% of added ceramic powder. On the other hand, the d_{33} was only 257 pC/N and the static capacitance was about 4.5 nF for added contents of 50 wt% and 60 wt%, because of the high resistance of the inner electrodes, as shown in Fig. 1, so the piezoelectric multilayers displayed a piezoelectric response like that of a monolayer ceramic.

The impedance of the first-order resonance frequency curve was measured for the multilayer sample, in which the inner-electrode layers has 30 wt% added ceramic powder, as shown in Fig. 8. By calculation, the mechanical quality factor (*Qm*) of the sample is 620 and the electromechanical coupling coefficient (*Kp*) is 0.489. The data confirm that the piezoelectric multilayers prepared at a low co-firing temperature present excellent piezoelectric properties, suitable for actuator applications requiring a low driving voltage.

4. CONCLUSION

In this study, the interface bonding strength of the piezoelectric multilayers was successfully improved. The critical mechanism is to form a gradient interface between the piezoelectric layer and the inner-electrode layer by incorporating ceramic powder of 0.90PZT-0.05PMS-0.05PZN into the silver paste. The measurements for electric and mechanical properties confirmed that the interface bonding strength increased with the addition of ceramic powder in the inner-electrode layer because of the improved interface combination. Under the optimized contents of 30~40 wt% ceramic powder additions, the multilayer ceramics kept excellent piezoelectric response as well as improved bonding strength. On the other hand, piezoelectric multilayers with too much ceramic powder added to their inner-electrode layers displayed a piezoelectric response like that of a monolayer ceramic, though their interface boding strength was largely increased.

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