Additive manufacturing of low-temperature co-fired ceramic substrates and surface conductors based on material jetting

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Abstract

Integrated manufacturing of ceramic substrates and surface conductors using 3D material jetting (MJ) technology is a novel additive manufacturing route for low-temperature co-fired ceramics (LTCC). This study evaluates the rheological and jetting properties of LTCC nanoceramic inks with varying solids contents. Ceramic inks with 35% solid content were found to be the optimal choice with high particle concentration and Ohnesorge numbers ($Oh$) below 1. The fabrication process used two piezoelectric printheads to inject nanoceramic ink and nanosilver ink to create a ceramic substrate and a surface interdigital electrode (IDE). The substrate sintering shrinkage was 21.5% and the surface IDE co-fired at the same shrinkage rate as the substrate thus ensuring all electrode pattern details. The electrode conductors demonstrated effective line widths of up to 0.21 mm. Microscopic characterisation of the interface between silver and substrate using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) confirmed the absence of significant elemental diffusion, ensuring the effectiveness of the silver electrode. The ceramic substrates exhibit good thermal stability below 400°C and have a coefficient of thermal expansion ($\sim$ 4.1 ppm/°C) similar to that of silicon, indicating reliability in packaging. A microstrip patch antenna with the design frequency at 9-11GHZ was made through the same MJ procedure, which was experimentally measured to have a resonant frequency of 10.1GHz, an S11 measurement of -24.6dB, a simulated radiation efficiency of 88.01%, and a high gain of up to 7.52dB.

Keywords: additive manufacturing, material jetting, low-temperature co-fired ceramics
1. Introduction

Low temperature co-fired ceramics (LTCC) devices have been widely used in microwave communications, aerospace and military electronics[1]. These applications mainly benefit from the good electrical and mechanical properties of LTCC substrates, thus meeting high reliability and stability[2]. However, the traditional manufacturing of LTCC devices is equipment-intensive and process-intensive[3], resulting in high manufacturing costs. Additive manufacturing (AM) technology offers a distinct advantage in producing ceramic parts[4], such as some intricate and complex components with sophisticated interlayer and internal structures, making it an ideal choice for rapid prototyping. Material jetting (MJ) is preferable over other technologies when considering the use of AM technology to produce LTCC devices. MJ technology selectively releases droplets from an array of nozzles, allowing for a line accuracy of a few microns to over ten microns with a single droplet, far superior to direct ink writing (DIW)[5] or fused deposition modelling (FDM)[6] based on extrusion. Additionally, the drop-by-drop printing of different materials makes MJ technology more suitable for achieving multi-material spraying, which is not the strong point of digital light processing (DLP)[7] or stereolithography (SLA)[8] technology. Considering the multi-material characteristics of LTCC equipment and the accuracy requirements, it is believed that MJ technology may be the most suitable way to produce LTCC structures with specific dielectric, conductive layers, and necessary support or sacrificial parts.

The formation of ceramic particle aggregates in ceramic ink can cause severe nozzle clogging, leading to inconsistencies and unreliability in the jetting process. To successfully produce ceramics using MJ technology, stable and uniform ceramic ink development is critical[9]. Rational formulation allows for a broad range of ceramics to be manufactured, such as ZrO₂ ceramic ink.
configured by Cappi et al.[10] for hot-foaming multiple-nozzle printhead, and Al₂O₃ ceramic ink reported by Chen et al.[11], jetted by piezoelectric multiple-nozzle printhead. MJ technology is also well-suited for manufacturing thin ceramic layers[12], which is very useful for miniaturizing ceramic devices. These works provide examples of partial high-temperature sintered ceramics fabricated with MJ. In our previous work[13], we developed low-dielectric LTCC inks adapted to piezoelectric inkjet printheads thereby fabricating LTCC substrates using MJ and demonstrating good low-temperature sintering properties. However, similar to other reports on the fabrication of ceramic structural components, this research has yet to report the realisation of ceramic electrical properties by means of AM. In recent years, material jetting using commercially available nanosilver inks has become a popular way to fabricate circuits. Jiang et al.[14] and Li et al.[15] have successfully achieved metallization on PDMS substrates and fabricated multilayer silver conductor bandpass filters using the MJ technique with nanosilver inks. Hence, combining commercially available nanosilver inks with nanoceramic inks may allow for the monolithic fabrication of devices with ceramic substrates and surface conductors. Fig.1 depicts the specific flow of this process, where the produced LTCC green body will undergo densification and electrical functionalization at a temperature below the conductor's melting point. This AM process is entirely different from the conventional manufacturing route of LTCC, promoting the flexible manufacturing and customization of LTCC components.
Fig. 1. Schematic diagram of LTCC substrate and surface circuit manufacture by material jetting

In light of this, the present study explores a method to produce LTCC substrates and their surface conductors using MJ technology. We present a comprehensive analysis of ceramic inks' jetability with varying solid contents, demonstrate co-jet moulding of the substrate and surface interdigital electrode, and assess co-fire shrinkage. We also evaluate the interface properties and thermal expansion of the substrate and fabricate a high-gain microstrip antenna to demonstrate its effectiveness.

2. Experiments

2.1 Materials

The composition of the printable LTCC inks has been discussed in previous work[13], with the main phase of ceramic particles being silica, supplemented with 25 wt% H_3BO_3 used to facilitate low temperature sintering. This work modified the type of solvent used in the ink formulation. As the solvent previously used was propylene glycol methyl ether with a boiling point of 120°C, the potential for excess solvent residue in the jetted green body would lead to micro-cracking of the green body during the degreasing low temperature section. To avoid this, isopropanol was chosen
as the new solvent type, with a relatively low boiling point, making it easier to achieve thermal
dissipation of the solvent during the jetting. The nanosilver ink for the metallisation of ceramic
surfaces was purchased from Broadteko, Beijing. It is compatible with a variety of piezoelectric
printheads and enables effective high-temperature sintering. Table 1 displays some of its physical
properties.

Table 1. Part of the physical properties of the nanosilver inks

<table>
<thead>
<tr>
<th>Product Type</th>
<th>Solids content *</th>
<th>Density *</th>
<th>Surface tension *</th>
<th>Viscosity *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ink550HT</td>
<td>35</td>
<td>1.52</td>
<td>27.6</td>
<td>10.5</td>
</tr>
</tbody>
</table>

* T = 20°C

2.2 Additive manufacturing procedure

In this work, we utilized a piezoelectric printhead (GH2220, Ricoh, UK) with 2 rows of 192
nozzles. A single row of nozzles can print at 150 dpi pixel addressing capability, while two rows of
nozzles produce two rows of droplets 84.5 µm apart when used simultaneously. During the additive
manufacturing process, we set the belt speed to 50 mm/s and kept the jet frequency below 1 kHz to
minimize the chance of nozzle failure due to sub-optimal rheology. The bottom heated substrate
coated with a Teflon fabric mesh deposited the part to be jetted as required. The substrate
temperature was set to 70°C to evaporate the solvent. After every three jetted layers, we used a UV
lamp equipped with a wavelength of 395 nm and a light power of 20 W to cure the pattern,
stimulating free radicals and promoting substrate formation. The initial nozzle height was 5 mm
from the substrate, and the nozzle rose approximately 3 µm in longitudinal height with each cured
layer. This process is repeated until the substrate jetting process is complete. During the nanosilver
jetting phase, the substrate temperature is increased to 140°C to promote nanosilver surface drying, the belt speed is reduced to 30 mm/s to ensure drop accuracy and the initial printhead height is 3 mm from the substrate. Due to the non-stick nature of the Teflon material, the cured structure is easily released from the Teflon substrate after printing and is then placed in a muffle furnace for debinding and pressure-free sintering.

2.3 Testing and characterization

A rotational rheometer (MCR 302, Anton pair, Austria) and a contact angle meter (JC2000 D1, POWEREACH, China) were used to test the rheological properties and surface tension of inks with different solids contents, respectively. A simultaneous thermal analyser (STA 449F5, NETZSCH, Germany) was used to investigate the sintering characteristics of green bodies in an air atmosphere, with the heating rate set at 5 K/min. The three-dimensional profilometer (Contour GT-K, Bruker, Germany) was employed to investigate the surface morphology of jetted samples and sintered samples. The microstructure and elemental distribution of the sintered samples were observed using field emission scanning electron microscopy (Apreo HiVac, FEI Inc., USA) and energy dispersive X-ray spectroscopy (EDS). A thermal expansion analyser (DIL402C, NETZSCH, Germany) was used to test the thermal expansion of the ceramic substrates. Design and simulation of microstrip antennas using high frequency structure simulator (HFSS, Ansoft). Testing the S-parameters of the antenna using a vector network analyzer.

3. Results and discussion

3.1 Inkjet printability

The rheological properties of ink, including viscosity and surface tension, play a significant role in determining the shape and speed of sprayed droplets. When viscosity and surface tension are
too high, ink droplets may not be driven out of the nozzle meniscus due to high resistance to flow. Conversely, low viscosity and surface tension can cause issues such as unwanted ink dripping, nozzle surface spreading, and the creation of satellite droplets. Therefore, to facilitate jetting, inks should exhibit appropriate rheological and dynamic fluid properties. It is generally accepted that whether and how droplets form depends on the Reynolds number \( Re \) and Weber number \( We \) of the fluid passing through the printhead capillary.

\[
Re = \frac{v \rho a}{\eta}
\]  \hspace{1cm} (1)

and

\[
We = \frac{v^2 \rho a}{\sigma}
\]  \hspace{1cm} (2)

where \( v \) is the velocity, \( \rho \) is the density, \( a \) is the characteristic length (i.e. capillary diameter), \( \eta \) the viscosity and \( \sigma \) the surface tension. To determine the printability of ink, the Ohnesorge (\( Oh \)) number can be calculated. It is defined as:

\[
Oh = \frac{We^{0.5}}{R} = \frac{\eta}{(\rho a)^{0.5}}
\]  \hspace{1cm} (3)

The suitable \( Oh \) values for inkjet printing are suggested to be between 0.1 and 1[14]. In order to calculate the \( Oh \) values of inks with different solid contents, the changes in the shear behavior and surface tension have been tested, and the results are shown in Fig.2. The suspensions exhibit non-Newtonian shear-thinning behavior, i.e., the viscosity decreases with increasing shear rate due to the destruction of the structure and shear-induced orientation of ceramic particles. No significant change in viscosity was observed when the shear rate increased to and above 100 s\(^{-1}\).
Table 2. Physical parameters and $Oh$ values of nanoceramic inks with different solid contents

<table>
<thead>
<tr>
<th>Solids content (wt%)</th>
<th>Viscosity $^a$ (mPa·s)</th>
<th>Surface tension $^a$ (mN/m)</th>
<th>Ink density $^a$ (g/cm$^3$)</th>
<th>$Oh$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>12.3</td>
<td>26.5</td>
<td>1.01</td>
<td>0.594</td>
</tr>
<tr>
<td>30</td>
<td>14.2</td>
<td>28.2</td>
<td>1.12</td>
<td>0.632</td>
</tr>
<tr>
<td>35</td>
<td>20.2</td>
<td>29.6</td>
<td>1.15</td>
<td>0.866</td>
</tr>
<tr>
<td>40</td>
<td>26.9</td>
<td>31.5</td>
<td>1.20</td>
<td>1.093</td>
</tr>
</tbody>
</table>

$^a T = 20°C$

$^b \gamma' = 1000$ s$^{-1}$

Table 2 presents the $Oh$ numbers at different solids levels, demonstrating that inks with 25%, 30%, and 35% solids exhibit $Oh$ values below 1, indicating suitable rheological properties for piezoelectric inkjet printhead jetting. Inks containing 40% solids have elevated viscosities, leading to $Oh$ numbers above 1 and were found to be unable to form droplets at the liquid meniscus of the
nozzle. To reduce shrinkage during sintering and optimize product quality, 35% solids ink is the most appropriate option for manufacturing LTCC parts. To further investigate the effect of jetting, we observed droplet generation and dropping at different frequencies using the developed droplet jetting observation device, as shown in Fig 3 (a). This was achieved by stroboscopic analysis of the real-time backlit images of droplet formation and jetting captured by a charge-coupled device (CCD) camera. The jetting frequency of 500 kHz is similar to the actual jetting frequency, and the generation and smooth extrusion (in the boxed area) reflect a good match of ink physical parameters under piezoelectric action. For some higher frequency jetting scenarios, the jetting effect was further examined at 2kHz and 4kHz, where snapshots were taken showing faster microdrop generation rates and denser flight paths without significant satellite droplet trailing. To determine the droplet fusion and monolayer curing phenomena on the substrate, a Xidian University badge pattern was jetted on PET film at 150 dpi, as shown in Fig. 3 (b). The dots are aligned into lines in the direction of jetting reflecting well-fused property. In the jetting cross direction, this gap is expected to be interpolated by a denser column of droplets when printing a complete layer at 450 dpi or higher thereby ensuring film formation characteristics.
Fig. 3. (a) Snapshots of drops falling at different frequencies (b) Detail of the Xidian University emblem jetted with ceramic ink at 150 dpi resolution

3.2 Jetting and co-firing of the green substrate and surface conductors

Fig. 4 (a) illustrates the fabrication process of the jet-sintered example, where a ceramic green substrate of size $32 \times 32 \times 1.2$ mm was first jetted with a configured ceramic ink, with the surface conductor pattern designed as interdigital electrodes (IDE) of different electrode widths. The substrate size after co-sintering was reduced to $25.1 \times 25.1 \times 0.92$ mm, where the line shrinkage in all directions in the XOY plane was uniform. The shrinkage in the Z-direction is slightly higher (23.3%), possibly due to gravity-driven effects.

For IDE jetting, two electrode lines were designed to have a 1 mm line width and were jetted 60 layers at 600 DPI accuracy. The profile and specific quantification of the jetted and sintered...
electrode lines are shown in Fig. 4 (b) and (c). The surface-dried nanosilver layer exhibits a slight print texture in the direction of jet intersection, while surface undulations are smoothed out after sintering. After jetting 60 layers, the wire height in the z-direction remained at approximately 27 µm and its width was approximately 1.0 ± 0.1 mm. As depicted in Fig. 4 (c), the sintered electrode wire shrinks to a wire width of approximately 0.84 mm, highly matching that of the substrate due to the similar solids content of the two inks. The height of the electrode wire after sintering was maintained at around 21 µm, meeting the LTCC's wire manufacturing guidelines for wire heights of typically 10 µm or more[17]. Further test results of the sintering effect for smaller jetted line widths (~ 0.25 mm) are shown in Fig. 4 (d) and (e), where the line width is reduced to 0.21 mm after sintering, while the height remains around 18 µm, maintaining the good appearance and conductivity continuity. Narrower effective line widths will require further testing. The synergistic shrinkage between the substrate and surface lines forms the basis for the co-fired manufacture of useful LTCC components with sintering shrinkage requiring advance dimensional compensation when using the LTCC process to manufacture dimensionally sensitive components like antennas. In this work, the nanoceramic and nanosilver inks fixed the shrinkage between different materials due to their similar solids content, resulting in co-fired LTCC devices that match the design values.

### 3.3 Interlayer properties

To ensure proper functionality of the devices, the substrate material must exhibit good chemical compatibility with low-resistance electrode metals like silver. Fig. 5 (a) presents a cross-sectional SEM image of the ceramic green sample after a 2-hour co-firing process with a silver electrode. The SEM image clearly displays the boundaries between the matrix and the Ag layer. Furthermore, the distribution of elemental Ag in the same area was measured using EDS mapping.
and presented in Fig. 5 (b). The EDS results indicated that Ag was primarily concentrated in the electrode area, with no apparent indication of a reaction between the composite and the Ag electrode. Thus, this confirms that the ceramic material exhibits outstanding chemical compatibility during cofiring with a silver electrode.

![Fig. 5. (a) SEM photograph of the interface between the LTCC substrate and the Ag layer (b) EDS mapping of silver and silicon elemental distribution in SEM areas](image)

3.4 Thermal expansion properties

To prevent a thermal mismatch between the substrate material and the chip, especially for large chip sizes, it is important that the coefficient of thermal expansion (CTE) value of the substrate material matches the CTE value of silicon (3.1 ppm/°C). Substrate materials that meet these requirements will enhance the performance of LTCC modules and improve the reliability of the package under different temperature conditions. The CTE of the substrate material was measured over a temperature range of 50-400°C and the results are shown in Fig.6 (a). The thermal expansion increases linearly with increasing temperature, which indicates that the substrate exhibits good stability. According to the thermal expansion coefficient curve in Fig.6 (b), the thermal expansion coefficient increases to 4.3 ppm/°C as the temperature increases from RT to 400°C. Compared to
commercially available LTCC materials, the present glass-ceramic composite has a lower thermal expansion coefficient and is comparable to the CTE value of silicon (3.1 ppm/°C)[17], indicating that the composite can be used for microelectronic applications.

![Graph](image)

Fig. 6. (a) Variation of thermal expansion from RT to 400°C (b) Variation of thermal expansion coefficient from RT to 400°C

3.5 Jetting and sintering of microstrip antennas

In order to quantify the contribution of the dielectric properties of the substrate to the performance of the LTCC device, a microstrip antenna was designed to operate at 9-11 GHz. The designed antenna is a power feed consisting of a combination of a microstrip transmission line and a microstrip radiating patch. In this case, the feed unit and the patch unit are set to be jetted and moulded in one go on a co-planar basis, using a waveport-side feed pattern to feed the centre of the wide edge of the rectangular patch, with the ground end again completely covered by jetted nanosilver material. When fabricating this antenna using MJ integration, shrinkage during the sintering of the substrate to the silver conductor needs to be taken into account, meaning that the antenna dimensions in the XOY plane need to be compensated for in advance. The physical dimensions and detailed parameters of the optimally determined sintered microstrip antenna are

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given in Fig. 7 (a) and Table 3. The dielectric parameters used for the simulation can be found in the previous work[13].

Table 3. Optimal parameters for the simulation of antennas

<table>
<thead>
<tr>
<th>Parameters</th>
<th>W_1</th>
<th>W_2</th>
<th>W_3</th>
<th>W_4</th>
<th>W_5</th>
<th>L_1</th>
<th>L_2</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values (mm)</td>
<td>18</td>
<td>16</td>
<td>6.7</td>
<td>0.8</td>
<td>1</td>
<td>9</td>
<td>1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Fig. 7. (a) Geometry and parameters of the microstrip antenna (b) Physical antenna made after co-fired (c) Simulated and tested S11 results (d) Simulated VSWR curves (e) Gain and radiation efficiency at different operating frequencies (f) 3D radiation pattern

Based on the obtained shrinkage, the green substrate dimensions were expanded to 22.8×22.8×0.66 mm and the central patch pattern to 20.2×11.4 mm, with careful compensation for the rest of the details. The physical dimensions of the antenna after integrated sintering were similar to design values, as shown in Fig. 7 (b). The antenna performance was evaluated based on S11,
which represents the ratio of input power to reflected power. Simulated and measured S11 profiles of the antenna were presented in Fig. 7 (c). The antenna resonated at 10.1 GHz with an S11 value of -30.41 dB, covering a -10 dB bandwidth of 280 MHz. The measured S11 profile was more consistent with the simulated one, exhibiting a resonant frequency of 10.1 GHz, a return loss of -24.6 dB, and a broad bandwidth of 263 MHz. The excellent S11 value indicated that almost all input power was radiated through the antenna. The voltage wave ratio (VSWR) curve (Fig. 7 (d)) presented an excellent value of 1.06 at a resonant frequency of 10.1 GHz, confirming the antenna’s good reflection coefficient. The simulated antenna signal gain and radiation efficiency as a function of frequency were illustrated in Fig. 7 (e), where a high signal gain of 7.52 dB and a high radiation efficiency of 88.01% were obtained at the resonant frequency. In addition, the antenna exhibited good radiation symmetry, as demonstrated by the simulated 3D radiation map in Fig. 7 (f). In conclusion, the integrated fabrication of LTCC antennas using MJ technology showcased great for wireless communication applications, given the antenna's excellent performance, microwave dielectric properties, and processing temperature.

**Conclusion**

In the current study, the first results of material jetting for the co-fabrication of LTCC and surface conductors are presented. The ceramic material is configured to be jetted with a nanoparticle ink and piezoelectric printhead to form the carrier layer, while the metallization is achieved on it employing nanosilver ink. In this way, the versatility and precision properties of material jetting are fully exploited. The main findings are as follows:

1. Matching the solids content of the nanoceramic ink to the nanosilver ink is critical to ensure simultaneous shrinkage by co-sintering. Ceramic inks containing 35% solids showed optimal
jettability and droplet fusion characteristics, while having a similar solids content to commercially available nanosilver inks. Co-sintering of the jetted LTCC green substrate with the interdigital electrode pattern on its surface confirmed the synchronous shrinkage phenomenon.

(2) The interface between the conductor and the ceramic substrate was observed by microstructure and elemental analysis to show no significant diffusion of silver elements after cofiring.

(3) The ceramic substrate possesses a stable thermal expansion rate with a coefficient of thermal expansion is consistent with that of silicon, with a value of 4.1 ppm/°C below 400°C.

(4) The fabrication process's reliability was exhibited through the injection and co-fire creation of a 9-11 GHz microstrip antenna. Both measured and simulated results show resonant frequencies at 10.1 GHz, and tests yield S11 parameters as low as -24.6 dB. The high gain value (7.52dB) is due to the substrate's excellent dielectric properties, highlighting the potential of the process and material for microwave device fabrication.

Acknowledgment

This work was supported in part by the National Natural Science Foundation of China under Grant 52035010, in part by Shaanxi Key Industry Chain Project under Grant 2020ZDLGY14-08, in part by the National 111 Project under Grant B14042, in part by the Nature Science Basic Research Plan in Shaanxi province of China under Grant no. 2019JQ-269, in part by the Fundamental Research Funds for the Central Universities under Grant no. JB210417, in part by Shaanxi Innovation Team Project under Grant 2018TD-012, in part by General Program of National Natural Science Foundation of China under 52275372.

Reference

This preprint research paper has not been peer reviewed. Electronic copy available at: https://ssrn.com/abstract=4493985


[10] B. Cappi, E. Özkol, J. Ebert, R. Telle, Direct inkjet printing of Si3N4: Characterization of ink, green


Supporting Information

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Figure S1. (a) Visualization of jetting thickness versus jetting time (b) Thermogravimetric curve of the ceramic green body (c) Debinding and co-sintering curve