Ceramic Honeycombs for Thermal and Process Engineering

Ceramic honeycomb structures are used in a multitude of applications and due to their technical potential the field of applications is still growing. Ceramic heat exchangers, which are also produced in a honeycomb shape, are used to store the heat of exhaust gases and to heat up the incoming raw air. Next to heat exchangers and flow rectifiers, ceramic honeycombs are also used as catalyzer substrates and in the dental industry as firing trays. Finally, in a multitude of applications and processes modified ceramic honeycomb structures are used as spark arrestor.

Introduction

Due to their material properties, their lifetime and their availability in various shapes and designs, ceramic honeycomb structures are used in a multitude of applications and the field of applications is still growing. Ceramic catalyzer substrates, firstly used in a small car for exhaust purification are widely used in chemical, electric power, metallurgy, petroleum, electronics, electrical appliances, machinery and other industries. Ceramic heat exchangers, which are also produced in a honeycomb shape, are used to store the heat of exhaust gases and to heat up the incoming raw air. This process is typically used at large burners, e.g. at waste incineration and processing plant and at chemical production plants to run a thermal after-burning unit to crack chemicals or to oxidize carbon monoxide to carbon dioxide.

Due to various technical developments during the last decade, ceramic honeycombs are also more and more used in biotechnical applications, but also in medical applications as well as in applications for energy recovery and energy storage.

Keywords
ceramic honeycombs, alumina ceramics, zirconia oxide ceramics, silicon carbide ceramics, cordierite ceramics, mullite ceramics

Materials

Ceramic honeycombs are typically made of alumina ceramics, zirconia oxide ceramics, silicon carbide ceramics, cordierite ceramics and mullite ceramics.

Alumina ceramics are one of the most widely materials for technical ceramics. Due to its highly strong ionic interatomic bonding, alumina offers good performance in terms of chemical and thermal stability, relatively good strength, thermal and electrical insulation characteristics at a reasonable price. Ceramics made of aluminum oxide can be produced with a purity of >99 % Al_2O_3. Compared with other materials for technical ceramics, aluminum oxide is more abrasive during the extrusion process which means a faster wearing of the extrusion tools. Mullite, cordierite, quartz porcelain and alumina porcelain are ceramics, which contain a significant percentage of aluminum oxide and silicon oxide.

Zirconia is one of the ideal materials of high-strength and high-toughness when proper compositions, such as magnesium oxide (MgO), yttrium oxide, (Y_2O_3), or calcium oxide (CaO), are added to control an otherwise destructive phase transformation. The microstructural features of zirconia ceramics also make it an engineering material choice of wear and corrosion resistance, damage and degradation tolerance in a wide range of applications.

Silicon carbide is notable for its hardness, high melting point and high thermal conductivity. It retains its strength at temperature up to 1400 °C and offers excellent wear resistance and thermal shock resistance. It is used in a wide range of industrial applications e.g. as support for ceramic gas and liquid filters, as catalyst supports and hot-gas or molten metal filters because of its low thermal expansion coefficient and good thermal shock resistance as well as excellent mechanical and chemical stability even at high temperatures.

Cordierite has a superior thermal shock resistance due to the intrinsic low coefficient of thermal expansion, combined with relatively high refractoriness and high chemical stability against acids. Therefore, it is often used for high temperature industrial applications, such as heat exchangers for gas turbine engines, catalyst carriers with honeycomb shapes in automobile exhaust system or large internal combustion engines like power generators and ships. More and more, small catalyzer substrates made of cordierite are also used in bio-

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technologies or other applications of environmental technologies.
Mullite occurs very rarely in nature because it only forms at high temperature, low pressure conditions. So as an industrial raw material, mullite has to be produced by synthetic processes. Mullite is a material on upscale pricing and known for its excellent thermal and mechanical properties: low thermal expansion, low thermal conductivity, excellent creep resistance, suitable high temperature strength and outstanding stability even under harsh chemical conditions.
Tab. 1 shows an overview of the typically used materials for ceramic honeycombs of the Rauschert® Group.

Production of ceramic honeycombs
No matter what ceramic material is used, the general production process for ceramic honeycombs is identical and shown in Fig. 1. The production process starts with the mixing of the masses. Typically, the raw materials are available as powders, during the mixing process, these raw materials are mixed homogeneously and converted into a pasty mass by adding water and other liquid agents. After this step, the mass is pressed through extruders to compact the mass, to remove entrapped air and to homogenize the mass again. Then, the mass is pressed through an extrusion tool to create the honeycomb shape. After extruding the honeycomb blocks, they are dried at smoothly elevated

Tab. 1
Overview of materials for ceramic honeycombs

	Unit	Quartz Porcelain	Alumina Porcelain	Cordierite, Dense	Mullite	Modified Cordierite a)
Rauschert® mass designation		C2	TS1	A2	M2	S1
Mass designation according to DIN EN 60 672		C110	C130	C410	C620	–
Density	$\frac{g}{cm^3}$	2,47	2,68	2,42	2,31	1,75
Open porosity	%	0,6	0,8	0,4	26	32
Specific heat capacity (20 – 100 °C)	$\frac{J}{kg \cdot K}$	890	990	940	995	800
Coefficient of thermal expansion (20 – 1000 °C)	$10^{-6} \frac{m}{m \cdot K}$	4,8	6,2	3,5	6,2	1,3
Thermal shock resistance*	K	500	500	500	550	650
Heat conductivity (20 – 100 °C)	$\frac{W}{m \cdot K}$	1,37	2,79	1,89	2,42	1,55
Recommended operating temperature	°C	1280	1400	1220	1480	1280
Softening temperature**	°C	>1380	>1500	> 320	>1580	>1380
Acid resistance***	%	0,3	0,2	5,0	2,5	28
Caustic resistance****	%	18	16	16	23	36
Content SiO_2/Al_2O_3	%	65/30	43/52	55/25	30/68	50/35

* Measured on test sample 6 cm × 6 cm × 3 cm, with two undamaged skins side by side, cut out of a honey comb.
** The softening temperature represents the temperature of beginning material damage, while the maximum application temperature represents the figure, which can be applied to the material without beginning deterioration.
*** Measured according to DIN EN 993-16: The material is prepared to a defined surface before being exposed to HCl during a defined period. The figures represent the mass reduction due to this influence (the lower the figure, the better the resistance).
**** Measured according to DIN EN 993-16: The material is prepared to a defined surface before being exposed to NaOH during a defined period. The figures represent the mass reduction due to this influence (the lower the figure, the better the resistance).
a) Modified cordierite is only suitable for the production of catalyzer substrates.

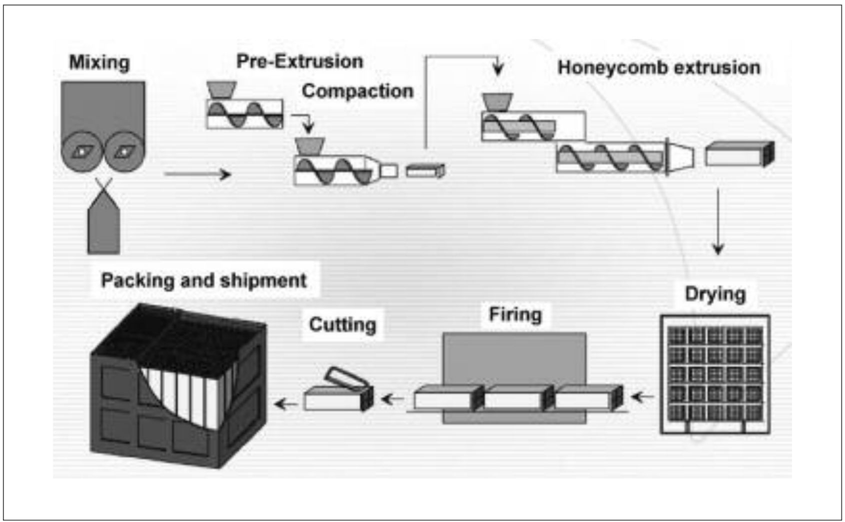

Fig. 1
Scheme of the production process of ceramic honeycombs

temperatures to remove the main content of liquid. The main firing process of the dried honeycombs is done at high temperatures, depending on the material up to 2000 °C. Alternatively to the firing process at high temperatures, also a freeze-drying process can be used. After the cooling down of the honeycombs, they are sawed to the required length. After a quality control, the honeycombs are packed.

The available diameters of ceramic honeycombs with round profile are various, depending on manufacturer and application. For ceramic honeycombs with square profile, an established size is 150 mm × 150 mm and established lengths are 150 mm and 300 mm. Fig. 2 shows an overview of typical designs for heat-exchanger honeycombs, Fig. 3 shows an overview of typical designs for catalyzer substrates.

Ceramic heat-exchangers for exhaust gas treatment

One of the major issues of industrial exhaust gases is the content of hazardous substances. To reduce this content and to crack molecules, a principle of post burning is used which is called “Regenerative Thermal Oxidation” (RTO). Like at standard thermal oxidation processes, the exhaust gases are heated up to 750–850 °C. At this temperatures and a defined dwell time in the heat chamber, organic compounds and also some inorganic compounds are oxidized and converted into water steam and carbon monoxide.

Regenerative burners are mostly used in foundries, refuse incineration plants, chemical production plants and pharmaceutical plants. The burners, which are equipped with heat accumulators, are always built in two identical groups of burners and operated alternated: while one burner group is in operation and takes in the combustion air via the heat accumulators, the other burner group heats up the heat accumulators by the heat of the treated exhaust air. After a defined period the operating mode is inverted and the burner groups change their function against each other. So, the principle technique is to make two regenerators operate alternating endothermic and exothermic by a reversing device.

In the beginning of the invention of this technologies, ceramic balls and saddles were used as heat accumulators and heat exchangers. By inventing ceramic honeycombs as heat exchangers, the process became much more effective due to a higher life time of ceramic honeycombs (compared to saddles and ceramic balls) and a lower pressure drop of the gas stream. Typically, ceramic honeycomb shapes with 40 × 40 channels or

Fig. 2
Typical designs of heat-exchanger honeycombs

Fig. 3
Typical designs of catalyzer substrates

50 × 50 channels are used, but also low channel densities like 25 × 25 channels are used for some kind of applications.

For some special applications, it is necessary to use modified ceramic honeycombs, which are called "Bridge block" and distributed by a multitude of manufacturers: either both or only one end of the faces is modified so that there is a cylindrical trench in the face to create an uneven surface. Therefore, when one block is installed directly on top of another, (crosswise) a trench will be formed between the layers which allows and supports cross flow in the intersection of the blocks.

When bridge blocks are installed in thermal regenerators, the air flow profile (air flow distribution) in the regenerator bed will be homogenized (uniformed), which has positive effects on the thermal efficiency, especially during the shut-down when the pressure drop of the bed becomes very low. In cases of local blockings, the bridge blocks allow to by-pass the blocking because the intersections are connected through the entire bed. Compared to conventional structured packings, which do not allow cross-flow inside of the packing and do show very often an inhomogenuous flow profile, a bridge block packing will promote cross-flow inside a regenerator packing what guarantees a very homogeneous flow profile in a regenerator packing also at partial load conditions.

In summary, the advantages of a bridge block packing are:

- nearly ideal air distribution in a regenerator packing
- nearly ideal temperature profile in a regenerator packing
- better energy efficiency in partial load situation
- less risk of complete blocking and fouling.

Fig. 4 shows a typical assembly of a heat exchanger packing with bridge block honeycombs.

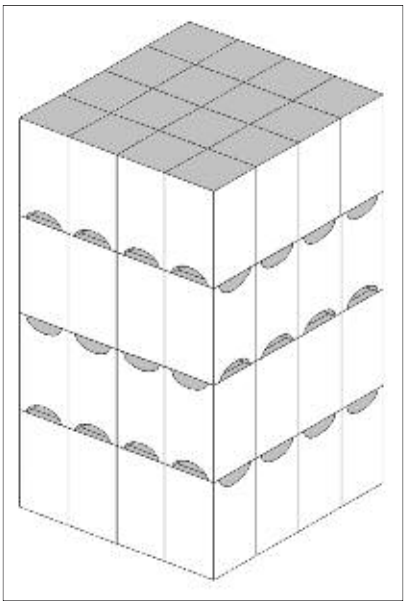

Fig. 4
Assembling of a heat exchanger packing with bridge block honeycombs

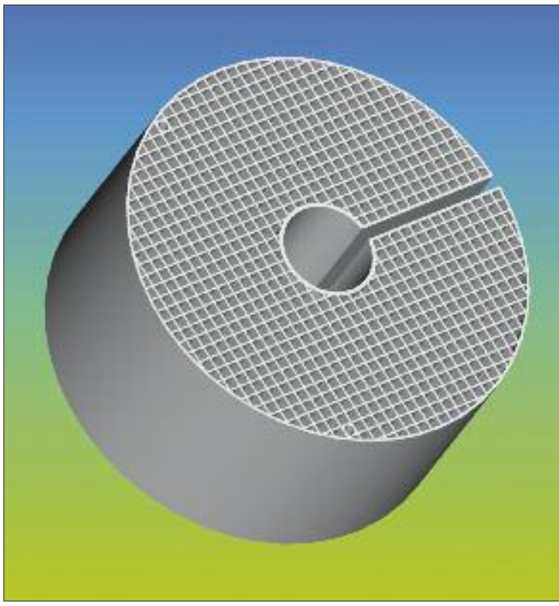

Fig. 5
Catalyzer substrate with central hole for sensor installation

Ceramic honeycombs for catalyzers

Next to heat exchangers and flow rectifiers, ceramic honeycombs are also used as catalyzer substrates. In this case, substrates means, that the ceramic honeycomb is the carrier which will be coated in further steps with wash-coat layers and materials (like e.g. rubidium, yridium) to run a catalysis process. The most popular application is catalyzers for cars and utility vehicles to treat the exhaust gases. The cell density of catalyzer substrates is usually given as "CPSI" which means cells per square inch. Typical cell densities for catalyzers are between 50–600 CPSI. A low CPSI number means low pressure drop combined with small surface, a high CPSI number means a high pressure drop combined with a large surface. Also, the coating process becomes much more complicated with an increasing CPSI number.

Next to this popular applications ceramic catalyzer substrates are also used for biotechnical and environmental applications. Depending on the country, also small combustion engines like lawn mowers and chain saws have to equipped with catalyzers. More and more, also the exhaust air of industrial kitchens and food production plants is leaded through a catalyzer to reduce stench by a catalytic post-treatment.

Depending on the application, a catalyzer step can be more than a static device. They can be manufactured in a shape that allows to install e.g. indicators for temperature, content of chemicals or humidity. Fig. 5 shows a round catalyzer substrate with a central hole for a sensor.

A very actual application of ceramic catalyzer substrates is "biological fuel cells": Some types of bacteria (e.g. some types of e.coli, rhodoferax ferrireducens, geobacter, pseudomonas aeruginosa) are able to metabolize hydrocarbons in a way, that hydrogen and electrons are available. By using a semipermeable membrane, which allows only hydrogen ions to pass through, a simple fuel cell can be built. To avoid, that the microorganism are washed out of the fuel cell by the metabolite flow stream, it is necessary to "fix" them in the fuel cell. Therefore, ceramic catalyzer substrates can be coated with an agent layer, which fixes them on the surface of the substrate. Next to this effect, the catalyzer substrates also provides a large surface which means a high amperage density of

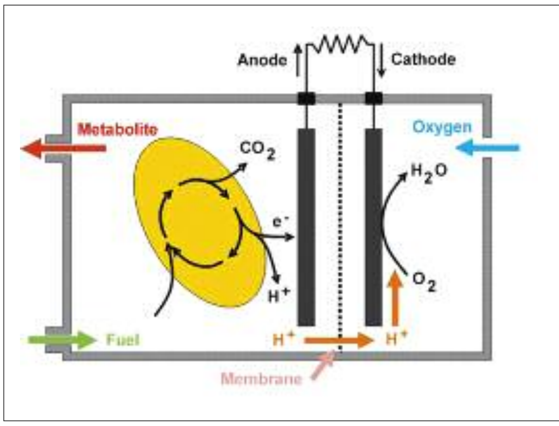

Fig. 6
Functional principle of a biological fuel cell

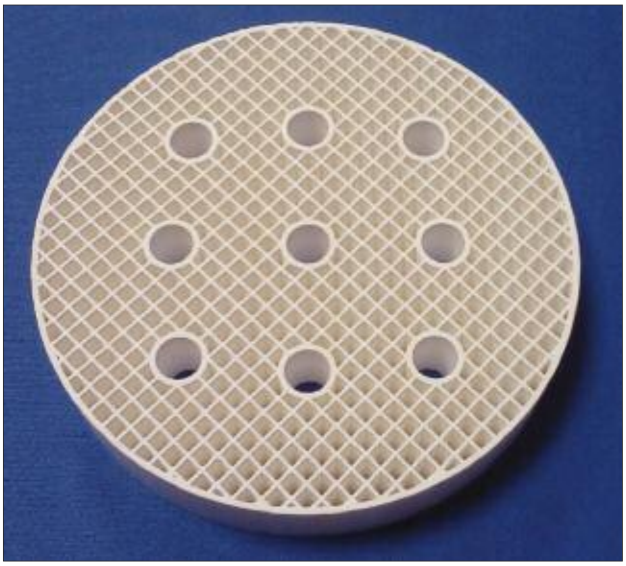

Fig. 7
A 2-loop ceramic honeycomb catalyzer substrate

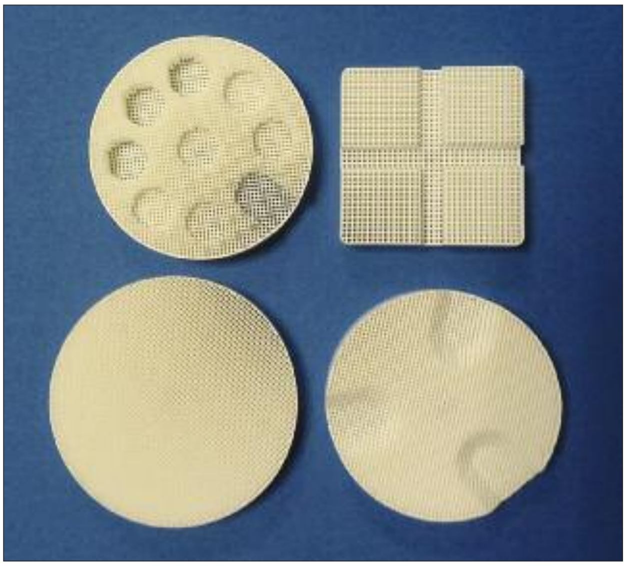

Fig. 8
Typical designs of dental firing trays

Fig. 9
Spark arrestor in cascade design

the fuel cell. Fig. 6 shows a schematic sketch of a biological fuel cell.

Ceramic catalyzers in 2-loop design

The usual ceramic catalyzers only handle one incoming gas or liquid stream. Nevertheless, ceramic catalyzers can be produced in a 2-loop design, to transport heat between two loops. Depending on the application the channels of each loop are coated with different types of catalytic materials. A very innovative layout is, to run one loop with an exothermal reaction and the other loop with an endothermal reaction which means: the upcoming heat of the exothermal process in loop 1 supports the endothermal process in loop 2, which means in total a significant reduction of the required energy input. Fig. 7 shows a typical design of a 2-loop ceramic honeycomb catalyzer substrate.

Ceramic honeycombs as firing trays

Next to the applications shown above, ceramic honeycomb structures are also used in the dental industry as firing trays: when using dental ceramics, the firing result largely depends on the individual firing procedure of the user, i.e. among other aspects, the type of furnace, the location of the temperature sensor, the firing tray as well as the size of the workpiece during the firing cycles. Solid firing trays absorb more heat during firing and can therefore influence the effect of firing on the ceramic as well they have a higher energy consumption for heat-up. The ceramic materials for honeycomb firing trays are very pure, so that no spotting will occur during the firing procedure. For this reason and to obtain the best possible results, honeycomb firing trays are used. Fig. 8 shows some typical details of firing trays.

Modified ceramic honeycomb structures as spark arrestor

In a multitude of applications and processes, it is necessary to avoid that sparks enter a process zone. Decades ago, regular ceramic honeycombs were used for this task: the principle was that the sparks will extinguish during passing the channels of the honeycombs. Therefore, the channels had to have a minimum length and the spark arrestors had a large constructed size. To minimize the size of the spark arrestors by the same probability of catching all flying sparks, ceramic cascades were developed. Fig. 9 shows a typical cascade spark arrestor. The advantages of this cascades are the compact and maintenance-friendly design, the lower prices and the excellent effectivity.

Outlook

The technical potential of ceramic honeycombs is significant and still growing. Next to the designs and applications shown above, Rauschert is still working in develop new shapes and geometries. Mainly the process technologies and chemical applications are still offering potential applications e.g. for catalyzers coated with photocatalytic layers or catalyzer structures with chemically adjustable surface loads or surface properties.