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# Bonding methods of ceramic materials with deposited carbon layers

***Abstract***. *In this paper, we present a proposed bonding technology of ceramic materials. It could be applied for manufacturing ~~the~~ excitation source for detection of elements by means of Optical Emission Spectroscopy (OES) method. The biggest challenge was choice of proper bonding technology for materials with screen printed carbon layers as an excitation electrodes. It was caused by a need to avoid a deterioration of electrical properties of the carbon layer during the bonding process. The bonding at low temperature with various glaze layers was verified with addition of noble elements and plasma modification. The results were promising, without any significant destruction of carbon layers.*

***Streszczenie.*** *W tym artykule przedstawiamy proponowaną technologię łączenia materiałów ceramicznych która może być zastosowana przy wytwarzaniu źródła wzbudzenia do detekcji pierwiastków w metodzie optycznej spektroskopii emisyjnej. Wybór odpowiedniej technologii łączenia materiału z warstwami węglowymi wytwarzanymi metodą sitodruku był wyzwaniem z powodu konieczności uniknięcia degradacji właściwości elektrycznych węgla podczas procesu łączenia. Zweryfikowano łączenie w niskiej temperaturze z różnymi warstwami szkliwa z dodatkiem pierwiastków szlachetnych i modyfikacją plazmową. Wyniki były obiecujące, bez znacznego zniszczenia warstw węglowych. (**Metody łączenia materiałów ceramicznych z naniesionymi warstwami węglowymi**).*

**Słowa kluczowe**: łączenie warstw, LTCC, $Al_2O_3$, plazma, szkło, węgiel
**Keywords**: bonding, LTCC, $Al_2O_3$, plasma, glass, carbon

## Introduction

The motivation of this research is to find the best and the most durable mechanical connection between two ceramic substrates: $Al_2O_3$ and LTCC. The foundations are based on needs to create a microfluidic chip that would be used to study the composition of a liquid sample excited during atmospheric glow discharge using Optical Emission Spectroscopy (OES). Such excitation sources based on microplasma discharge between a reservoir with analyte and a solid electrode have been developed for years in chemical laboratories. The process used typical laboratory glasses and makeshift constructions for suspending the solid electrode above the liquid. This research presents a summary on the next step of development of the miniaturized system for complex analyses of liquid samples.

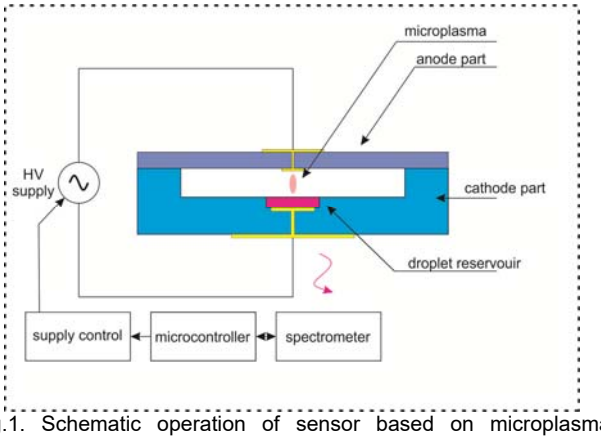



Fig.1. Schematic operation of sensor based on microplasma generator

In most of analytical systems the detection method consists of electrochemical manner, such as electrophoresis [1] or other like voltammetry [2]. Very promising source for detection in analytical chemistry is plasma as an excitation source of aqueous analytes. Research on this subject started in 90's [3, 4] when the Atmospheric Pressure Glow Discharge (APGD) was developed. In this type of discharge, plasma is generated between a liquid cathode and a solid anode, where the cathode is an analyte. Many works present good results with many different constructions as an evolution of the electrolyte-cathode discharge reactor [3, 4]. This excitation source has very promising Detection Limits (DLs) [5] comparable to the big laboratory setups. Such miniaturized microAPGD reactor could be made in Low Temperature Cofired Ceramic technology combined with thick-film technology with droplet analyte reservoir. Simplified schematic of the system is presented in Fig. 1.

The principle of operation of the chip is to excite the sample pipetted into the droplet reservoir during the atmospheric pressure discharge, and then to record the emitted spectrum.

First built prototypes were based on enclosure flowed liquid reservoirs [6], but their lifetime was not too long. – After about 1 hour of operation the anode got almost completely etched/sputtered. However, the study on the reliability of the microplasma generator has been continued. First efforts presented wide spectrum of experimented thick-film layers [7]. One of these focused on carbon-based layers [8] and those promising results required suitable technology for chip fabrication. In that case – low temperature bonding technology for the LTCC chip and the alumina substrate with carbon layer. In the literature some standard methods for joining the LTCC ceramics with other materials are presented:

Bonding of the LTCC with PDMS (polydimethylsiloxane) – reliable bonding thanks to the oxygen plasma surface activation of the LTCC and the PDMS surfaces [9]. The method is widely used technique for microsystems with optical detection.

a) Anodic bonding method - known as bonding method between a silicon and a glass which is also applicable for the LTCC and the silicon [10, 11]. The method of bonding ~~the~~ LTCC to silicon has been well-known topic for years as the LTCC materials were widely used as ~~the~~ materials for encapsulating the silicon structures.
b) Firing a ceramic substrate with an intermediate layers e.g. with glass. Bonding carried out at the temperature below 650˚C is a criteria for selecting the technological process.

One of the methods of improving the quality of ~~the~~ joining between successive layers is adding grains of precious metals such as platinum or gold [12]. The glazes can be fired in the co-firing process, i.e. together with green-state LTCC ceramics, or separately in the post-firing process, where the glaze is applied on the already fired

ceramics (LTCC, HTCC, $Al_2O_3$) or e.g. resistive fired layers. The $Al_2O_3$ ceramics was bonded with LTCC through the glaze layer. The glaze is the coating glass deposited on ceramic substrates. The addition of 1 wt. % Au or Pt particles to the enamel, due to the heterogeneous nuclei that create new crystallization centres, should increase the adhesion of $Al_2O_3$ to LTCC [12].

The issues concern making the joint resistant to thermal stresses, taking into account the appropriate time-temperature firing profile and the gas atmosphere present during the joining process. These limitations result from the usage of a graphite-glass composite [8] as the electrode material. Preparation of the ceramic surfaces has been performed by the plasma treatment. Materials treatment by plasma improves the adhesion, affects the hydrophobic properties and the wettability angle. During the modification process ions hit the surface of materials which eliminates the particles formed in the post-production process and micropollutants from the room. Besides they can also lead to changes in the chemical structure of the modified surface, which in many cases is justified [9].

**Technology**

The chip technology was based mainly on the LTCC and thick-film technologies, where the standard method of applying conductive and connecting layers was screen-printing. A simplified flow of the process of preparing the layers for joining is shown in Fig. 2. The left and right sides presents the technology for an anode and a cathode parts, respectively. GreenTape 951PX (DuPont) sheets with a thickness of 254 μm before firing were used for preparation the cathode part. In case of the anode, chips from LTCC (GreenTape 951PX) had also been manufactured from $Al_2O_3$ substrates as well (Rubalit® 708S, CeramTec). Cofired LTCC part presented in Fig. 3 (top and bottom side view) were used.

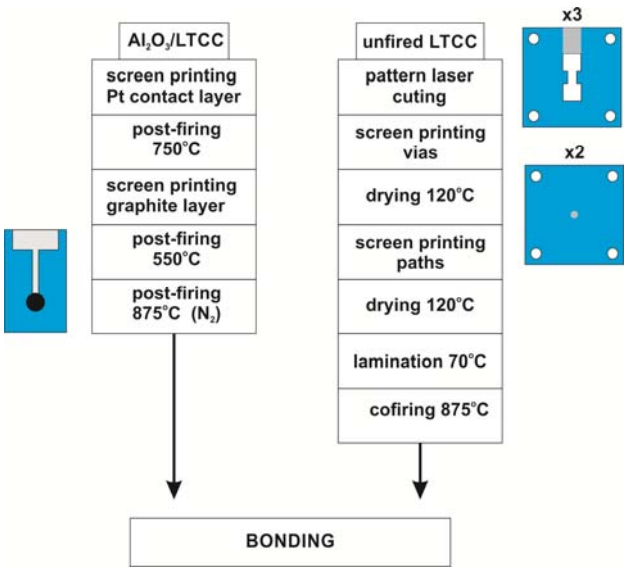



Fig.2. Technology of preparing structures for bonding tests

Table 1. Firing temperature of each glaze material

| Glaze type | Datasheet $T_{max}$ peak [°C] | Experimental $T_{max}$ peak [°C] | Time of max peak [min] |
|---|---|---|---|
| Heraeus SG683K | 600-650 | 550 | 5-10 |
| DuPont 9615 | 850 | 550 | 10 |
| DuPont QQ550 | 510-525 | 525 | 1-2 |

The firing temperature $T_{max}$ did not correspond to the firing temperature suggested by manufacturers. During the experiment it was decided to not exceed the firing temperature over 550 °C. In case of firing at a higher temperature, it had to be done under an inert atmosphere e.g. in nitrogen, which would make the process more complicated. However, firing in the air was problematic as the graphite oxidized at temperatures over 550 °C. On the other hand, the deterioration of the LTCC surface in the nitrogen atmosphere was also problematic. Thus, the LTCC anode were not used in experiments.

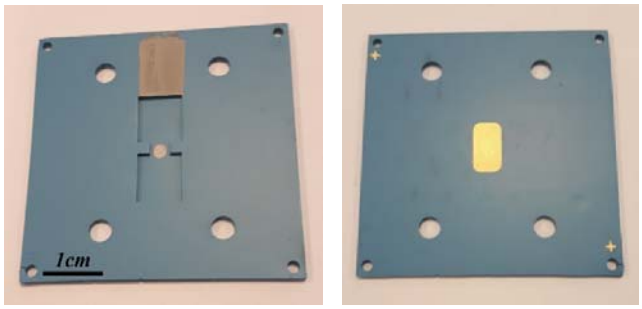
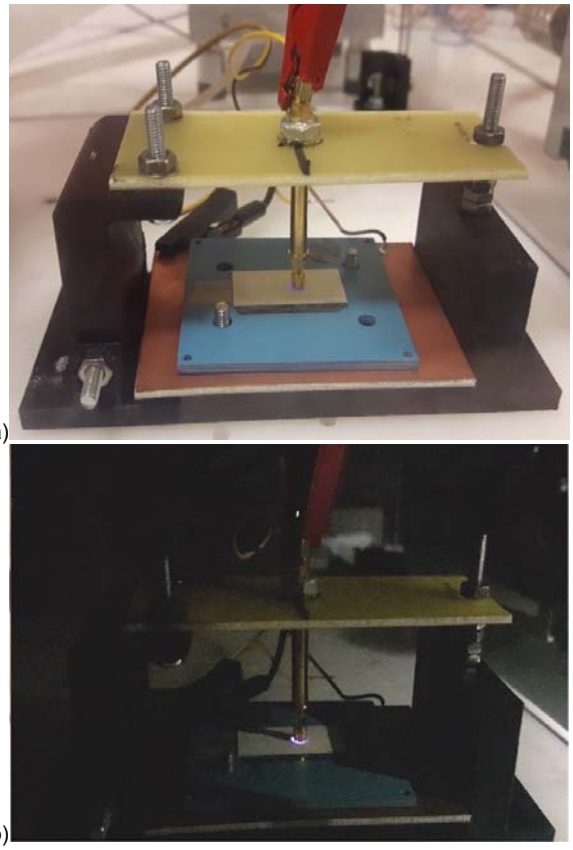



Fig.3. LTCC part with cofired metallizations: top side – bonded side (a) and bottom side (b).

In case of the plasma surface modification, the stand has been prepared for proper alignment of each part during the process. The stand before and during process is presented in Fig. 4.a and Fig. 4.b, respectively.



(a) (b)

Fig.4. Stand for plasma surface modification before operation (a) and during modification (b)

**Experimental details**

Heraeus (SG683K) and two DuPont's (9615 and DuPont QQ550) glaze pastes were used for the connections. The differences in the mechanical strength of the joints were

investigated for each of the glass. Effect of plasma modification on the joints was tested and the theoretical influence of noble metal additives such as platinum and gold was verified. Glass with addition of noble metals should increase the adhesion between the alumina ceramics and the LTCC thanks to creation of new crystallization points by heterogeneous metal nuclei.

In order to minimize the number of necessary experiments, the Taguchi method of experiment planning was applied. The Taguchi method began with defining the parameters that influenced performed research. Three two-tier factors were selected. Experiment with more repetitions of individual trials was planned. In case of carried out experiment, these factors were:

- no modifications / additions,
- doping with gold,
- doping with platinum,
- plasma modification.

Then, the levels of chosen parameters were determined, which were in fact the values of these parameters, such as gold doping at the level of 1%, or plasma modification taking place at a voltage of 10 kV AC. After defining the parameters, the orthogonal matrix was selected from the Taguchi method [13].

Table 2. Levels of Taguchi method

| Influence level of parameter | Level 1 | Level 2 | Level 3 |
|---|---|---|---|
| Au | 1 % | 0% | - |
| Pt | 1 % | 0% | - |
| Plasma AC | 10 kV | 5 kV | - |

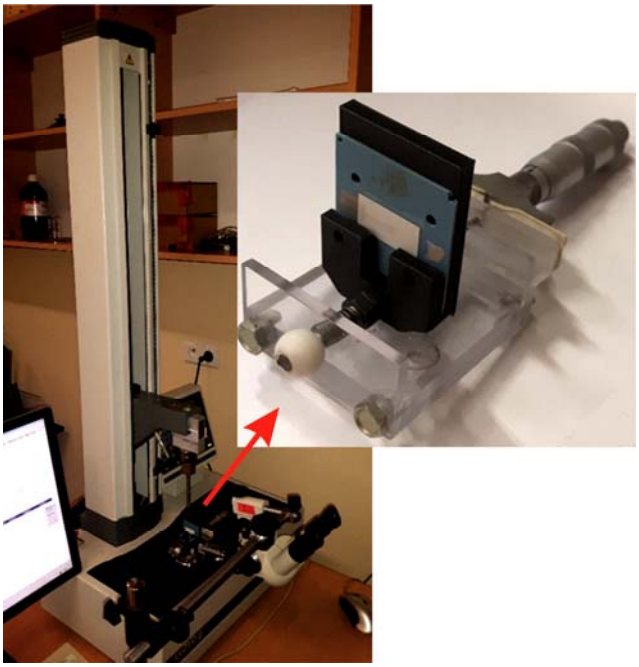


Fig.5. Machine testing the strength of the connection with the zoom of the sample fixing

For the influence of the addition noble metals and the plasma modification on the strength of the connection examination it was decided to choose signal to noise ratio (S/N). The tests were characterized by examining a force needed to break off the joint in the sample, so the higher the force value, the better the strength. Determining the S/N ratio allowed further targeting of research.
According to the literature [13], the adopted *S/N* ratio criterion remained to "the bigger, the better" was represented by formula (1).

$$\frac{S}{N} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y^2}_i\right) \tag{1}$$

where: *S/N* – signal to noise ratio, $y_i$ – measured force for each method of bonding, $n$ – number of measured samples for each measuring method.

Prepared samples were subjected to mechanical strength tests on the Lloyd Instruments LRX Testing Machine shown in Fig. 5.

Single-column testing machine allowed to test the shear force needed to break off bonded materials. The current force value during single uniaxial tension was recorded by ~~the~~ tester and presented as a function of time in Neyxgen software. The measurement was carried out using a breaking tooth that pulls the test piece vertically upwards until it breaks off. The number of tested samples (*n)* was set to 10.

**Results**

In Fig. 6. obtained results of mean forces for ~~the~~ joining methods are presented. No measurement values were obtained for the DuPont 9615 glaze as the glass did not crystallize during the firing of the layer. This was due to the reduction of ~~the~~ firing temperature to 550 ˚C, followed by ~~the~~ firing ~~of~~ the layers in the nitrogen atmosphere. As a result, powdered enamel layer was obtained between the joined materials. Results from the experiment calculated by the formula (1) are presented in Tab. 3.

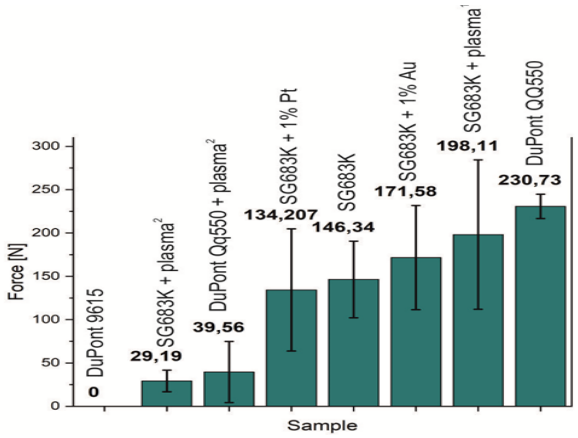



Fig.6. Average value of the forces obtained for individual methods of joining with their standard deviation ([1], [2] plasma modification of the surface for 5 and 10 minutes, respectively)

Table 3. Results of S/N values for each parameter

| Examined material | S/N [dB] |
|---|---|
| SG683K +~~z~~ 1% Pt | 55.72 |
| SG683K +~~z~~ 1% Au | **57.45** |
| SG683K | 55.85 |
| DuPont QQ550 | **59.32** |
| DuPont 9615 | -* |
| SG683K + plasma[1] | 56.35 |
| SG683K + plasma[2] | 42.48 |
| DuPont QQ550 + plasma[2] | 39.29 |

* - deterioration of glaze layer during firing

The tests were characterized by checking the shear force required to break off the alumina ceramics from LTCC module. If the force used for the sample breakage was bigger, the connection obtained between the materials was better. The best S/N value was obtained for the connection made with DuPont QQ550 glaze, which was also visible in Fig. 6 where the highest average force value and the smallest dispersion for this connection method is observed.

## Discussion

The results of experiments on bonding method using ~~the~~ intermediate glaze layers have been presented. The tests showed that the addition of precious metals can affect the strength of the joint. While the addition of platinum to the glaze did not significantly change the mechanical resistance, in case of gold the force needed to break the specimen was on average 30 N higher than in the case of the glaze alone. One-percent addition of gold to the glaze volume, as well as the plasma modification of $Al_2O_3$ ceramics under a variable voltage 10 kV AC, improved the adhesion between the substrates. DuPont 9615 paste did not set substrates after exposure to the temperature applied in the experiment. DuPont QQ550 paste showed the highest mechanical strength without any additives. Unexpectedly, the SG-683K glaze, as a typical sealing glass, did not give~~n~~ the best results for all configurations and exhibited very large spread of the force value.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