Application of Reactive Bonding Methods on LTCC Substrates

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Abstract - This paper discusses the application of reactive bonding for the area of Low Temperature Coffired Ceramics (LTCC) assemblies. The goal is to reduce the thermomechanical stresses during soldering by transferring heat only locally to the solder joints without heating the entire component. Such a reactive multilayer system (RMS) consists of alternating nanolayers (10-300 nm) of at least two metal components which produce an exothermal reaction after ignition. Although the deposition of an RMS is established on silicon substrates for the use in micro-electromechanical systems (MEMS), it is very challenging to create them on LTCC substrates. One of the main obstacles is to overcome all issues connected with the significant roughness, because it is not an optimum territory to deposit nanolayers. In this paper, different methods like chemical mechanical polishing (CMP) and laser ablation, to modify the surface morphology, are presented. A direct relation between the morphology and the exothermal reaction can be observed. In addition, 3-D Computational Fluid Dynamics (CFD) simulations were conducted to analyze the process in more detail. These simulations make use of a shoebox model with different layers and an adjustable user-defined function for the heat release of the RMS to adapt the reaction front velocity and the combustion temperature to the experimental values.

Keywords - LTCC, RMS, reactive multilayer systems, Al-Ni, joining.

I. INTRODUCTION

The chemical reaction of nitrogen monoxide (NO) with ozone leads not only to the formation of nitrogen dioxide and oxygen, but also to the emission of radiation in the wavelength range between 600 to 2600 nm with a maximum in the infrared area at 1200 nm [1]. Measuring this radiation can be used to determine low concentrations of NO in gas flows. Therefore, a measurement device was developed and presented in [2]-[4] using LTCC (Low Temperature Coffired Ceramic) technology (see Fig. 1). It consists of three different modules: first, there is an ozone generator with a high voltage source, that is applied to a gas flow using an embedded electrode. Then, the ozone is transported via microfluidic channels to a chemiluminescence detection reaction chamber where it is mixed with the gas that contains an unknown amount of NO. An infrared transparent window is bonded onto the LTCC substrate, and a photo diode that measures the emitted radiation is placed on it. The last module is an exhaust gas treatment to decompose the ozone into nonhazardous oxide.

Therefore, a heating structure was embedded in the LTCC substrate and a platinum paste, that can be applied to the substrate, was used as a catalyst.

Fig. 1. Measurement device for low concentrations of nitrogen monoxide in gas flows, realized using LTCC technology.

The LTCC technology is an excellent candidate for such devices because it enables the possibility of three-dimensional structuring [5]-[7] and shows very good hermetic sealing properties [8], [9]. Additionally, it provides not only excellent robustness under harsh environmental and mechanical conditions [10], [11], but also chemical resistance [9]-[13]. Due to these properties, LTCC technology can even be used in automotive and aerospace. It is also possible to add passive elements using conventional surface mounting technology like reflow soldering. Therefore, both the component and the substrate need to be heated up to a temperature above the melting point of the used solder, which can be critical for heat sensitive components. Adding heat locally to the solder joints can be an option to avoid damages during this process e.g., through using a reactive multilayer system (RMS). While the use of an RMS is well established on silicon substrates [14], it is very challenging to deposit such a system on LTCC substrates due to their high roughness in the range of 0.4 to 1 m [15]-[17].

An RMS consists of at least two different materials that are applied on a substrate in an alternating way e.g., through...
magnetron sputtering [10]. The thickness of every single layer is in the range of 10 to 300 nm [19] and the total stack thickness varies in the range of 0.1 to 300 μm [20]. After the system is ignited (e.g., by providing sufficient heat, by using an electrical spark or by using a laser pulse) the materials begin to intermix on atomic level building a new intermetallic phase. This leads to a self-propagating reaction [21] that is profoundly exothermal [22]. The released heat of this process can be used for joining processes by melting an additional solder layer, among other things. The propagation speed will depend on the materials used, the bilayer thicknesses, the ratio of the materials, the total stack thickness and the amount of heat released. However, the mechanical pre-processing of the substrates also has an influence on the speed of the reaction, what should be discussed here.

II. SAMPLE PREPARATION

A. Reference sample and laser ablation

As described in [23] the samples were prepared in different ways. For the reference samples, and the samples that were modified by laser ablation, a standard LTCC technology was processed using 6-layer DuPont 951 P2 resulting in a thickness of 817 nm ± 2.5 nm. Without further processing a roughness of 390 nm ± 16.6 nm was reached for the reference samples.

To achieve other roughnesses the surface of the LTCC substrate was laser ablated in a grid-like way using a 355 nm picosecond UV laser system. Different cutting distances between 5 and 30 μm and a laser power between 0.5 W and 1 W were used, which resulted in a roughness between 572 nm ± 14.4 nm and 874 nm ± 20.5 nm. Finally, the samples were cut into pieces of 15 mm × 7 mm. After that a 20 nm thick layer of titanium was sputtered onto the samples as an adhesion layer, followed by the subsequently deposition of the RMS. With a total thickness of 10 μm, 100 layers were chosen with a thickness of 60 nm for the aluminum and 40 nm for the nickel. After processing the samples, they were ignited by an electrical spark using two electrodes and a power supply limited to 25 V and 4 A.

B. Chemical/mechanical lapping and polishing (CMP)

The other possibility for the sample preparation persists in using a CMP machine to achieve lower roughness. An 8-layer DuPont 951 P2 was processed in a standard LTCC technology resulting in a thickness of 1080 μm. The substrates were lapped down chemically/mechanical on both sides to achieve a plane surface with a thickness of 810 μm ± 5.5 μm. Further polishing led to a roughness in the range between 105 nm ± 19.5 nm and 258 nm ± 16.5 nm. As before the samples were cut into smaller pieces and both the adhesion layer and the RMS were deposited.

C. Laser ablation with additional metallization

Some samples obtained an additional AgPd metallization between the LTCC substrate and the RMS [24]. Therefore, a standard LTCC technology was processed using 4-layer DuPont 951 PX resulting in a thickness of 839 μm ± 2.6 μm. The surface morphology was modified using the laser system in the same way as before. The reference sample (without further processing) reached a roughness of 525 nm ± 30 nm, whereas the other ones reached a roughness of 537 nm ± 12 nm (LS 3) and 773 nm ± 29 nm (LS 5). Finally, the samples were cut into pieces of 15 mm × 7 mm and the RMS was deposited.

D. Roughness characterization

The roughness of the surface was characterized by using a laser scanning microscope [23], [24]. An area of 250 μm × 250 μm was chosen for the measurements. The lowest roughness of about 100 nm was found for the CMP samples without metallization whereas the laser ablated samples show the highest roughness with a maximum of about 870 nm. Without processing the roughness is about 400 nm (see Fig. 2). For the samples with metallization, a roughness of 525 nm (reference respectively 537 nm and 773 nm were reached (laser ablated samples).

![Fig. 2. Resulting surface roughness for some samples with different preparation methods, measured by LSM [23], [24].](image)

III. CFD MODEL

A. CFD model description

To achieve more information about the reactive joining process a suitable CFD model was already developed and presented in [25]-[27] (see Fig. 3). It consists of the aluminum-nickel bilayer (blue), the LTCC substrate (green) and the isolation layer (green) between, some simulations also contain a solder layer. The base of the model has a primary surface of 4 mm × 4 mm with a surrounding air environment of the dimensions 10 mm × 10 mm × 5 mm to avoid interactions between the region of interest and the boundary conditions. Due to stability and convergence reasons no titanium layer was considered in the simulation model.

![Fig. 3. The CFD simulation model mainly consists of the reactive multilayer system (blue) and the LTCC substrate with an isolation layer (green) [25].](image)
The material properties and the dimensions of the individual layers are shown in Table I. The properties of the LTCC substrate and the isolation layer were assumed to be identical (GreenTape™ DuPont DP951), which is why the effective thickness of the LTCC substrate is 860 µm. The properties of the RMS match with an unreacted multilayer [28], and the properties for the solder and the silicon chip were taken from the ANSYS Fluent material databases.

### Table I. Dimensions and properties of the layers used in the CFD simulation model [26], [28].

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness [µm]</th>
<th>ρ [kg/m³]</th>
<th>λ [W/mK]</th>
<th>υ [J/kgK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTCC</td>
<td>825</td>
<td>3100</td>
<td>3.3</td>
<td>600</td>
</tr>
<tr>
<td>Isolation</td>
<td>35</td>
<td>3100</td>
<td>3.3</td>
<td>600</td>
</tr>
<tr>
<td>RMS</td>
<td>30</td>
<td>5500</td>
<td>152</td>
<td>830</td>
</tr>
<tr>
<td>Solder</td>
<td>200</td>
<td>7000</td>
<td>63.2</td>
<td>230</td>
</tr>
<tr>
<td>Chip</td>
<td>400</td>
<td>2500</td>
<td>100</td>
<td>710</td>
</tr>
</tbody>
</table>

A 3x3 matrix of temperature probes was used to measure the temperatures during the movement of the reaction front. The probes in the same vertical position (e.g., P1, P2, P3) gave information about the reaction velocity (through the time delay in the recorded values), and the probes in the same horizontal direction (e.g., P1, P4, P7) can be used to determine the peak temperature. For additional information the temperatures were also measured in the middle of the RMS, at the interface between the RMS and the solder, and at distances of 10 and 20 µm in the solder starting from the interface.

![Fig. 4. Locations of the platinum temperature probes (P1 to P9) and the measurement points in the solder and the RMS.](image)

All the structures were meshed in ANSYS Workbench 2023R1 with a length of 100 µm for the mesh edges in x- and y-direction, and with a length of 10 µm in the z-direction leading to a total number of 5,001,000 cells. The time-step size was fixed to $10^{-6}$ s for 10,000 time-steps which results in a simulation time of 10 ms. For a more detailed view see [25], [26]. To simulate the propagation of the reaction front, a probability density function in the form of (1) was used.

$$f(x) = \begin{cases} 
A e^{-\frac{x}{B}} & x \leq 0 \\
C & 0 < x < 1 \\
D e^{-\frac{x}{C}} & x \geq 1 
\end{cases}$$

The four parameters A, B, C and D are used to control the heat release function, where A and B approximately correspond to the amplitude and width, C is an offset for the alignment with the leading edge of the reactive multilayer system and D corresponds to the velocity.

### IV. Results

#### A. Experimental analysis

As described in [23], all the samples showed a good adhesion behavior before ignition (see Fig. 5). After ignition, a peel-off effect could be observed at both the un machined reference sample and the CMP prepared samples with low roughness (105 µ 390 nm). In contrast the samples that were laser ablated with a roughness between 572 nm and 874 nm still show a good adhesion even after ignition, but SEM images show the occurrence of micro cracks within the RMS. Both the micro cracks and the peel-off effect are mainly caused by the different coefficients of thermal expansion of the materials. As an additional factor, there is a shrinkage in volume of approximately 12 % in the RMS due to lattice-spacing reduction [29] which may also affect the adhesion.

![Fig. 5. Reflected light microscopy image reveals a good adhesion of the reactive multilayer on the LTCC substrate (blue) before ignition.](image)

To determine the peak temperatures and the reaction speed, high velocity pyrometer measurements and high-speed camera measurements were done simultaneously [23], [24]. The pyrometer measurements show that the un machined LTCC substrate reaches the highest peak temperature (1092 °C), followed by the samples that were Prepared by CMP with nearly the same temperature (1067 and 1062 °C). The samples that were prepared by laser ablation reach the lowest temperatures (811 and 803 °C). It is remarkable that there is nearly no difference within the laser ablated samples although they differ in their roughness (572 nm to 873 nm). It can be assumed that the higher temperatures occur due to the peel-off of the RMS; the heat cannot be dissipated through the air as fast as if the RMS was still in contact with the substrate.

In case of the laser ablated samples with AgPd metallization, the lift-off effect was not as pronounced as in the other samples without the metallization. There is a punctual adhesion of the reactive multilayer, whereas some areas are separated from the metallization (see Fig. 6). The reference sample reaches a peak temperature of 854 °C whereas the laser ablated samples reach 847 and 793 °C. This temperature drop (compared to the first samples) may be caused by the additional metallization layer that absorbs some of the released heat.
The high-speed measurements show a velocity of around 5 m/s for the reaction front of both the reference sample and the CMP prepared samples. In contrast, the laser ablated samples show a reduction in velocity down to 3.7 m/s (roughness 572 nm) and 2.9 m/s (roughness 873 nm). The same effect can be observed on the samples with AgPd metallization: the velocity reduces from 3.7 m/s (roughness 525 nm) to 2.8 m/s (roughness 537 nm) and 2.2 m/s (roughness 773 nm). The measured values are clearly represented in Table II.

Table II. Overview of the reached peak temperatures and reaction front velocities depending on different substrate preparation methods and resulting surface roughness [23, 24].

<table>
<thead>
<tr>
<th>Substrate preparation</th>
<th>Surface roughness [nm]</th>
<th>Peak temp. [°C]</th>
<th>Reaction front velocity [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMP 1</td>
<td>105</td>
<td>1067</td>
<td>5.1</td>
</tr>
<tr>
<td>CMP 2</td>
<td>257</td>
<td>1062</td>
<td>4.7</td>
</tr>
<tr>
<td>Ref.</td>
<td>390</td>
<td>1092</td>
<td>5.1</td>
</tr>
<tr>
<td>LS 1</td>
<td>572</td>
<td>811</td>
<td>3.7</td>
</tr>
<tr>
<td>LS 2</td>
<td>873</td>
<td>803</td>
<td>2.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate preparation</th>
<th>Surface roughness [nm]</th>
<th>Peak temp. [°C]</th>
<th>Reaction front velocity [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgPd + Ref.</td>
<td>525</td>
<td>854</td>
<td>3.7</td>
</tr>
<tr>
<td>AgPd + LS 3</td>
<td>537</td>
<td>847</td>
<td>2.8</td>
</tr>
<tr>
<td>AgPd + LS 5</td>
<td>773</td>
<td>739</td>
<td>2.2</td>
</tr>
</tbody>
</table>

B. CFD comparisons

Simulations were performed for a model with solder (Fig. 7) and for a model without solder (Fig. 8). A velocity for the reaction front of 1 m/s and a time-step size of 10^-6 s was chosen for the temperature recordings.

As depicted in Fig. 7 the maximum temperature of about 260 °C was reached within the RMS which is only slightly above the required temperature of 240 °C [26]. At the interface between the RMS and the solder it reaches around 240 °C and the lowest value with around 220 °C is reached at a distance of 20 μm within the solder.

Fig. 8 shows the temperature plot for the model without a solder layer. The reached temperature within the RMS is raised by more than 200 % up to 820 °C while the temperature at the interface between the surrounding air and the RMS is above 750 °C. By comparison to the previous model, it can be assumed that the melting and solidification of the solder is responsible for this significant drop of the RMS peak temperature, so the amount of solder deposited on the RMS should be a good parameter to control the peak temperature during reactive bonding. A similar relation was already considered by Wang [30].

V. CONCLUSIONS

This paper discusses the application of reactive bonding methods on LTCC substrates. Therefore, a reactive multilayer system (RMS) consisting of alternating nanolayers of
aluminum and nickel with a total thickness of 100 μm was deposited after two different surface modifications were applied. Then, the samples were electrically ignited which was recorded by a high velocity pyrometer and a high-speed camera for temperature and velocity measurements. The first preparation method is chemical mechanical polishing (CMP) of a LTCC substrate, without metallization, which lowers the surface roughness down to around 100 nm. Compared to the reference sample (roughness 390 nm), the CMP does not seem to influence the peak temperature or the reaction front velocity. In addition, there is a peel-off of the RMS structure. The second method uses a picosecond laser to modify the LTCC substrate morphology, whereby the roughness can be increased up to 873 nm. This leads to a decrease in the peak temperature by nearly 300 °C and a decrease in the reaction front velocity by around 27 - 43 %.

In case of the laser ablated surfaces no peel-off effects could be observed but some micro cracks in the RMS could be found. Both the peel-off effects and the micro cracks occur due to different coefficients of thermal expansion and the volume shrinkage during the exothermal reaction. An additional reason for the problems in adhesion is the lower thermal conductance of the LTCC substrate compared to silicon substrates.

Laser ablation was also done for samples with an additional AgPd metallization between the LTCC substrate and the deposited RMS. After ignition, less peel-off effects could be observed. The drop in the RMS peak temperature is not as high as in the other version, but the velocity of reaction front was slowed down by around 24 - 41 %.

Experimental data show that the adhesion still has to be improved.

CFD simulations were conducted to analyze the process in more detail. A shoebox model with the different layers (LTCC, RMS and solder) was presented and compared to another model without a solder layer. An adjustable user-defined function for the heat release of the RMS during the reaction was used to adopt the reaction front velocity and the combustion temperature to the experimental values. The temperature during the exothermal reaction was recorded at different positions with a time-step size of 10⁻⁶ s. The measurements suggest that the solder layer can be used to control the peak temperature during the reactive bonding process.

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