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Functionalization of additively manufactured ceramic components via thick-film technologies

Highly integrated functional components for electronics, analytics, sensors and process technology

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Content

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1. Introduction

Additive manufacturing processes open up entirely new possibilities for a wide range of different materials such as plastics, metals or ceramics with regard to geometrically complex components. For certain applications, there is also a high level of interest in providing these components with additional functions. These approaches are often associated with electrical, sensor or actuator functions. This results in the need to "functionalize" the additively manufactured components with corresponding layer systems, for which the approach of multi-material printing is pursued in various scientific studies. This means that different processing heads are used simultaneously for the production of these multi-material components. These are filled with different materials. In the case of ceramics, for example, this makes it possible to print both the unfired ceramic slurry and the electrically functional layers at the same time. After the green bodies are printed, the entire body is burned in a joint thermal process and the desired multifunctional component is created.

In this paper, an alternative approach based on ceramic materials is presented, in which the multi-functional components are realized in two separate technological steps. In a first step, the ceramic component is manufactured, including sintering. In a second technological step, this ceramic component is functionalized. For Al_2O_3 as well as other ceramics, the thick-film technology established in electronics and microsystem technology is a good solution. This technology can be used to print and fuse electrical conductors, resistors, heating elements or sensors onto the ceramic substrates. The electrical connection contact is realized by proven methods of the packaging technology of electronics. The advantage of this approach is that the materials required for functionalization are available on an industrial scale. Extensive technological know-how with regard to both processing and further processing is also available. Thus, applicational implementations are possible in a timely manner.

The white paper provides a simplified overview of the basics of thick-film technology and its adaptation to additively manufactured ceramic components based on aluminum oxide (Al_2O_3).

2. Thick-film technology in electronics and microsystems technology

In electronics and microsystems technology, defined electrical functions are realized by electrical components that are arranged in a circuit. It is necessary to mount these components on wiring supports and connect them electrically. The wiring carrier is a mechanical carrier that simultaneously carries the required conductor tracks, enables contacting of the components and is integrated into a higher-level system. Due to economic conditions in the field of low-cost and consumer electronics, wiring carriers based on organic materials are mainly used for these applications. These are generally known as printed circuit boards.

In addition to this printed circuit board technology, ceramic materials can also be used for the construction of such wiring carriers in the high-performance sector or for applications under harsh environmental conditions. These offer individual and material advantages:

- Increased thermal conductivity combined with excellent electrical insulation properties, even at higher operating temperatures
- Thermal expansion coefficient adapted to active semiconductor devices
- Higher process temperatures
- Possibility of mounting houseless components

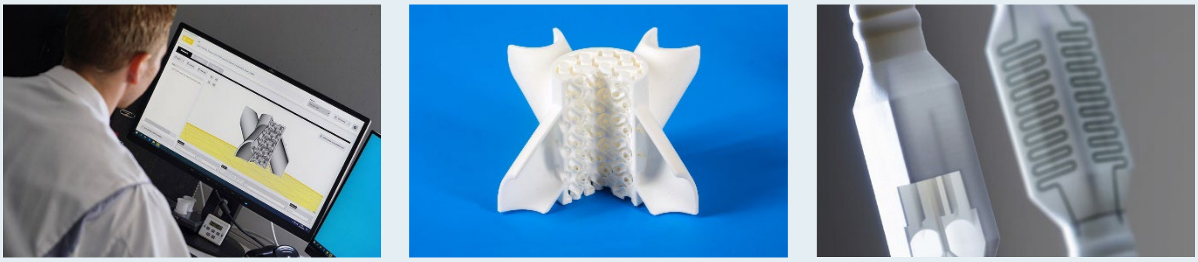

Figure 1: Print job preparation of a three-chamber fluid mixer (left), 3D-printed three-chamber fluid mixer with different wall thicknesses and hidden channels (center), additively manufactured fluid heater with printed conductors (right).

In principle, there are various ways of producing conductive tracks on ceramic substrates in order to use them as ceramic wiring carriers. One of these possibilities is thick-film technology. It is therefore also suitable for functionalizing additively manufactured ceramic components – e.g., adding further properties, such as heating or sensor elements.

3. Principles of thick-film technology

If we look at the possibilities of using ceramic materials for the realization of wiring carriers, it becomes clear that there are also different technological paths in this case. Each of them has specific advantages and disadvantages for individual requirements and is selected according to the target application. The requirements differ fundamentally, for example, whether a power module for power electronics or a module for high-frequency applications is to be developed. In DCB/AMB technology, flat copper tapes are bonded to the ceramic substrates either by sintering processes (DCB) or on the basis of special solders via soldering processes (AMB). The aim is to produce conductor tracks with a very high conductor cross-section. The technologies are used in the construction of power modules in power electronics. Diametrically different requirements exist for the conductor geometries in high-frequency technology. Here, a finely resolved conductor pattern with thin layer thicknesses is required. These are produced using various thin-film processes, such as vapor deposition or sputtering. Technologically, thick-film technology is positioned between these two variants. It is based on pasty materials – the so-called thick-film pastes. These pastes are printed in a structured manner onto ceramic substrates using suitable printing techniques and then sintered together in defined processes at temperatures of approx. 850 °C. The pastes are then applied to the ceramic substrates. Thick-film technology can thus be used to produce a ceramic substrate with a conductor pattern of any complexity.

4. Thick-film pastes

The thick-film pastes, which have different electrical properties such as conductivity or resistance, provide a distinctive "construction kit" that can be used to represent different functionalities. The individual pastes are described below. In principle, thick-film pastes always consist of four components: functional materials, glasses, organic binders and solvents. The individual components determine the electrical and mechanical properties of the final layer and the processing parameters of the paste during printing.

The solvents and organic binders form the printing substance and determine the printing behavior. They are removed during drying and sintering. The inorganic binders serve to ensure the adhesion of the particles of the active phase to each other and to the substrate.

The functional material determines the electrical property of the paste. A distinction can be made between conductive, insulating and resistive pastes. The construction of a thick-film circuit from several pastes – a so-called paste system – requires that the pastes can be processed with the same firing profile, for example, and that they are chemically compatible with each other. Commercial paste systems consist of conductive, insulating and resistive pastes. There are also pastes for special applications, e.g. sensor pastes or pastes for special substrates (steel, aluminum, glass).

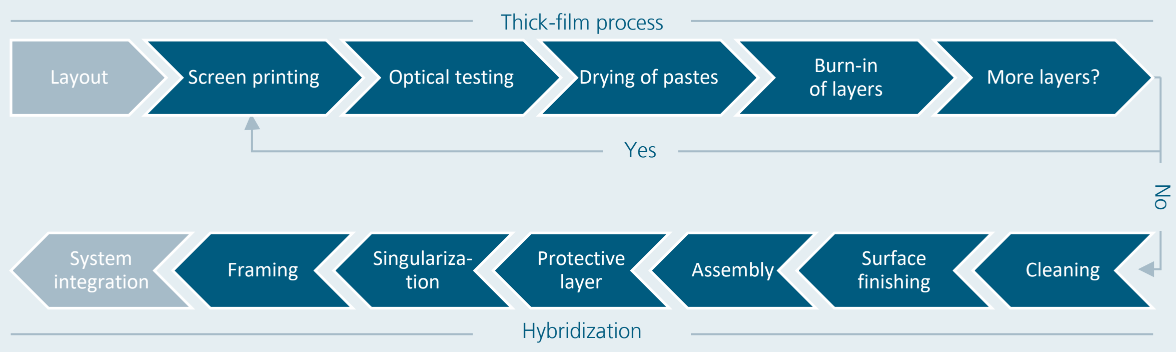

Figure 2: Process diagram thick-film technology.

In addition to the electrical properties of the burned pastes and their compatibility, the flow behavior (rheology) of the pastes to be printed must also meet the special requirements of screen printing. On the one hand, the paste pressed through the individual meshes during the printing process must bond to form a cohesive structure, and on the other hand, this structure should not flow further apart. This good flowability over a short period of time is achieved by the structural viscosity and thixotropy of the paste, which can be specifically influenced by the selection of organic binders and solvents. Thixotropy is the reversible decrease in viscosity under constant shear stress.

Figure 3: Thick-film paste for screen printing on ceramic substrates.

Conductive pastes

Pastes with precious metals, such as gold or silver, as the main component are mainly used for the production of conductive structures. The electrical properties can also be specifically influenced by the addition of palladium or platinum. Precious metal-free conductive pastes made of copper are an alternative. To avoid oxidation during firing, these pastes must be burned under inert gas (usually high-purity nitrogen). However, the advantage of saving precious metals is largely offset by the higher cost of producing the copper powder and the necessary use of an inert gas.

The burned conductive structures must meet the following requirements:

- Sufficient adhesive strength
- Good electrical conductivity (RF = 1,5–50 mΩ/qm)
- Solderability and bondability (if required)
- Low tendency to diffusion and migration
- Corrosion resistance

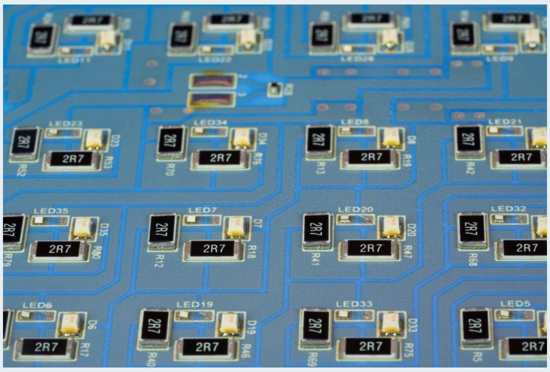

Figure 4: Ceramic thick-film substrate assembled with electrical components (assembly techniques, soldering, bonding and wire bonding).

Resistance pastes

In resistor pastes, mainly ruthenium oxide (RuO_2) and bismuth ruthenate ($Bi_2Ru_2O_7$) are used as functional materials. This allows for good electrical properties to be achieved (temperature coefficient, long-term stability, noise) and a resistance in the range of 10 Ω/square to 10 MΩ/square to be covered.

The reproducible production of thick-film resistors with defined properties requires knowledge of all influences and exact adherence to the specified processing. Most resistor pastes may only be burned once. Therefore, when using several resistor pastes with different surface resistances, they are printed one after the other, dried and then sintered as one.

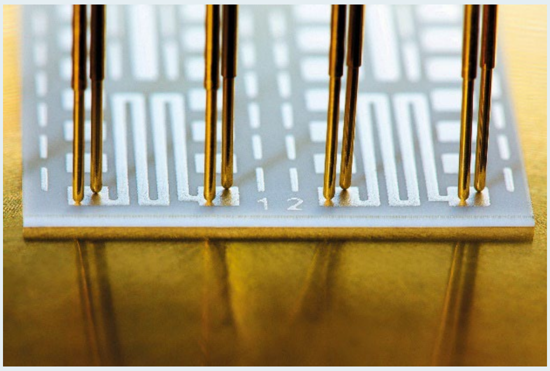

Figure 5: R(T) measurement on a resistive paste.

Dielectric insulation pastes

The main components of these pastes are special glass and ceramic frits which, in addition to the respective desired dielectric constant, also have the highest possible insulation resistance. They can be divided into three groups:

- Insulation pastes with low dielectric constant for multilayer assembly
- Dielectric pastes with high dielectric constant for the production of printed capacitors
- Low-sintering masking pastes for surface protection and as solder resist

Insulation pastes with a low dielectric constant are used for conductor crossings (cross-over technology) and for insulating several conductive layers (multilayers). To minimize the unwanted capacitive coupling of the insulating conductor structures, the functional material is optimized for a minimum dielectric constant (7 to 9). The insulation layers are printed at least twice, as multiple printing closes any pores and improves the density of the layer.

Dielectric pastes are used to manufacture printed capacitors. In order to keep the required area for such capacitors small, a higher dielectric constant (up to about 2000) is required here. However, the capacity of such printed capacitors varies considerably. Since no satisfactory balancing technique is known, only limited circuit tasks can be solved with such roughly tolerated capacities. Therefore, chip capacitors are usually used in hybrid circuits.

Masking pastes are used to protect printed resistors from environmental influences and improve their long-term stability and reliability. They consist of low-melting glasses and can therefore be sintered already at 500 °C. At these temperatures, the previously burned-in resistors are only slightly affected. When printing masking pastes, only the contact surfaces are kept free. The masking paste thus acts as a solder stop.

5. Screen printing of thick-film pastes and heat treatment

For the structured deposition of thick-film pastes, there are various printing processes, such as stamp printing, stencil printing or aerosol printing. However, screen printing is the most commonly used process. This is a print form-based process. It means that the structure to be transferred is mapped as a kind of "negative" in the printing form. As a consequence, a separate printing screen is required for each functional layer to be printed. Screen printing plates consist of a stable metal frame in which fine-mesh screen cloths are glued. These screen cloths are coated with photopolymer, which is exposed and developed. During this process, the areas to be printed are exposed in the screen structure.

Figure 6: Screen printing form.

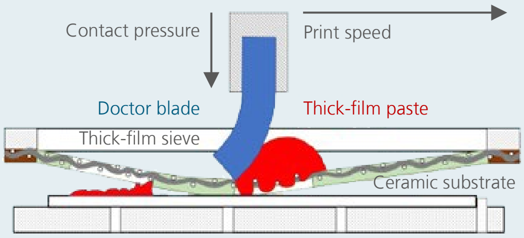

Figure 7: Principle of screen printing with thick-film pastes.

During the printing process, the printing screen together with the paste is positioned above the substrate at a defined distance. After the start of the printing process, the doctor blade is lowered and moved over the printing screen at a defined speed. In this process, the printing paste on the stencil carrier is pressed through the open meshes of the screen cloth onto the substrate. Screen printing is possible on flat substrates as well as on cylindrical surfaces of pipes, for example.

Figure 8: Circular screen printing for functionalization of tubular structures for heaters or flow sensors.

The printing process is followed by heat treatment. First, the printed layers are dried. This is followed by sintering at 850 °C.

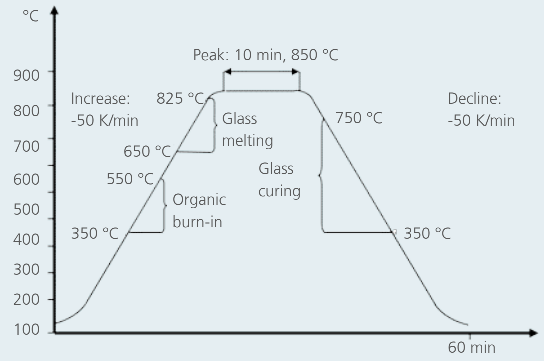

Figure 9: Example of a firing profile at 850 °C.

Figure 10: High-temperature packaging technology for reliable contacting of ceramic heating elements.

6. Assembly

The assembly of further components and sensors usually takes place on the conductor tracks. The electrical contacting of the entire component can then also take place at these contact points. Typical processes in packaging technology are:

- Soldering with soft solders and soldering with hard solders at higher operating temperatures
- Thermosonic wire bonding with gold wires and ultrasonic bonding with aluminum or copper wires
- Sintered assembly of power semiconductors based on nano-silver sintering
- Use of electrically conductive or electrically insulating adhesives

Commercial thick-film pastes are designed for these processes, but the operating temperature of the assembled components is limited as a result. Typical operating temperatures in the field of electronics are below 200 °C. Therefore, common material systems are only designed for this temperature range. However, special material solutions have already been realized that can withstand temperatures of up to 600 °C.

7. Application examples

As described above, the functionalities of thick-film technology can be combined with those of additive manufacturing of ceramic components to realize highly complex functional components. Important functionalities can include, for example, the application of conductive materials to these functional components.

These can be used, among other things, to realize electrical connections or additional components on these components. They can also be used to contact other thick-film functional layers. These can be both heaters and temperature sensors applied by means of thick-film technology.

One possible application for such functionalized ceramic elements is in the field of active heating and cooling. Here, both the use of ceramic materials and functionalization can bring their benefits to the fore. The basic functionalities always consist of rapid heating up to application temperatures of 350 °C and rapid cooling of the temperature down to room temperature. The combination ensures fast temperature cycles.

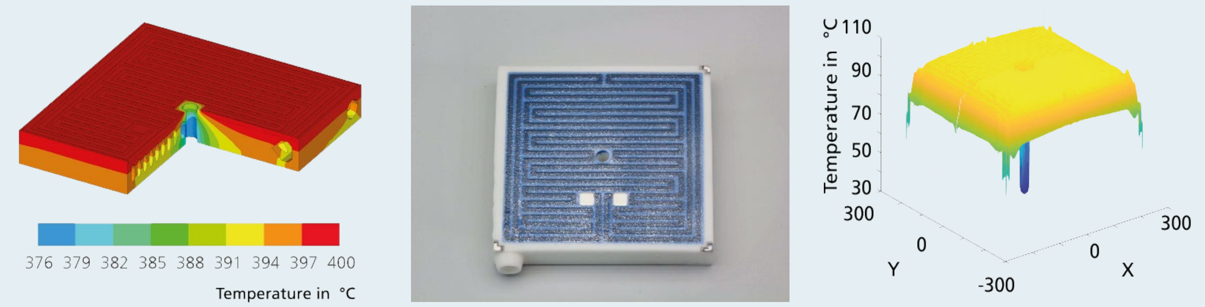

Figure 11: Design of the highly dynamic ceramic matrix heater using finite element modeling (left), additively manufactured ceramic base body with thick-film functionalization (center), temperature field over a heater pixel (right).

The physical structure consists of additively manufactured ceramic structural elements made of alumina (Al_2O_3) with integrated cooling channels, which enable effective cooling of the modules. The basic bodies can be manufactured as plates or as tubular elements using the CerAM VPP (Vat Photo-Polymerization) process. After the firing process, the components are functionalized by means of screen printing. Since the operating temperature of the components is up to 600 °C, the use of platinum-based thick-film pastes is required. Due to this temperature, the heating elements had to be contacted using a modified welding process – double gap welding. Platinum was also used for the connecting wires.

In addition, a wide variety of other applications have been successfully demonstrated to date. Among other things, geometrically adapted sensor housings for applications under harsh environmental conditions have been demonstrated. Another field of application is actively cooled components for power electronics. In all the cases mentioned, geometrically adapted ceramic AM assemblies are always combined with functionalization using thick-film technology.

8. Conclusions

Harsh environmental conditions with high thermal, chemical and/or mechanical loads are a particular challenge in almost all areas of industry. Here, for example, highly integrated sensor systems with metallic or polymer components reach their limits and make real time-based data acquisition difficult. Functionalized 3D ceramic components, on the other hand, meet the requirements in terms of robustness, miniaturization and reliability. Through the targeted selection of materials and the combination of additive manufacturing and thick-film technology, they combine advantages, such as chemical and thermal resistance, high hardness, low density or certain biological properties, with complex geometries, such as different wall thicknesses or concealed heating and cooling channels.

9. Transferability to other material groups

On the basis of the information presented in this article, the question inevitably arises as to whether the described approach of two-stage functionalization can also be applied to other material groups, such as glasses, polymers or metals. The key to answering this question lies in the thick-film pastes used, and the answer is: "In principle, YES". The general prerequisite, however, is the material compatibility of the "base bodies" with those of the functional layer. However, since there are many material variations in the material groups mentioned, this point cannot be answered generally for all material combinations. Some examples are shown below.

Plastics: Low-temperature pastes can be used for this purpose. These pastes are modified in such a way that the glass as an adhesion promoter to the substrate is replaced by a polymer matrix. During processing, the structured layer application of these pastes is also carried out by the printing techniques mentioned. However, these pastes are not burned at 850 °C, but cured at significantly lower temperatures. The adhesive strength between the layer and the substrate is achieved by the adhesive effect of the polymer component introduced into the paste. Compatibility of the pastes with the plastics to be coated is a basic prerequisite for this functionalization and must be tested in each case. Paste systems of this type are technically available

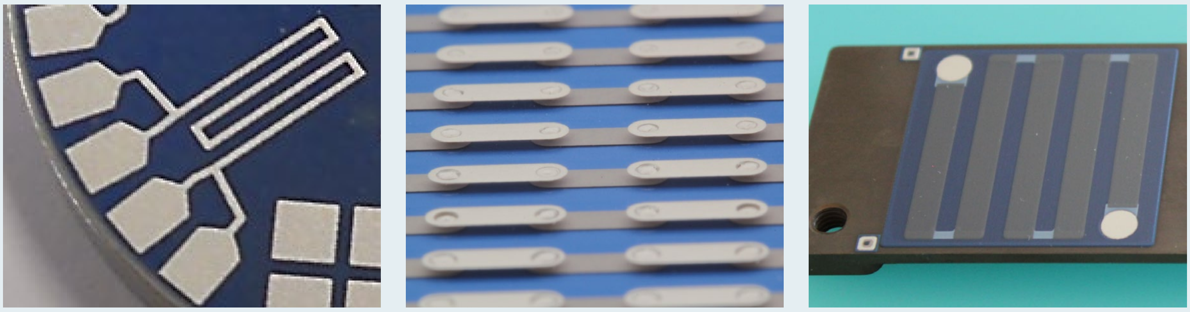

Figure 12: Test structure made of polymer paste in multilayer printing (left). Test structures on glass substrate. On the top and bottom side there are metal coatings which are connected by vias (center). Thick-film test structures on insulated steel substrate (firing at 850 °C, right).

for a number of combinations and are mostly suitable for assembly.

Glasses: Either polymer pastes or thick-film pastes with reduced burn-in temperatures are suitable for functionalizing glasses. These pastes are modified in such a way that the usual glasses, which are processed at 850 °C, are replaced by glasses that can be burned in at reduced temperatures, e.g. 500 °C. The pastes are also commercially available for these material systems. However, the range is limited to insulation and metallization pastes.

Metals: An important difference between the ceramics described and, for example, steel is their electrical conductivity. In order to produce electrical functional layers, such as heaters or temperature sensors, on the steel, it is necessary to insulate the steel in a first technological step, i.e. to apply an insulating layer. In the following step, conductors, heaters or sensors can be printed on. Here, too, there are paste systems that can be used for selected steels.

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Fraunhofer IKTS in profile

For more than 30 years, Fraunhofer IKTS has been demonstrating the potential of ceramic materials in a steadily growing range of applications. It is our drive to develop complete system solutions and services, but also to solve specific challenges within the processes of our partners from industry and science. Our expertise in the characterization and analysis of materials, components and systems along their life cycle provides us with a unique data pool to carry out new developments more efficiently and faster.

Fraunhofer IKTS has a staff of more than 800 at its three main sites in Dresden and Hermsdorf as well as numerous external locations. This makes it the largest ceramics research institute in Europe. Researchers have access to 40,000 m^2 of floor space with excellently equipped laboratories and pilot plants. These include both pilot lines suitable for industrial use and application centers in which new developments can be tested under conditions that are close to industrial practice.

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