Electrically Heated Oxide Ceramic Tubes for High Temperature Reactions

Jörn Matthies*, Thomas Schall, Walter Pritzkow, Ute Tuttlies, and Ulrich Nieken

DOI: 10.1002/cite.202200186

Endothermic high temperature reactions are usually carried out in metal tubes heated by gas burners. Electrical heating allows substantial reduction of CO₂ emissions. We propose the usage of a composite tube, where a thin metallic layer is embedded between an inner and outer ceramic layer. While monolithic ceramics suffer from brittleness and low tolerance to thermal stress, only the inner layer is made from monolithic ceramics, while the outer layer is made of fiber reinforced oxide ceramics. In first tests the hybrid ceramic tube was electrically heated to 1250 °C with a maximum heat release of 85 kW m⁻².

Keywords: Electrical heating, High temperature, Oxide ceramic matrix composites, Resistive heating

Received: October 14, 2022; revised: February 14, 2023; accepted: February 27, 2023

1 Introduction

The chemical value chain starts with endothermic syntheses, which require very high temperatures to achieve economical conversions and high reaction rates. State of the art is to carry out the endothermic reactions at high flow rates and elevated pressure in metallic tubes, which are heated by a combustion reaction in an external firebox. The maximum temperature is limited to approximately 900 °C on the outside of the reactor tube [1] due to limited tensile strength of the metal tubes. In addition, metallic tubes are corroded by carburization, hydrogen embrittlement [2, 3] and metal dusting [4]. The metallic reactor wall catalyzes undesirable reactions, such as carbon formation, resulting in a growing coke layer inside of the tube. Approximately half of the supplied heating energy is needed to compensate the temperature decrease of the endothermic reactions, the other half is withdrawn with the exiting flue gas of the burner.

To avoid the combustion of fossil fuels in the external fire box, the use of electric resistance heating is considered. Attempts have been conducted to apply resistive heating in reactor design [5]. Direct resistive heating of the reactor tubes seems to be a simple solution but fails due to high electric conductivity of the massive tubes. Usage of metals for resistive heating requires small cross-sectional areas, but reduction of wall thickness of the tubes is not feasible due to loss of mechanical stability.

To apply electrical heating the demand for “mechanical stability” should be separated from the function “heat release from resistance heating”. In direct electrical heating of metallic tubes both functions are linked. This substantially hampers tube design or even makes it impossible.

Electrically heated tubes should thus consist of an electrically conducting material, which is used for resistive heating and can be designed such that total ohmic resistance is sufficiently high to avoid very high currents. This can be achieved by low cross-sectional areas and geometric design of a metallic layer.

Whereas resistance heating by metal is straightforward, what kind of materials are suitable for pressurized tubes at very high temperatures? State of the art are metals, but this would imply the use of electrical insulation between the different layers of heater and the pressurized reactor tube. Using ceramic materials has several advantages at a first glance: they are non-conducting, can withstand very high temperatures, are not prone to corrosion, and are chemically inert. The major drawback is the low tolerance to thermal stress and their brittleness, which leads to sudden fracture [6]. Therefor it is hardly applied in high temperature synthesis today.

The presented new multi-layer ceramic tube consists of an inner, dense monolithic ceramic tube, a thin metal layer and an outer layer made of so-called oxide ceramic matrix composites (OCMCs).

1 Jörn Matthies (joern.matthies@icvt.uni-stuttgart.de), 2 Thomas Schall, 3 Walter Pritzkow, 4 Dr. Ute Tuttlies, 5 Prof. Dr. Ulrich Nieken 1 University of Stuttgart, Institute of Chemical Engineering, Böblinger Str. 78, 70199 Stuttgart, Germany. 2 Justus Liebig University Gießen, Institute for Physical Chemistry, Heinrich Buff Ring 17, 35392 Gießen, Germany. 3 Walter E. C. Pritzkow Spezialkeramik, Adam Opel Str. 6, 70794 Filderstadt–Sielmingen, Germany.
While ceramics are usually associated with dense materials, a new class of ceramic materials are oxide fiber-oxide ceramics. OCMC layers can be applied to metal or ceramic tubes by wrapping layers of fabrics, which are infiltrated by a slurry, around the tube. During the sintering process a micro porous fiber reinforced ceramic layer is formed. Due to the porous structure the layer is no longer brittle and shows a more damage tolerant and flexible behavior. This property is important to compensate the thermal expansion of the metal layer during heating. The second important property is shrinkage of the OCMC layer during sintering. This applies a compressive stress to the thin metal layer and to the inner, dense ceramic layer. While monolithic ceramic materials are very sensitive to tensile stress, they can withstand high compressive stress [6].

In the following chapters we describe material properties, the manufacturing process, and tests of the electric heating in a laboratory setup.

The main purpose of this work is to make the best use of the advantages of ceramics and to counterbalance the disadvantages. We have developed and tested a novel hybrid ceramic tube with an integrated metallic heater that enables high operating temperatures and heat fluxes at technically relevant voltages and currents. The construction compensates the brittleness and unfavorable failure characteristics of conventional monolithic ceramics. [7–9]

2 Reactor Concept

The reactor prototype is designed to withstand high temperatures of >1200 °C, is electrically heated and can be operated under flexible conditions due to a good thermal stress resistance. The heater material and shape can be designed to meet a wide variety of voltage and current specifications while maintaining a high heat release due to the special construction involving an outer armoring with OCMC (see Fig. 1).

Tests have been carried out in a test setup with prototypes at temperatures exceeding 1250 °C, a heating power of 85 kW m⁻² and a heating rate of 2 K s⁻¹ at the same time. These performance characteristics are comparable to known high performance materials like nickel-based high-alloy steel [10] from industrial processes, which are typically found in, e.g., steam-crackers [1].

The combination of both high heat transfer due to direct contact between heating conductor and reaction space at high operating temperatures makes this reactor design very advantageous and is an alternative to conventional reactors, which are limited to lower maximum temperatures.

2.1 Material Choice

The reactor concept is built in three layers as shown in Fig. 1. A monolithic inner tube on which the resistance heater is applied, and a reinforcement made of OCMC material. The monolithic inner tube made of Al₂O₃ is gas-tight. It has good thermal conductivity (25 W m⁻¹K⁻¹ at 100 °C, decreasing at elevated temperatures), resistance to high temperatures and pressure resistance. Any direct exposure to tensile stress must be avoided, as the monolithic tube may suddenly fail in a brittle manner and therefore has a low fault tolerance [6].

In oxide ceramic matrix composite (OCMC) endless oxide ceramic fibers are embedded in a matrix of filler powder (Al₂O₃) and binder powders (Al₂O₃, SiO₂ and 3YSZ/ZrO₂). The ceramic fibers reinforce the matrix [11–13], which in itself is a weak phase that exhibits large strain to failure and low stiffness [14]. Due to this combination of weak matrix with stiff and brittle ceramic fibers, OCMC exhibits quasi-ductile fracture behavior in contrast to monolithic ceramics [14, 15]. Thus, OCMC is not affected by the problematic drawback of brittle fracture behavior, because microcracks and delamination within the OCMC structure can locally dissipate stress peaks. This enables fiber-reinforced ceramics to react to corresponding loads with deformation [13, 14]. Disadvantages of OCMC structures are the porosity and the lack of experience in handling and construction for applications of chemical industry. For this reasons, fiber-reinforced ceramics have been rarely used in the past. Examples of relevant usage in this context include furnace tubes, burner nozzles, furnace sliding carriages or hot engine solutions [6, 16–18].

Heating with an additional functional layer as resistance heater offers the advantage that the electrical resistance can be designed by the heater shape and material.
In this study, the following materials, inter alia, were investigated: a) V2A (1.4301), b) molybdenum, c) carbon fibers, d) woven Kanthal® wire and e) Aluchrom Y Hf (1.4767).

Materials a) to d) were excluded here due to their disadvantageous material properties. All four materials are not resistant in oxidative atmosphere at 1200°C. In addition, molybdenum proved to be too stiff for use as a heating conductor. Carbon fibers are problematic due to a lack of proper connection to the electric wiring. When heating using carbon fibers, a material change of the metallic conductors by carbon diffusion into the metal could be observed [19]. Fine Kanthal® wire woven into a fabric of oxide ceramic fibers has turned out to be not resistant to oxidative atmosphere at high temperatures and is, like carbon fibers, problematic to connect to a power source.

The best results were achieved with 1.4767 Aluchrom Y Hf. Aluchrom Y Hf is a ferritic chromium steel with aluminum, yttrium and hafnium added. At high temperatures, a well-adhering aluminum oxide protective layer is formed [20, 21]. For this reason, Aluchrom Y Hf is suitable for use under extreme conditions for temperatures up to 1200°C. Sinter firing of the ceramic parts under oxidizing atmosphere is possible with Aluchrom Y Hf present.

Therefore, a meander-shaped (for a long conducting distance) sheet of Aluchrom Y Hf (1.4767) with a thickness of 0.11 mm was selected as the heating conductor in the heated functional layer. Since the heating conductor is located between the monolithic tube and the OCMC reinforcement, the heater can also be operated at temperatures above the softening point of the metal without deformation or delamination of the metal structure (see Sect. 2.3).

2.2 Manufacturing

The heating conductor is manufactured by laser cutting from a sheet of Aluchrom Y HF with a thickness of 0.11 mm. A piece of OCMC fabric (Nextel 610 DF-11) is cut and infiltrated with slurry. Since the metallic meander has sharp edges, the OCMC fabric must be protected during manufacturing. For this purpose, a fleece of ceramic fibers was positioned on the OCMC fabric. The meander is placed in the center of the fleece. The contact lugs protrude beyond the fabric. A ceramic tube is then placed on the meander and the fabric with fleece and meander is wrapped around the tube with slurry (see Fig. 2). With a peel ply, the OCMC armoring is pressed firmly onto the pipe. After drying of the OCMC the peel ply is removed. The hybrid tube is then sintered at 1200°C. Tab. 1 shows a summary of the components in the reaction tube.

In Fig. 3 a manufactured OCMC tube after the sintering step and a successful heat-up cycle is shown. On the left the low resistance lug of the heater protrudes the ceramic tube. The contacts are inserted at the outer edge between the monolithic inner tube and the OCMC armoring. The constriction in cross section of the contacts to the high resistance section of the metallic heater is covered by the OCMC to protect the flexible heater construction from mechanical stress. The thermal stress to the ceramic tube is reduced by a V-shape of the heater at the beginning of the high resistance area and therefore a gradually increase of electrical resistance results in a gradually increase of heat release. In the area of the inserted metallic heater a risk of delamination of the OCMC composite from the ceramic tube due to lack of contact between OCMC and ceramic tube was suspected. Multiple X-ray photographs of a used hybrid tube have been taken. However, these delamination effects were not observed in our experiments. In fact, the conducted X-ray photographs (see Fig. 3) show that the heater underlying the OCMC composite is well in place with parallel and equidistant space between the heater lines. Corrugation or displacement of the heating elements due to thermal expansion could not be observed.

Table 1. Detailed information on the components in the reaction tube.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material and geometry</th>
<th>Thermal expansion 20–1000 °C [K⁻¹]</th>
<th>Maximum service temperature [°C]</th>
<th>Thermal conductivity at 100°C [W m⁻¹K⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic tube</td>
<td>Alsint 997</td>
<td>8.0·10⁻⁶ [22]</td>
<td>1650 [22]</td>
<td>25 [22] (decreasing with increasing temperatures)</td>
</tr>
<tr>
<td></td>
<td>ø50 mm × ø40 mm × 500 mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heating</td>
<td>Aluchrom Y Hf (1.4767); meander shape; length of the heating zone: 276 mm; length of parallel conductors: 250 mm; total length 600 mm</td>
<td>15.0·10⁻⁶ [23]</td>
<td>1200 [23]</td>
<td>13.5 [23]</td>
</tr>
</tbody>
</table>

Figure 2. Components of an electrical hybrid OCMC tube with embedded electrical heater.
2.3 Theory of Functional Principle

For the first time, the combination of a rigid inner tube, a metallic heater, and a stress-resistant fixation with OCMC makes it possible to heat a ceramic tube directly with electrical power at arbitrary voltages and currents at an industrially relevant level. It is assumed that this is caused by the functional separation which enables to retain the desired individual material properties in a combined structure. This is achieved by shrinking the OCMC layer onto the monolithic ceramic tube during the manufacturing process, thus applying a static pressure to the inner tube (illustrated in Fig. 4). This leads to a pressure-only stress to the rigid tube and the flexible metallic heater. Since high pressure stress is appropriate for dense ceramic shapes, this construction makes the monolithic ceramic-based material resistant to external influences such as mechanical or thermal stress [7–9]. The contraction stress of the fiber to the inner tube is compensating occurring stress resulting in a net pressure stress to the monolithic ceramic. At the same time, the metallic heater is placed between the ceramic monolithic tube and the OCMC layer. This approach provides thermal contact of the metallic heater with the ceramic inner tube. The metallic heater is mechanically supported by the outer OCMC reinforcement. Different coefficients of thermal expansion of the metal- and ceramic-based materials are compensated by the OCMC reinforcement. Softened metal due to extreme temperatures are fixed in position while pressed to the surface for heat conduction.

3 Experimental Setup

3.1 Test Setup

To test different types of heater materials, a dual-use test setup was developed. A drawing of both setups is shown in Fig. 5. A ceramic protection tube with a one-sided opening was used. The protection tube is sealed by a high-grade steel cap equipped with one centrally arranged exhaust tube reaching into the OCMC hybrid test prototype and eight tubes arranged in a circle serving as service lines and safety devices.

In the first setup the reactor is sealed air-tight and purged with a flow of inert gas. The heat loss to maintain the temperature of the prototype at given power input results from the heat losses through the outer protective wall. In this case an oxidation of the heater material can be prevented due to the inert atmosphere. It is possible to test prototypes at maximum operation temperature up to 1800°C restricted by the temperature resistance of the insulation material.

In the second test setup, a gas inlet is used to provide a flow along the outer surface of the prototype. The gas flow is inverted at the tip of the protective tube and flows back inside of the OCMC hybrid test prototype. The gas flow is channeled in an axial exhaust pipe, which is open to an ambient pressure exhaust hood to avoid any pressure buildup inside the setup.

In both setups the OCMC hybrid tube prototype was monitored by type K and N thermocouples placed on the outside and inside to receive information of the temperature distribution of the prototype. The electrical power was provided by a high-performance laboratory transformer (Elek-
4 Results

4.1 Experimental Procedure

The experiment shown here in detail is a heat-up cycle. In this case the goal was to reach a high temperature of at least 1200 °C with a fast heat-up rate of at least 1 K s⁻¹. Also, the maximum heat output was monitored based on the input power of the electrical heater. The resistance of the heater can be calculated with Ohm’s law given by

\[ R = \frac{U}{I} \]  

(2)

where the voltage \( U \) and current \( I \) was given by the measurement. The resulting electrical resistance \( R \) refers to the entire circuit including the cables and contacts, which is neglected due to their low electrical resistance of < 0.01 Ω. The power consumption of the transformer is related to the heat production of the heater based on the Joule heating given by

\[ P_{\text{Heating}} = \frac{RI^2}{A_{\text{Heater}}} \]  

(4)

with

\[ A_{\text{Heater}} = \pi DL = \pi \cdot 50 \text{ mm} \cdot 250 \text{ mm} = 0.039 \text{ m}^2 \]  

(5)

The diameter \( D \) of the monolithic ceramic tube as well as the length of the high resistance area \( L \) is identical for all used OCMC hybrid tubes.

In preparation of the experiment the setup was purged 12 h with \( \text{N}_2 \) to remove any residual air. Subsequently the prototype was heated up by slowly elevating the heating power while regulating the voltage.

The measuring results of the heat-up performance test are shown in Fig. 6. The temperature of three thermocouple sensors (see Fig. 5) is shown as follows: A sensor placed on the inside of the ceramic monolithic tube in the heated area (sensor 1), placed inside of the ceramic monolithic tube in small distance above of the heated area (sensor 2) and outside of the OCMC hybrid tube in the heated area (sensor 3). All shown sensors were placed to be in direct contact with the surface of the OCMC hybrid tube.

For the heat-up to 1200 °C the voltage was raised in 25 V steps manually while temperature and resistance were closely monitored. A slight rise of the resistance of the heater could be measured up to a temperature of 800 °C. The maximal heat intensity could be measured in the heat-up phase...
with 165.5 V and a peak power input of 84.5 kW m$^{-2}$. A heat-up rate of 2 K s$^{-1}$ could be exceeded over several minutes. The mean heat-up rate of sensor 1 over 1000 s is 1.18 K s$^{-1}$ and thus higher than expected.

After reaching 1200°C, the temperature was held for 60 min. The voltage was lowered to control the temperature accordingly. The electrical resistance remained nearly constant indicating a steady state of the heater.

At the end of the constant heating the voltage was again risen to test the maximum temperature limit. The experiment was stopped when a temperature of 1250°C was reached to prevent a failure of the metal heater.

To initiate a cool-down the voltage was lowered incrementally by 5 V and held constant to be able to monitor the change of the electrical resistance. The mean electrical resistance over time does decrease slightly as can be seen in Fig. 6 at 4800 s.

5 Conclusion and Outlook

The demand of electrically heated reactors for use in high temperature reaction is evident. We were able to develop and test a novel electrically heated hybrid ceramic tube at 1250 °C with a maximum heat release of 85 kW m$^{-2}$ while the resistance of the heater remained at an industrial relevant level over the total temperature range tested. It is considered that the exceptional performance of the ceramic reactor is inherent in the functional separation of the components (dense ceramic tube, heater foil and OCMC-layer).

The manufacturing process has been described for different materials. In this study a combination of Aluchrom Y HF and Nextel 610 DF-11 fiber matrix has proven to be a robust set of material. The stability of the heated tube after the conducted experiments could be verified with the aid of X-ray images.

In principle, any reaction with high demand in thermal energy is suitable for this reactor concept. Preferably reactions with the demand of high temperatures such as reforming, cracking reactions or pyrolysis of, e.g., plastic waste in industrial scale might be beneficial compared to other approaches.

This proof of concept demonstrates the general feasibility but at this stage not an industrially applicable reactor. In further studies the impact of a catalytic reaction will be investigated. In particular the impact of chemical atmosphere and coke formation to the fiber and the heater is to be studied.

Acknowledgment

Open access funding enabled and organized by Projekt DEAL.

Symbols used

\[ A \quad [m^2] \quad \text{surface (outer surface of the monolithic)} \]
\[ D \quad [mm] \quad \text{diameter} \]
\[ I \quad [A] \quad \text{current} \]
\[ L \quad [mm] \quad \text{length} \]
\[ P \quad [W] \quad \text{(electrical) power} \]
\[ R \quad [\Omega] \quad \text{electric resistance} \]
\[ U \quad [V] \quad \text{voltage} \]

Abbreviations

MFC mass flow controller
OCMC oxide ceramic matrix composites

References
