Design of LTCC-based Ceramic Structure for Chemical Microreactor

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Abstract. *The design of ceramic chemical microreactor for the production of hydrogen needed in portable polymer-electrolyte membrane (PEM) fuel cells is presented. The microreactor was developed for the steam reforming of liquid fuels with water into hydrogen. The complex three-dimensional ceramic structure of the microreactor includes evaporator(s), mixer(s), reformer and combustor. Low-temperature co-fired ceramic (LTCC) technology was used to fabricate the ceramic structures with buried cavities and channels, and thick-film technology was used to make electrical heaters, temperature sensors and pressure sensors. The final 3D ceramic structure consists of 45 LTCC tapes. The dimensions of the structure are 75 × 41 × 9 mm^3 and the weight is about 73 g.*

Keywords

Chemical microreactor, LTCC ceramic, 3D structure.

1. Introduction

Low-temperature co-fired ceramic (LTCC) technology was used for many years for interconnections technology in the electronics industry. The main advantage is its compatibility with thick-film technologies. Electronic devices and systems based on a combination of these two technologies are reliable and the characteristics are stable. In comparison with other technologies the LTCC and thick-film technologies enable a fast and easy fabrication of electronic devices and systems. Therefore, it could both reduce the cost of devices and shorten the development time [1-9].

LTCC technology is a three-dimensional ceramic technology for interconnection layers and electronic components. Thick-film technology is used for the lateral and vertical electrical interconnections, and the embedded and surface passive electronic components (resistors, thermistors, inductors, capacitors). LTCC materials in the green state (called green tapes, before sintering) are soft, flexible, and easily handled and mechanically shaped. A large number of layers can be laminated to form high-density interconnections and three-dimensional structures. The fabrication process includes several steps, which are named LTCC technology. The separate layers are the mechanical shaping of mesosize features (0.1-15 mm), and then the thick-film layers are the screen-printing. All the layers are then stacked and laminated together with hot pressing. This laminate is sintered in a one-step process (cofiring) at relative low temperatures (850–900°C) to form a rigid monolithic ceramic multilayer circuit (module). With the non-conventional application of LTCC technology different three-dimensional (3D) structures, such as cantilevers, bridges, diaphragms, buried channels and cavities can be realized [1-9].

Microsystems are one of the fastest-growing technologies, and most microsystems are made by the micromachining of silicon. On the other hand, complex microsystems combine different materials (silicon, ceramic, metal, polymer, etc.) and technologies (semiconductor, thin and thick film, etc.). In some demanding applications thick-film technologies and ceramic materials are a very useful alternative. In comparison with silicon microsystems they are larger, more robust and operate over a wider operating-temperature range [1-12].

A chemical reactor is typical device or system where the chemical stability, the thermal stability and the mechanical stability are important factors. Microreactors (the dimensions are in the millimeter and micrometer ranges) in comparison with large conventional reactors have a higher surface-to-volume ratio, and higher rates of reaction, mass and heat transfer [7-9]. Therefore, the combination of LTCC (low-temperature co-fired ceramic) and thick-film technologies is suitable for the fabrication of ceramic chemical microreactors.

Chemical microreactors are used in fuel-cell technology for fuel processors for the conversion of liquid fuels into the (pure) hydrogen used for portable polymer-electrolyte membrane (PEM) fuel cells. They consist basically of fuel and water evaporators, fuel reformers, gas clean-up units (to remove the excess carbon monoxide) and heat exchangers (recuperators). A schematic outline of the fuel processor is shown in Fig. 1. The first part consists of fuel and water inlets, fuel and water evaporators, the mixer, and the reformer. The second part consists of air and water vapour inlets, the desulphurizer, the WGS (the water gas shift rector) and the PrOx (the partial oxidation reactor) for removing the carbon monoxide from the gas mixture by reactions with water and oxygen, respectively [13]. The third part is a heating system, which consists of two inlets for fuel and air, the evaporator of the fuel, the air/fuel mixer, and the combustor. LTCC technology provides mechanical and chemical stability, while the thermal stability of the system is guaranteed by the proper design.

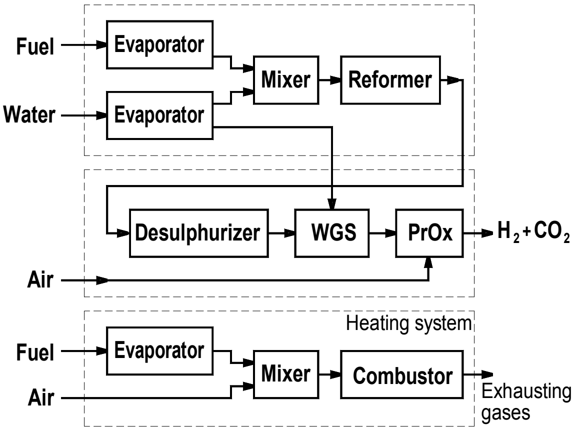


Fig. 1. Schematic outline of the complete fuel processor [13] (WGS – water gas shift; PrOx – partial oxidation).

This article presents the design and fabrication process of a relatively very complex LTCC structure for a chemical reactor. The LTCC structure integrates the first and the third part of the complete fuel processor presented in Fig. 1. The main aim of this article is to present the technological solution for making the complex 3D ceramic structure, and not an evaluation of the functional operations of the reactor.

2. Architecture of the Microreactor

The architecture of the microreactor for the production of hydrogen for portable polymer-electrolyte membrane (PEM) fuel cells is schematically presented in Fig. 2. The microreactor was realized as an EMRC system (abbreviation EMRC means evaporator, mixer, reformer and combustor).

The top view of the LTCC-based microreactor is presented in Fig. 3 where six inlets and outlets, electric contacts, functional area and vertical exhausting channels are presented. The liquid reagents of the microreactor are fuel and water. The liquid fuel – methanol – enters the system through Inlet 1 and the liquid water enters through Inlet 4. The two reactants then evaporate and mix together. The vapor then flows through the channels of the reformer where the catalyzed chemical reaction (1) takes place.

$$CH_3OH + H_2O \rightarrow CO_2 + 3\ H_2. \quad (1)$$

The resulting gas comes out through Outlet 3. There is also a service Inlet/Outlet 5, which is used as the middle control point and for the deposition of the catalyst during the fabrication process.

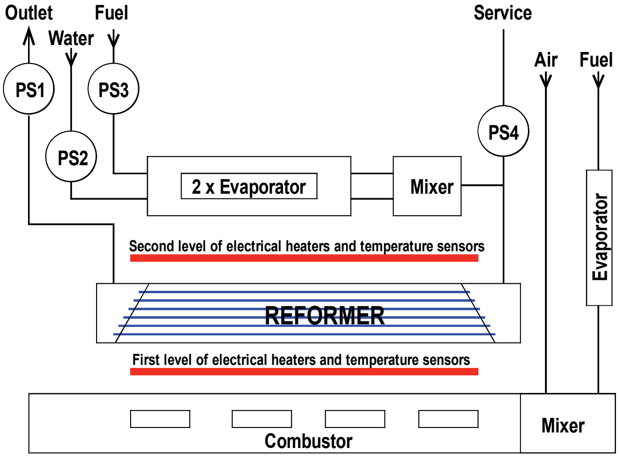


Fig. 2. Schematic architecture of the microreactor

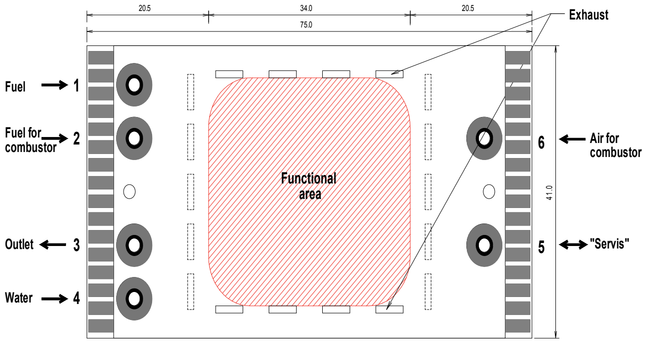


Fig. 3. Schematic top view of the LTCC-based microreactor

Four heaters for the start-up process and six temperature sensors for the temperature control are located in the system at two levels. The system also includes four pressure sensors (PS) for control fluidic, which are presented in Fig. 2.

Another important part of the system is the combustor, which supplies the thermal energy for the chemical microreactor. The distribution of the temperature through the 3D structure is managed with the position of eight micro-burners and with the integration of numerous thermally isolating cavities in the ceramic structure. Thermal management enables the required vertical temperature distribution through the system and the relatively homogenous temperatures in the functional area (Fig. 3). At the same time the temperature in the periphery of the system is relatively low.

3. Components of the Microreactor

In the first development phase the components of the EMRC system were designed and fabricated as separate (stand-alone) components. In the pre-engineering process the required functionality and characteristics were defined for each component (the evaporator, the mixer, the reformer and the combustor).

3.1 Evaporation and Mixing Systems

The requirements for the evaporator are a methanol flow rate of 50 ml/h, an equivalent water flow rate and operating temperatures over 100°C. The key function of the mixer is an effective mixing of the reactants with no significant reduction of the flow rates and temperatures of the reactants.

The liquid fuel and liquid water enters the system through two channels formed as a meander to extend its length. The evaporator for the fuel and the evaporator for the water are located in the functional area of the system. In both evaporators the 3D mesh of the channels was designed to prevent the pulsing of liquids. A similar structure is used for the mixing of the reactants. This enables a good mixing of the vapors.

3.2 Reformer

In the reformer the catalyzed chemical reactions at required flow rates and at temperatures around 300°C are necessary. The reformer consists of channels, which are coated with the catalyst. The LTCC structure of the reformer consists of 108 channels at 6 levels with a total length of 3.5 m. The dimensions of the rectangular cross-sections are 500 × 200 µm. The channels are located in the functional area of the system and are connected in parallel and series. The channels are linked with the distribution chamber and the inlet on one side and with the collection chamber and the outlet on the other side.

3.3 Combustor

The main purpose of the combustor is to supply the thermal energy for the entire system. The combustor consists of two inlets for fuel and air, the evaporator of the fuel, the air/fuel mixer, eight micro-burners, and the exhaust system. The fuel evaporates in the channel within the functional area of the system and mixes with the air through several T-type mixers. The mix of air and fuel is distributed as symmetrically as possible to the eight symmetrically distributed micro-burners. The micro-burner is designed as a cavity with dimensions of 11.5 × 4.5 × 0.6 mm. The catalyst, which incites and supports the burning process, is deposited on the bottom of the cavity. The mixture of air and fuel enters from one side of the micro-burner. At the other side the exhausting gases go through the exhaust vertical channels.

3.4 Pressure Sensors

For the pressure monitoring four ceramic (piezoresistive) pressure sensors were integrated into the ceramic structure (Fig. 4). All four pressure sensors were designed to measure the relative pressure in the range from 0 to 100 kPa. A thick-film piezoresistive pressure sensor is based on the piezoresistive properties of the thick-film resistors that are screen-printed and fired onto the deformable diaphragm. The diameter of the diaphragm is 7.0 mm, and the thickness of the diaphragm is 150 µm. The piezoresistive sensor has four thick-film resistors with dimensions of 1.0 × 1.0 mm. Each of these resistors acts as a strain gauge and is electrically connected in a Wheatstone-bridge configuration [14], [15]. The output voltage versus the applied pressure is shown in Fig. 5.

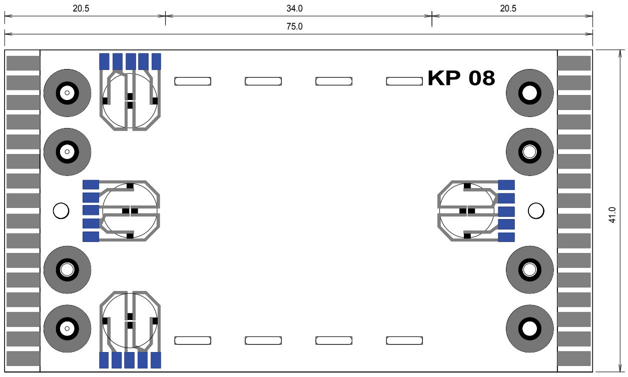


Fig. 4. Four ceramic pressure sensors are additionally integrated on the top of the LTCC structure.

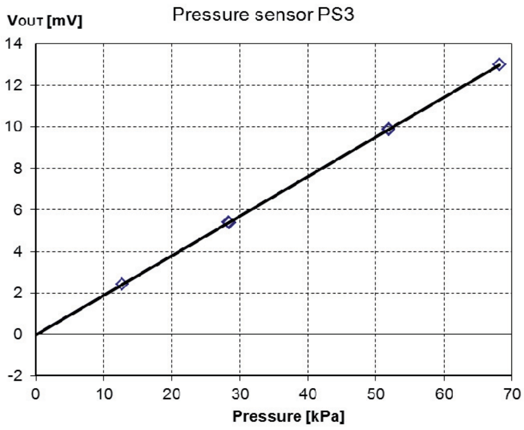


Fig. 5. The output voltage versus applied pressure of the pressure sensor PS3 (Fig. 2) as a part of the entire LTCC structure. The excitation voltage is 5 V.

The output voltage at a pressure of 70 kPa and at an excitation bridge voltage of 5 V is 13 mV, and the pressure sensitivity from the measured data is about 38 µV/V/kPa. The temperature coefficient of the sensitivity is 350×10^{-6}/K. The bridge resistance is about 8 kOhms and the temperature coefficient of resistivity is better than 50×10^{-6}/K.

4. Ceramic Microsystem

Each stand-alone component was developed and tested, and then optimized to fulfill the requirements for the integrated EMRC system. The final 3D ceramic structure is presented in Fig. 6.

The LTCC structure for the microreactor was made from 45 layers of LTCC tapes. The dimensions of the structure are 75 × 41 × 9 mm^3 and the weight is about 73 g. In the central part of this ceramic structure is a functional area (presented in Fig. 3), which includes two inlet channels (for the fuel and the water), two evaporation chambers, a mixing chamber, a reformer consisting of 3.5 m of channels coated with a catalyst, and a combustor (an air/fuel mixer, 8 micro-burners, and an exhaust system). In the structure, 4 platinum-based electrical heaters and 6 platinum-based temperature sensors are integrated. Outside of the functional area 4 ceramic pressure sensors, 6 inlet/outlet tubes, and the electrical contacts for the sensors and heaters are located.

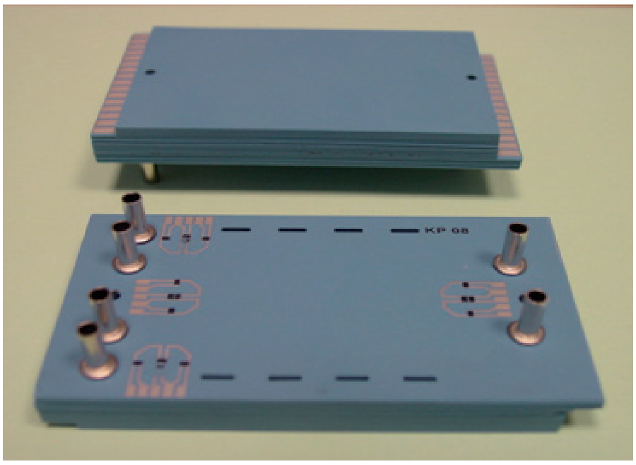


Fig. 6. The final 3D LTCC structure of microreactor (dimensions of the LTCC structure: 75 × 41 × 9 mm^3).

In Fig. 7 three cross-sections of the LTCC structure is presented. The cross-section A shows three cavities of pressure sensors on the top, followed by two evaporating chambers, distribution channels for the reformer, and two channels for air and fuel on the bottom of the structure. The cross-section B shows the mixing chamber on the top followed by six levels of channels for the reformer. In the middle of the bottom of the cross-section the mixing channels for air and fuel are presented. Symmetrically, on the left- and right-hand sides the micro-burners and exhaust vertical channels are shown. The cross-section C shows the mixing chamber on the top followed by vertical cannels connecting the above-mentioned horizontal channels. On the bottom of the structure the two channels for air and fuel are shown.

5. Conclusions

A design and fabrication of LTCC-based microreactor for fuel processing was described. The microreactor was developed for the steam reforming of liquid fuels with water into hydrogen, which will be used for low-temperature fuel cells.

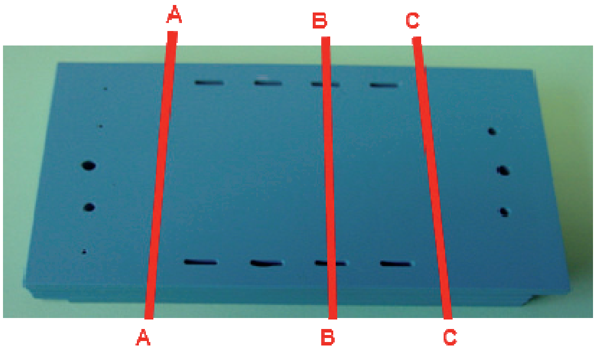
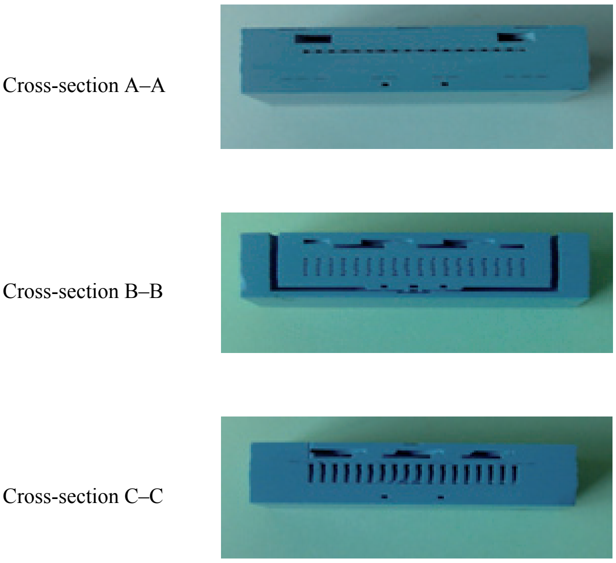


Fig. 7. Top view of the LTCC structure.


Cross-section A–A

Cross-section B–B

Cross-section C–C

Fig. 8. Cross-sections over lines A–A, B–B and C–C in Fig. 7.

The microreactor was designed and fabricated using LTCC (low-temperature cofired ceramics) technology. The 3D LTCC structure with buried cavities and channels, including two evaporators (fuel and water), the mixing chamber, the reformer and the combustor was realized. Ceramic pressure sensors, platinum-based heaters and platinum-based temperature sensors were integrated into the structure.

The fabrication of three-dimensional ceramic (LTCC) structure confirms that the combination of LTCC and thick-film technology is suitable for the fabrication of chemical microreactors. Result of the experimental work shows that relative complex three-dimensional ceramic structure can be designed and fabricated with LTCC technology.

The ceramic microreactors are larger in comparison with silicon based microreactor. Therefore they are suitable for the use in fuel-cell technology for the electrical power in the range between 50 and 300 W. Additional important parameter in the design issue is the different thermal properties of the materials (ceramic, LTCC, silicon, etc.) [12], [16].

Acknowledgements

The authors wish to thank Stanko Hocevar (National Institute of Chemistry, Ljubljana, Slovenia) and Iztok Stegel (Ministry of Defense, Republic of Slovenia) for outstanding and significant contribution in functional and conceptual design of fuel processors for the conversion of liquid fuels into the hydrogen.

The authors also wish to thank Mr. Mitja Jerlah (IN.Medica) for printing, laminating and firing the LTCC structures and Mr. Primoz Fajdiga (Jozef Stefan Institute) for functional testing the separate (stand-alone) components of chemical microreactor.

The financial support of the Ministry of Defense of the Republic of Slovenia through the project RR-07-018 is gratefully acknowledged. The part of the research work was also included in the Centre of Excellence NAMASTE and Development Centre IN.Medica. Both centers are financially supported by the European Union (European Regional Development Fund), and the two ministries of the Republic of Slovenia (the Ministry of Higher Education, Science and Technology, and the Ministry of the Economy).

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