A Ceramic Tubular Probe for Online Substance Concentration Measurement, Manufactured by Ceramic Injection Molding

Dr.-Ing. Matthias Hartmann* and Prof. Dr. rer. nat Bertram Schmidt
Otto-von-Guericke University of Magdeburg
Institute of Micro and Sensor Systems (IMOS)
P.O. Box 4120
39016 Magdeburg, Germany
Phone: +49 391 67 52857 Fax: +49 391 67 12609
E-mail: matthias.hartmann@ovgu.de
www.ovgu.de/imos/mst/doc/cms/
*corresponding author

Abstract

The current research presents recent respective to the work development of a ceramic tubular probe for online substance concentration measurements. The aim was to develop a robust and acid-resistant sensor device, which can be easily included in existing procedural pipeline systems. To archive those goals a lot of factors had to be checked. For the substance concentration measurements a capacitive sensor effect was chosen. With this method even low substance concentrations down to one-tenth of a per cent can be indentified.
For the package material zirconium oxide (tetragonal zirconia polycrystal – TZP) was used. Zirconium oxide is a technical ceramic which is wear-resistant, acid-resistant, has a low thermal conductivity, is electrically isolating and can be uses in a ceramic injection molding (CIM) process. In the phase of the sensor design process multiple geometries for the sensor effect and integration space for the evaluation electronics had to be considered. A standardized DN 10 DIN 32676 flanged joint was also added for an unproblematic connection to the pipelines. All these needed geometries had to be integrated into one ceramic element. As a result of these requirements a 3D CAD model of the sensor element was designed. The CAD-file has shown that there was only the CIM technology left to comprehend developed sensor geometry. CIM is a low cost process for large-scale production which is distinguished by high size accuracy. In the CIM process the material shrinkage, this is caused by the needed debindering and sintering steps, had to be considered.
The developed ceramic tubular probe was successfully tested in multiple fluidic systems. It has left the test phase and is now ready for maturity phase.

Key words

three-dimensional ceramic tubular probe, online substance concentration measurement, ceramic injection molding

Introduction

In nearly every procedural processes it is desirable to know the in stock substance concentration. Thereby the product quality can be fit into close tolerances, for example to produce polystyrene spherules with a constant diameter of some micrometers. In other applications like a clothes washer the needed washing powder can exactly be charged to the measured degree of pollution. This will help the environment protection and reduce the costs of the used washing powder.
For each application area different geometries and sensor effects as well as materials will be needed for an exact measurement. The presented clevis sensor was developed for online concentration measurement. This sensor can be used in procedural pipeline systems where corrosive acid or alkali fluidics are present. As sensor effect dielectric spectroscopy was chosen. Furthermore the sensor design will be derived from the sensor effect and technical boundary conditions.

Frequently used Sensor Effects

Several sensor effects can be used to measure fluidic concentration levels. Here ultrasonic sensors are well known as optical systems. X-ray sensors are seldom used. Each of these measuring principles got its own advantages and disadvantages.
When using ultrasonic sensors the acoustic properties of the used fluid have to be known exactly. Because of the complexity of ultrasonic signals a high effort in signal processing is needed. For long-term operations, as needed in procedural systems, the risk of having coating formations on the sensory housing surface is present. These coating formations might lead to render ultrasonic sensors unusable.

Optical measurement systems can only be used if there is a technically option to get the measuring beam into the pipeline system. For example if hydrofluoric acid is present optical measurement is impossible. The acid would corrode the needed optical fiber. In addition a concentration measurement in emulsion will not be able.
Radioactive seeds and x-ray source open a good ability for highly accurate measurements in fluids. They can also be used to measure in emulsions. But even if these sources are good shielded and harmless a lot of customers are afraid of using them.

DIELECTRIC SPECTROSCOPY

The chosen dielectric spectroscopy in a frequency range of 1 MHz to 100 MHz is an other measurement principle [1]. With this concept dielectric changes of the fluid can be detected by capacity measurement. As a further development of the ceramic clevis sensor prototype [2] a coaxial configuration of the sensor electrodes has been chosen (Fig. 1). Based on the permittivity changes, depending on the fluid, the substance concentration can be determined. No complex signal processing is needed.

SENSOR HOUSING DESIGN

The idea was to integrate a coaxial electrodes design into one pipeline; in between the fluid will flow. The behavior of the sensor will be like a capacitor, where the fluid is the changing dielectric. However it had to be ensured that non of the both electrodes will have contact to the fluid at any time. Although a solution had to be found for electric connectivity of the inner electrode. The sensor housing had to be made of electric isolating material to avoid short circuits. Furthermore the housing had to be resistant against chemical bases and acids. Hence zirconium oxide was chosen as housing material. Two flanged joints, standardized in DN 10 DIN 32676, were chosen as fitting. This choice was founded on the requirement of easy mounting into existing pipeline systems, without a lot of technical complexity and costs. By this way the sensor can be removed easily for maintenance (Fig. 2).
Next to the specifications the housing has been designed in CAD-Systems. Because of the housing design complexity and the high mechanical strength of zirconium oxide, the sensor housing is quite robust. That is why it can not be machinable and work on CNC milling. Consequently a realizable and cost-effective 3D forming technology for the chosen zirconium oxide had to be found. Here the ceramic injection molding (CIM) technology was chosen [3].

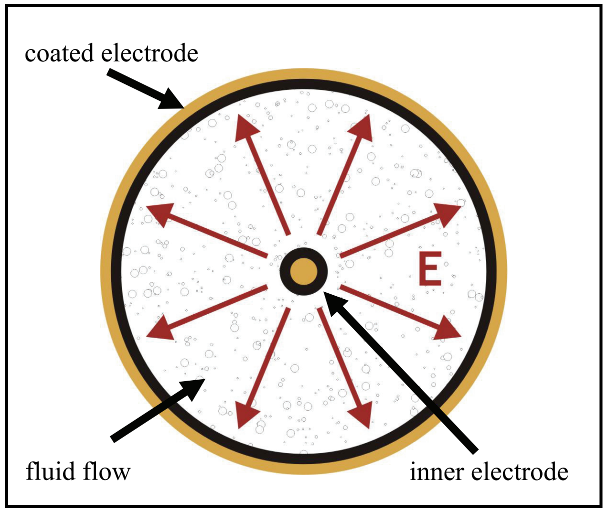

Fig. 1: cross section - schematic of sensor effect

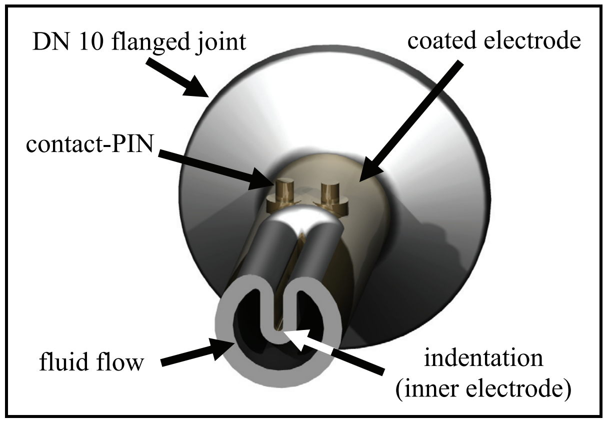

Fig. 2: cross section tubular ceramic sensor

SIMULATION

Very important for the sensor effect is a homogeneous streamline field. Before the sensor design has been finished an *Ansys* FE simulation of the streamlines of the field was done (Fig. 3). Here all material parameters like the thickness of the housing or the permittivity of the desired ceramic and fluid were taken into consideration. Some redesigns were done, e.g. like some rounding-offs are added to create a homogeneous field.

As next step in the development process the redesigned housing geometry was imported into *Moldflow*®, a FE injection molding simulation. This tool helps to determine the best injection molding point. Furthermore the filling behavior (Fig. 4) was analyzed and possible air traps were indentified. Air traps would cause damages in the ceramic sensor housing in later sintering steps. They would although have influence on the streamlines of the field and strictly had to be avoided.

Process Chain of Ceramic Injection Molding

The ceramic injection molding is a special method adapted from the polymer injection molding technology. Here the concept is to build a molding tool where the geometry of the desired part is included as a negative (cavity). The polymer melts at temperatures between 140°C and 350°C and is shot into the cavity beneath high pressure. When the polymer cools down the finished 3D shaped part can be easily deformed. With this technology nearly every shape can be manufactured in mass production within a few seconds (Fig. 5).

To use the injection molding technology with ceramic materials some ruses had to be used. First the ceramic was milled to a fine powder. Then the powder was mixed with a thermoplastic binder system to a feedstock. Because of the special binder system the feedstock had thermoplastic properties and could be used in a commercial injection molding machine.

Subsequently to the forming process the binder system had to be removed from the "green" parts. This was the most critical part in the process chain. Here it had to be ensured that the parts were heated slowly. Otherwise the binder could not exhaust fast enough and the inner pressure would have grown until the parts cracks. Debindering can be done by thermal treatment or in a catalytic way. The method is depending on the chosen binder. After the binder has been removed, pores occur in the structure on the surface. The pore size d_p depends on the used grain size distribution and can be defined [4] as:

$$d_p = 0{,}612 \cdot (1 - F) \cdot d_{50} \qquad (1)$$

where F is the solid content and d_{50} is the middle-sized grain distribution.

For the tubular sensor housing a commercial feedstock called "*Catamold® TZP-A*" made by BASF® was chosen. Here the debindering process had to be done catalytically at 120°C with 99.9% nitric acid and a subsequently second thermal debindering step. But by several process optimizations it has become obvious that 70% nitric acid can be used. By using this lower concentrated acid the debindering time had to be increased by approximated two hours. But the total debindering process cost were decreased significant because of the much cheaper acid. After all the sensor housing was sintered at temperatures up to 1560°C to compress the ceramic to 99.99% theoretically density. These thermal treatments caused a compaction of the ceramic sensor housing and hence shrinkage. The known shrinkage of approximately 17.1 % (Fig. 6) was considered in designing the molding tool as an oversize [3] [4].

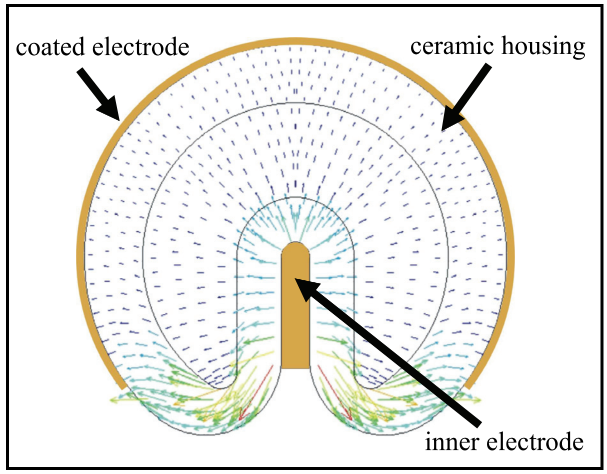

Fig. 3: simulation – streamlines of the field

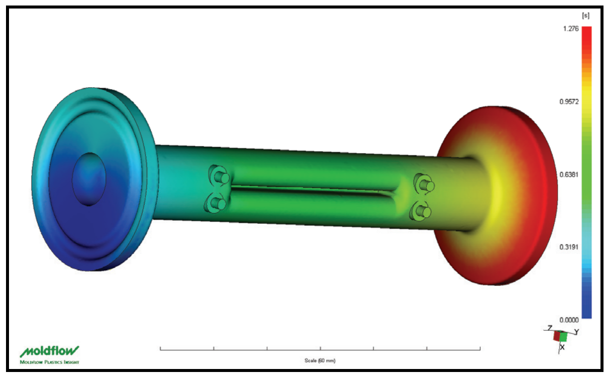

Fig. 4: simulation – filling behavior for CIM

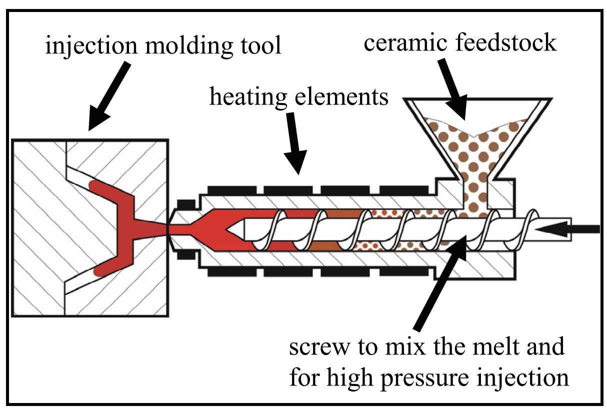

Fig. 5: Schematic of injection molding process

Packaging of Sensor Electronic

It turned out that the realization of the electrodes on the 3D ceramic surface was quite complex. Sputtering and pad printing could not be used because of the 360° metallization of the coated electrode and the aspect ratio of the inner electrode. As solution airbrush technology with a special silver conductivity paint was chosen. This method is state of the art in dental laboratories by preparing ceramic prostheses. Finally thermal treatment was used for burning-in the electrode structure into the ceramic substrate.

A PT 1000 thermo element was also added into the pipelines indentation of the inner electrode to be able to correct the temperature drift. For data logging a spectrum analyzer was used. This system was equipped with a CF-Flash card for data storage and a LAN adapter for digital control integration into existing control systems. The four metalized pins on the pipeline surface were used for contacting the measurement electrodes with the spectrum analyzer. In the future a PCB-board with first stage signal amplification will be placed on these pins.

System Test And Measurement Value Acquisition

A closed loop pipeline system was chosen as setup for test measurements. The regular fluid flow was realized with a peristaltic pump. Also a heating system has been added to test the measurement performance at different fluid temperatures. Multiple concentration levels of methanol and distilled water were determined in the pipeline.

Before the measurement could start, the evaluation unit has to be calibrated. For this the sensor was put into 100% methanol at 20°C. Once the evaluation unit was calibrated to the connected sensor, measuring could start.

The measurement started with 100 % methanol at 20°C and a constant flow of 1 l/min. For each concentration level the flow-rate was changed at constant temperature up to 5 l/min in 0.5 l/min steps. Then the fluid temperature was increased in 5 K steps up to 50°C and measurements were done at the same flow-rate steps.

When all these series of measurements were finished the fluid was diluted with distilled water and the concentration level of methanol was changed down to 50 % with a step size of 1 %. For each case of concentration level the measurements were done at same flow-rate and temperature profiles as described before. All measured values were checked against theoretically values. It turned out that the developed sensor and evaluation unit were able to measure the methanol concentration in distilled water within accuracy of 0.1 Mol-%.

The same measurement principle was used for measuring various fluids in a frequency range of 1-1.000 MHz. It has been shown that the fluids dielectric permittivity changes could be distinguished up to 100 MHz (Fig. 7).

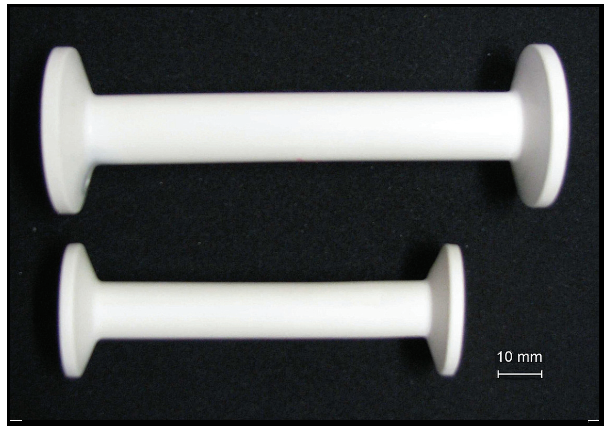

Fig. 6: ceramic sensor housing – green part after injection molding (top), finished part subsequent to sintering (bottom)

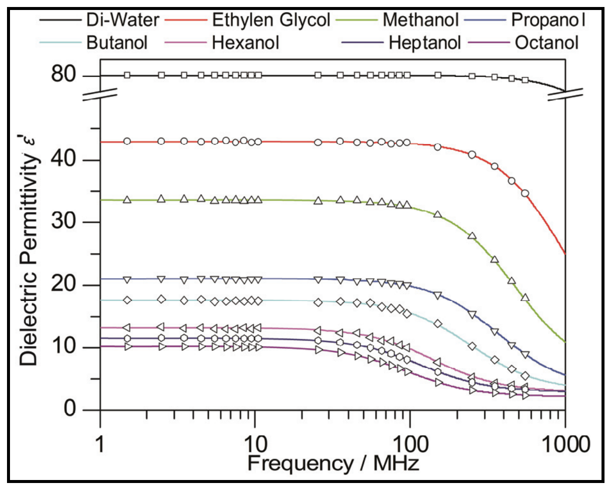

Fig. 7: measured data of various fluids

Conclusions

A tubular sensor housing was developed for online concentration measurement. To realize measurement in base and acid fluids a ceramic was chosen as housing material. For an easy mounting into existing pipeline systems standardized DN 10 DIN 32676 flanged joint was included as fitting. It has been shown that the designed housing could not be manufactured with standard CNC milling technologies. To ensure a low cost mass production the ceramic injection molding technology was chosen as forming technology for the housing. Based on the chosen dielectric spectroscopy as measurement principle a spectrum analyser was used for data logging and interface unit to existing control systems. The complete measurement system was tested successfully in a pipeline test bench. Different fluid concentrations were measured successfully. The results corresponded with the theoretically concentration levels. Even the temperature drift could be corrected by using a PT 1000 sensor element.

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