EUROSENSORS 2015

A Novel Co-casting Process for Piezoelectric Multilayer Ceramics with Silver Inner Electrodes

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Abstract

The presented process offers a simplified method for manufacturing multilayer ceramics (MC) in comparison to the conventional multilayer ceramics technology (MCT). It combines the tape casting of ceramic green tapes and the subsequent screen printing of electrodes into one single co-casting process. Since the co-casting process circumvents also the stacking and laminating of single ceramic green tapes, MC with layer thicknesses as thin as 20 μm could be manufactured by this technique. To create an easy contacting of the inner electrode in the MC, the generation of an interdigital electrode structure has been aspired. By means of the specific innovation, to fix a shadow mask by magnetic forces on top of the ceramic green tape, this was realized. With the intention to manufacture piezo generators for vibration energy harvesting, triple-layered bending transducers have been manufactured successfully from a hard-doped PZT powder and inner electrodes made of pure silver via this new co-casting process. The material compatibility for the co-firing step of PZT and the cost-effective base metal silver was achieved by means of the liquid phase sintering technology, using a combination of Li\textsubscript{2}CO\textsubscript{3}·Bi\textsubscript{2}O\textsubscript{3}·CuO (LBCu) as sintering additives.

Keywords: Piezoelectric bending transducer, PZT multilayer ceramics, co-casting, co-fired Ag electrodes

1. Introduction

The piezo ceramic lead zirconate titanate Pb(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3}, abbreviated as PZT, is still the standard material for a variety of piezoelectric MEMS like actuators, sensors, generators as well as capacitors. Compared to other ferroelectrics, PZT shows the highest electro-mechanical constants and is the most common material despite its lead...
content. PZT-based multilayer ceramics, such as stack actuators, are industrially fabricated according to the powder-based multilayer ceramics technology (MCT). It includes the preparation of a pourable ceramic slurry, fabrication of single ceramic green tapes from this slurry by the tape casting method, which are subsequently screen printed to apply internal electrodes. The lower limit of layer thickness that can be achieved by MCT lies in the range of about 40 μm. A further decrease in the layer thickness is hampered due to the stacking operation of the very thin green tapes. For manufacturing MC with layer thicknesses about 20 μm, free-standing green tapes with thicknesses below 100 μm have to be processed. However, precisely stacking of such thin green tapes has proved difficult due to their increased tendency to corrugation. Two ceramic green tapes with different thicknesses are shown in figure 1 for comparison of their form stabilities. In addition, a stacking operation entails the risk of including air bubbles into the layer structure which is important to avoid for maintaining well-functioning components.

Another challenge is to replace the high-temperature stable internal electrodes in PZT multilayer devices that are generally made of Pt [1] or Ag/Pd alloys [2,3], with the more cost-effective and more conductive Ag electrodes. However, for co-firing pure silver electrodes together with the PZT ceramic, the sintering temperature of PZT has to be lowered from about 1200 °C to at least 900 °C to perform co-firing of the MC below the melting point of silver. This requires the development of a low temperature co-firing PZT-based powder composition (LTC-PZT) that sinters densely below 900 °C. With the objective to manufacture a piezoelectric triple-layered bending transducer for vibration energy harvesting with layer thicknesses below 50 μm and internal electrodes made of silver, the following co-casting process was developed and performed using a LTC-PZT composition.

2. Co-Casting Process

The novel co-casting process offers a simplified technique for an alternating buildup of ceramic and metallic layers without stacking of single green tapes as it is carried out industrially according to the conventional MCT process chain [3]. The new process flow of the simplified co-casting method is schematically depicted in figure 2. After casting a ceramic film on top of a hard-magnetic underlay that was previously covered with a self-adhesive teflon tape or a graphite film, a laser-structured steel foil is attached magnetically on the dried ceramic green tape. This soft-magnetic foil serves as a firmly fixed mask for casting a diluted metal paste directly on top of the dried ceramic layers. The next ceramic layer is cast, when the silver layer is dried again directly on top of it. By that way air inclusions between the layers are avoided and an adequate junction of the layers is created so that no further mechanical assembly is required. Repeating the steps a) and b) for several times leads to a co-cast MC. To guarantee uniform thick layers a PMMA panel was used as plane base on which the hard-magnetic foil can be directly adhered. This co-casting technique can be extended analogously to other ceramic materials, since it is a powder-based process.
2.1. Equipment for co-casting

A main advantage of the co-casting process is that an entire green multilayer stack can be fabricated only by means of a precision squeegee, as it is depicted in figure 3, or a lab-scaled tape casting plant with a mobile doctor blade. In comparison, manufacturing MC according to MCT requires a tape casting plant, a screen printing set-up, a heated isostatic press for the lamination step as well as component specific pressing tools for each device geometry. Especially, for MC manufacturing in a lab scale the co-casting process is much easier to perform. Moreover, a self-adhesive hard-magnetic underlay and a laser-structured steel foil are needed. The magnetic attraction of the mask combines the following advantages. First, the fixation of the mask is removeable and it can be taken off completely residual-free. Second, an once laser-structured mask is several times re-useable.

2.2. Realizing an interdigital electrode structure

For casting the patterned metallized areas, a soft-magnetic steel foil is used as a shadow mask and a hard-magnetic foil as an underlay. The strong magnetic forces of the magnetic underlay bring the mask into tight contact to the ceramic tape and guarantee a firm fixation of the mask. Using this special innovation, metallized areas with high edge definition can be generated, since it effectively prevents an underrun of the pourable silver paste successfully. By shifting the steel mask by a small distance for casting the electrode layers, as it is illustrated in figure 2, a lateral offset of every second electrode can be generated. This offset Δx is shown in figure 4a. After dicing and co-firing of the MC, the electrode offset results in an interdigital electrode structure, as shown in figure 4b.
2.3. Formulation development of the ceramic slurry and the metal paste

In general, polymeric binders with high molecular masses are used for preparation of ceramic slurries that are processed via MCT, since the single green tapes need to have a high E-Modulus to stay form stable for a precise stacking. As shown in figure 5a, the E-Modulus of single green tapes increases with the polymer chain length. That was found by performing tensile tests on specimens with different binder types. These specimens have been punched out in and orthogonal to the casting direction of single green tapes. For manufacturing MC according to the co-casting process, it should be considered that a binder type with increased polymer chain length requires also a higher content of solvent to set the slurry viscosity in an optimum range of 6-8 Pa·s. This is illustrated more detailed in figure 5b. A higher solvent amount entails more drying shrinkage and even though the shrinkage takes place mainly in z-direction, the lateral shrinkage becomes proportionally larger when the solvent amount is increased and that should be avoided. Since no free-standing green tapes are processed while co-casting a MC, it is perfectly sufficient to use a binder type with a middle molecular mass for preparation the slurry in that case. For the MC presented in this work the polyvinylbutyral binder type Mowital B 45 H (Kuraray Europe GmbH) was used. With regard to the debinding step the same binder type was used to modify the commercial silver paste. Without addition of a binder micro-fissures have been observed in the dried electrode layers.

![Fig. 4. (a) Topview on four ML stacks during co-casting procedure; (b) Cross section through an already co-fired triple-layer.](image)

![Fig. 5. (a) E-Moduli of PZT single green tapes made of slurries containing the same polyvinylbutyral binder with different molecular masses and (b) required solvent amount for setting a slurry viscosity of 7 Pa·s as function of binder type.](image)
2.4. Layer thicknesses

The new co-casting technique offers an outstanding approach for manufacturing MC with very thin layers, since it circumvents the problem of stacking very thin and less form stable green tapes. The measured layer thicknesses in their wet, dried and co-fired state are listed in Table 1. Figure 6 shows a co-fired PZT-based MC with internal silver electrodes and layer thicknesses below 20 \( \mu m \). For controlling the thickness of the ceramic layers, the layers drying shrinkage in z direction must be known. Otherwise the height of the precision squeegee can not be set precisely. As mentioned before, the shrinkage depends directly on the solvent content in the slurry. That applies equally for the electrode layers whose height can be controlled by mask thickness.

Table 1: Resulting average layer thicknesses of one layer after its shrinking during drying or co-firing.

<table>
<thead>
<tr>
<th>State of layer</th>
<th>PZT layers (( \mu m ))</th>
<th>Ag layers (( \mu m ))</th>
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<tbody>
<tr>
<td>Wet</td>
<td>300 200 100</td>
<td>100 50</td>
</tr>
<tr>
<td>Dried</td>
<td>120 ± 10 83 ± 8 40 ± 6</td>
<td>55 ± 4 28 ± 2</td>
</tr>
<tr>
<td>Fired</td>
<td>73 ± 5 36 ± 4 20 ± 3</td>
<td>9 ± 2 5 ± 1</td>
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Fig. 6. Co-fired piezoelectric ML with silver inner electrodes and layer thicknesses below 20 \( \mu m \).

3. Co-firing PZT and Ag

The low temperature co-fired PZT-based ceramic (LTC-PZT) composition that has been used for manufacturing the depicted MC by using the liquid phase sintering technology consists of the same commercial PZT powder with hard piezoelectric characteristics (PIC 181, PI Ceramics) and 1.2 vol.-% of the sintering additive LBCu which was mixed in a ratio 1:1.4, as recommended by Wang et al. [4]. An investigation of the piezoelectric and mechanical properties of ten sintering additives for hard-doped PZT that has been performed in a previous work, turned out that the ternary system LBCu, consisting of a combination of \( Li_2CO_3 \cdot Bi_2O_3 \cdot CuO \), is able to lower the sintering temperature of hard PZT significantly. It was found that the sintering additives, though impurities in the PZT matrix, only negligibly affected the electrical and mechanical properties of the pure PZT [5]. Figure 7 shows that PZT with 5 vol.-% LBCu sintered at 900 °C exhibits even a 27 % higher characteristic breaking strengths of 77 MPa than the PZT sintered at 1200 °C without any sintering additives. Thus, a material compatibility of PZT and silver for co-firing the MC with internal electrodes made of Ag was achieved.
Fig. 7. Comparison of characteristic breaking strengths of hard PZT (PIC 181, PI Ceramics) with and without addition of the sintering additive LBCu, measured by performing 3-point-bending tests on single layered specimens after sintering at 900 °C or 1200 °C for 3h.

4. Conclusion

A novel technique for co-casting multilayer ceramics with layer thicknesses down to 20 μm has been developed. It can be integrated in the conventional multilayer ceramics technology for manufacturing multilayer devices where the novel co-casting technique offers a convenient alternative to tape casting, screen printing, stacking and lamination of single green tapes by including the metallization step into the tape casting step. The via co-casting fabricated multilayer stacks have an interdigital electrode structure, since patterned electrode layers with high edge definition were cast directly on top of the ceramic green tape using a laser-structured steel foil as shadow mask. The most important innovation of this co-casting process is that the steel mask is fixed magnetically on top of a previously cast ceramic green tapes by using a hard-magnetic foil as underlay.

References