Crushable Ceramics – or how a Knot Can be Tied in a Ceramic Pipe

Crushable ceramics or just "crushables" for short, are a highly unusual niche application for ceramics. With conventional ceramics, the usual aim is to achieve a high level of mechanical strength. With crushable ceramics however, the aim is to achieve a defined level of mechanical strength that is generally very low in comparison to conventional ceramics. The mechanical strength is defined within certain limits, such that this strength is sufficient for the necessary production steps during manufacturing and processing, but is also sufficiently low for the later compaction. In the following section, commonly used materials, their manufacturing, properties and their typical applications will be described in more detail.

Fig. 1
Overview of typical crushable ceramics manufactured by Rauschert

Materials

There are only a few ceramic materials that have established themselves in the manufacturing of crushable ceramics.

Keywords
steatite, magnesium oxide, steatite porous C230, crushable ceramics

Probably the most commonly used in the manufacturing of crushables are magnesium oxide C820 and the porous steatite C230. Additional materials that are used to a lesser extent in the manufacturing of crushables are: aluminium oxide (Al_2O_3), spinel (ideally: $MgO \cdot Al_2O_3$), hafnium oxide (HfO_2), silica (SiO_2), porous forsterite C240 (ideally: $2MgO \cdot SiO_2$) and there are possibly other exotic materials that have not been mentioned here. The author is also aware of applications with boron nitride (BN). Just the fact that the materials porous steatite C230 and magnesium oxide C820 are mentioned in the international standards for ceramic and glass-insulating materials (DIN EN 60672-3:1999-02; VDE 0335-3:1999-02 [1]) demonstrates the economic importance of these two materials for electrical engineering, even if they are something of a niche product in terms of the amount produced, in comparison to other materials that are mentioned there.

Typical applications for the individual materials are as follows (details below):

Magnesium oxide C820: Heater elements, coil cartridge heaters, sheathed thermocouples, heating cables, fire-proof cables, signal cables in rough environments, etc.

Porous steatite C230: General heating elements, cartridge heaters, coiled heaters and micro-coiled heaters (only in the connection area), temperature-resistant seals, etc.

Porous aluminium oxide: Sheathed thermocouples for nuclear power stations (as it can compensate better for exposure to radiation in use than MgO can. Nowadays however, special MgOs can also be used at these locations) and in very rare cases also as heating elements, etc.

Spinel: Signal cables in neutron accelerators (as it decomposes less than MgO under strong neutron radiation), etc.

Hafnium oxide: Maximum temperature sheathed thermocouples, etc.

Silica: Intrinsically safe mineral-insulated cables in mining (as it possess a lower specific permittivity than MgO, and thus a lower electrical capacity is generated for each length unit of a cable. There is thus a lower risk of a spark, as a cable also acts as a capacitor), etc.

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As the specific properties of the materials (electrical properties in particular and thermal conductivity) are different depending on the materials, the temperature distribution in a heating element for example can also be set by using specific combinations of materials.

Manufacturing

The overwhelming majority of crushables are manufactured via extrusion, as it is mostly tubular components that are needed for later applications (Fig. 1). Depending on the geometry required, Rauschert can also manufacture components from the crushable ceramics MgO and steatite C230 by dry pressing (typically flat components), isostatic pressing (tubes with large diameters and narrow tolerances) or injection moulding (complex components). All three alternative forming methods to extrusion are already used in the large scale production of components from crushables. As these methods are of lesser importance, we will only focus on extrusion here.

Raw materials made of Fused Magnesia (also known as FM) are used for the manufacturing of ceramics from magnesium oxide, as it is only this material that has a low tendency to react with water. MgO reacts with water to form magnesium hydroxide ($Mg(OH)_2$). The reactivity continually decreases when moving from caustic calcined magnesia (CCM), via Dead Burnt Magnesia (DBM) to fused magnesia. MgO materials with different purities are used depending on the application. It should be stressed that it is less the MgO content itself, and more the type and the relationship of the impurities to each other that plays an important role in determining the electrical properties. Impurities such as boron (B) or sulphur (S) can cause problems in the later products in quantities as low as 30–50 ppm (these components will embrittle and/or corrode the heating conductor materials and will thus sometimes drastically shorten the life cycle of the heating elements). Other impurities such as SiO_2, Al_2O_3 or ZrO_2 will have a neutral effect, or will even improve the electrical properties, even at higher levels [2]. In the case of iron, it depends strongly on whether it is present as an impurity in the grain boundaries (and thus typically a negative effect) or whether it is finely dispersed in the structure of the grain (typically a neutral effect, or even a positive tendency in quantities up to 0,10 % [2]. High levels of purity in terms of iron content, e.g. 0,05 % or 0,02 % will provide no benefits in terms of the electrical properties and will merely drive the price of the materials drastically higher. The grain size of MgO is always a compromise between the later application – smaller grains are of course to be preferred for tubes with a small diameter – and the highest possible thermal conductivity and good electrical insulation capacity.

In order to be able to satisfy all applications, Rauschert has a variety of grain sizes in its product range, the smallest grain size is even suitable for producing sheathed thermocouples with an external diameter of 0,25 mm. For use in sheathed thermocouples, it must be ensured that there are no oversized particles present in the material, as even one single oversized particle will cause damage to the sheathed thermocouple and will thus be rejected by the processors of the ceramic.

The MgO material is plasticised with organic binders and water during preparation for production to create an extrudable mixture. The organic additive is selected to ensure that it can be completely removed during the ceramic firing.

The plasticised mixture is then pressed through a corresponding ceramic die using piston or screw extruders and processed to make endless strands. The design of the die has an enormous influence on the final contour accuracy of the extruded tubes. In particular, the position of the pins that later determine the location of the bore-holes is of great importance. Rauschert can guarantee a high level of positional accuracy here via special tool designs. As MgO reacts with water, which will ultimately lead to a strong hardening of the mixture after a few hours (setting!), all production facilities must be cleaned daily.

After extrusion the strangs are cut to length and slowly and carefully dried on appropriate dry underlays to avoid any tears. After drying, which can take up to a week for larger diameters, the dried strands are cut to the length and assembled on kiln furniture for firing. The goods are then fired in gas or electric kilns. In the case of crushables, it is normal to specify the strength specifically for each article. Mostly, the breaking load for an article is specified in N for a defined support distance spacing and a defined alignment of the article. Small fluctuations in the composition of the raw material and the grain size distribution within the tolerance limits are compensated for via an adjustment of the firing temperature. This ensures that uniform products are always produced for the customer.

After firing, an additional cutting process takes place if required, before the article is then subjected to 100 % to a sorting.

Moulding for other materials, such as porous steatite C230, is performed in a similar manner, however the influence of the composition and grain size is, however, lower here. Therefore, only two standard materials are used here at Rauschert. As steatite does not react with water and set, there is no daily and time-consuming cleaning work of the production facilities required for this material. The firing temperature for steatite is lower than that for MgO materials. All additional work steps for porous steatite C230 are carried out in a similar manner to the procedure described above.

Properties

Magnesium oxide (MgO) has a very high melting point at approximately 2800 °C. In mineralogical terms, it is known as periclase (there is only the one crystal structure known) and crystallises in the face-centred cubic system. The cleavage planes are thus defined and hence milled MgO grains typically possess a more or less cubic form. The density is specified as 3,55–3,65 g/cm³ [3].

As the most important properties of crushables in most typical applications are the electrical insulation capacity and the thermal conductivity, both of these should also be considered dependent on the temperature.

An overview of the electrical insulation capacity (caution: the conductivity value is given in [S/cm] in the chart) for several oxides important for ceramics is provided in Fig. 2. It is clear to see that the electrical conductivity increases with increasing temperature and, in turn, the electrical insulation capacity decreases.

The powder samples represented as dashes are relevant for the applications as crushables, the values for monocrystals

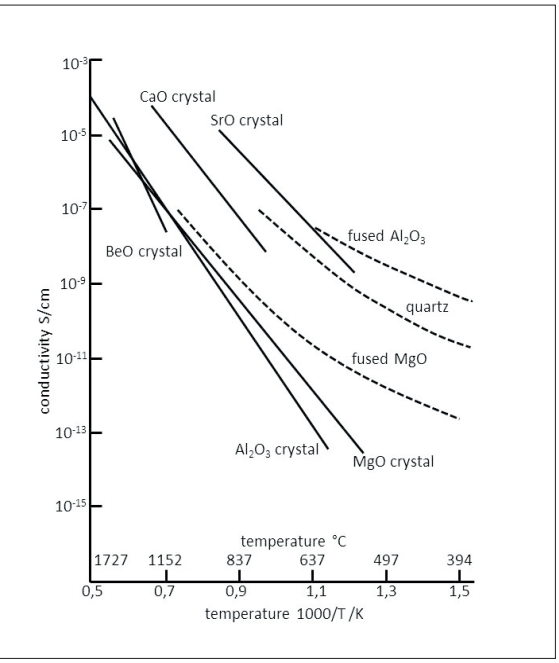

Fig. 2
Thermal conductivity of various oxides as a function of temperature [2]

that are also represented show the optimal level (that cannot be achieved in technical products). It is also clear to see that compacted MgO powder possesses a level of electrical conductivity that is between 100 and 1000 times less that of SiO_2 and Al_2O_3 at the same temperature.

An additional influencing factor on the electrical insulation capacity of MgO that should not be ignored is the grain size of the MgO. The finer the powder is milled, the lower the insulation capacity. This is shown in Fig. 3, where the grain size is represented as the specific surface area. The grain size of the powder decreases with increasing specific surface area. The temperature dependency of the electrical resistance that is described above can be read off clearly in this chart. The values represented are applicable for a packing density of approximately 70 % of the theoretical density [4].

As has already been mentioned, in most applications, the thermal conductivity of the crushable ceramics plays an important role. In principle, heat can be transported via three mechanisms:

- via thermal conduction
- via thermal radiation
- via convection.

The amount of convection can be ignored in ceramic bodies, as the pores are mostly very small. The main proportion of heat transfer takes place via thermal conduction. At increasing temperatures, the proportion of heat transfer via thermal radiation continues to increase.

Like electrical conductivity, thermal conductivity is also temperature-dependent, as shown in Fig. 4 [3]. It is clear to see that monocrystal MgO possesses the highest thermal conductivity of all of the typically used ceramics – BeO can largely be ignored, as it is considered to be highly toxic and its processing is strictly monitored. Powders in particular are considered to be very dangerous due to the risk of entry in the body. The conditions of the monocrystal also apply in principle for the multi-crystalline, porous crushable ceramics, i.e. with the same grain size and the same porosity, a crushable ceramic made from MgO will still possess a higher thermal conductivity than that of Al_2O_3, spinel or quartz for example. Of course, the thermal conductivity of the moulded body decreases due to the porosity and the many monocrystals, as pores have an insulating effect and the thermal transfer resistances from grain to grain also have to be added. This raises the question: What is preferable at the same packing density (= total porosity) of the ceramic: many small pores (a fine-grained raw material) or fewer but larger pores (= coarser raw material)? It should be noted once again that the total porosity and the packing density are the same. The answer is provided by Fig. 5: In particular at higher temperatures, it is more beneficial for the thermal conductivity if there are large pores present and large grains are used. The manufacturer of the ceramics can only influence the pore

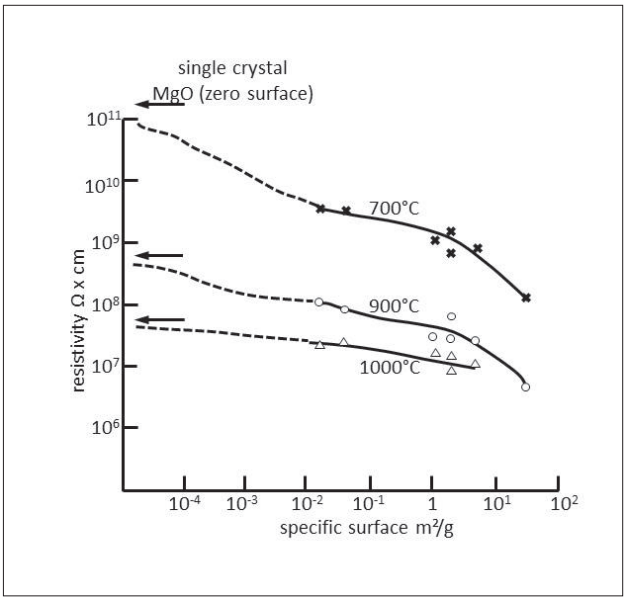

Fig. 3
Variation of resistivity of MgO as a function of specific surface and grain-size [2]

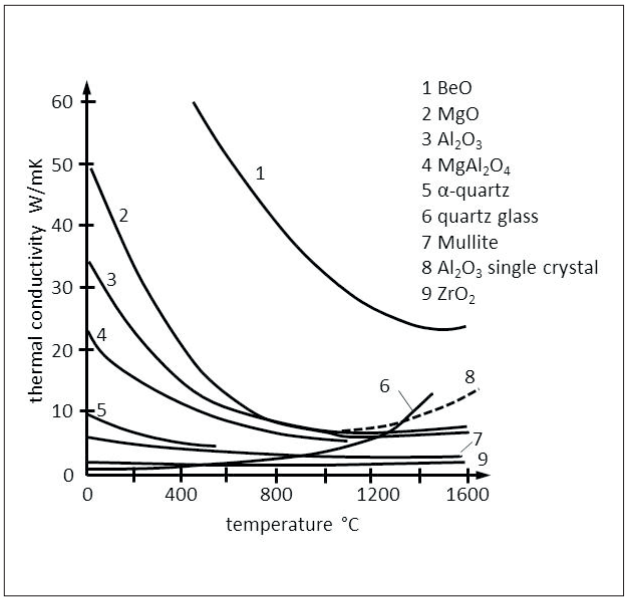

Fig. 4
Thermal conductivity of various non-porous materials as a function of temperature [3]

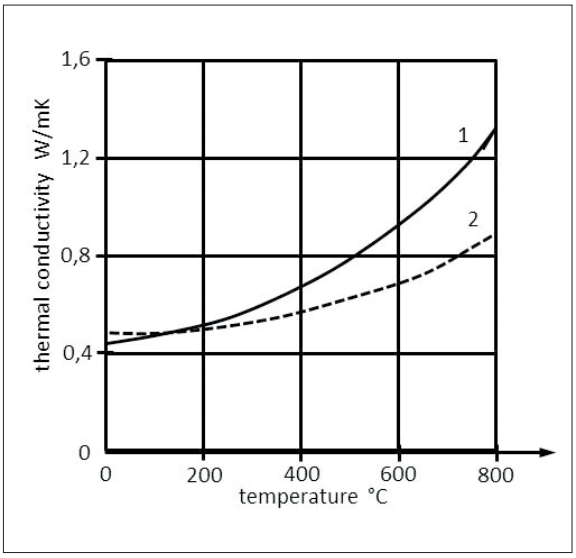

Fig. 5
Thermal conductivity as a function of pore-size and temperature [3]; both materials 1 and 2 have the same total porosity, but the mean pore-size of 2 is smaller than that of 1

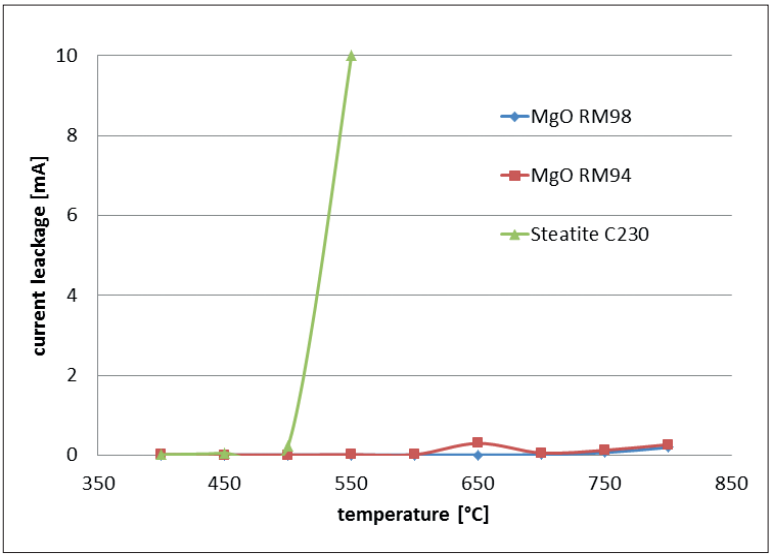

Fig. 6
Leakage current of MgO and porous steatite C230 as a function of temperature

size and the total porosity within certain limits by selection of the grain size of the raw material. The processor of the ceramics also has enormous possibilities to influence these properties during the compaction of the ceramics.

Alongside these effects, which in daily practice can only be separated from other effects in daily practice with great difficulty, the packing density and its reciprocal value, the porosity, also of course play an important role.

The aim should be to drive the packing density to be as high as possible in order to obtain the best possible level of thermal conductivity. In summary, the following statements may be made [3]:

- The proportion of thermal transfer via radiation increases significantly more quickly than that via thermal conduction with increasing temperature.
- The proportion of thermal transfer via thermal conduction reduces at a constant temperature with increasing total porosity → you should attempt to achieve the highest packing density possible.
- The proportion of thermal transfer via radiation is lower at a constant temperature with smaller pore sizes → You should attempt to achieve large pores rather than small pores; smaller pores are created by the use of fine-grained powder.
- Textures and preferred directions (mostly production-related) have an influence on the thermal conductivity, this can differ depending on the direction.

In addition to MgO that has been described in detail above, porous steatite C230 is often used in electric heating technology. It is a multi-phase material that consists of partly sintered steatite raw materials. Steatite consists of the natural materials soapstone (talc) with additives of clays and possibly BaO. The composition can vary depending on the materials used. The electrical insulation capacity of porous steatite C230 reaches such low levels at approx 500 °C (Fig. 6) that it can no longer be used in heating elements.

The thermal conductivity of porous steatite C230 is considerably lower than that of MgO, this is 1,5–2 W/m·K at 30–100 °C [1]. Nevertheless, this crushable has its own area of application. Steatite C230 is used:

- For applications which take place at temperatures under approximately 500 °C.
- It is installed at locations in heating elements where little heat should be emitted and where there should be thermal insulation, e.g. mandrels (see below).
- Due to the lower firing temperatures, lower raw material costs and simpler processing, it often offers a very large cost benefit. It is therefore used in combination with the highly thermally conductive MgO where possible.

An additional benefit of the most frequently used materials MgO and porous steatite C230 is their good cohesion when they are compacted during processing (see below). These crushables can only be removed from a metal sheath with a great deal of effort, while Al_2O_3 for example can be trickled out again easily. It is therefore only used in exceptional cases – particularly as it can offer no benefits in terms of thermal conductivity or its electrical properties for example.

Processing of crushable ceramics

Crushable ceramics are always inserted into metallic casings. There they form the electrical insulation between the heat conductors or the thermal element conductors, or between them and the metallic casing. The crushables must always be compacted to achieve their beneficial properties. The tubes and moulded parts supplied by Rauschert are just one preform that can be handled easily by the customer, but is also so soft that it will not be splintered or be irregularly crushed during the compaction. The heat conductors, thermal element conductors and other components will therefore be embedded with no damage. Three procedures are used for compaction:

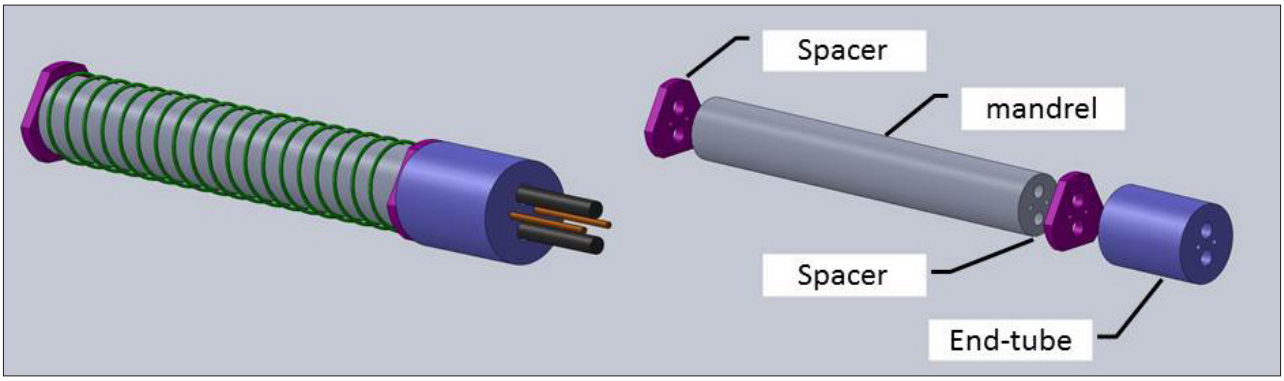

Fig. 7
Schematic design of a cartridge heater

- compaction by drawing;
- compaction by hammers/rotary swaging;
- compaction by rolling.

Compaction by drawing is used mostly in the manufacturing of sheathed thermocouples, heating cables and fire-proof cables. Therefore, Rauschert supplies tubes of corresponding cross-sections (most frequently with external diameters of approximately 15 mm, 20 mm or 25 mm) and with one, two, four or six boreholes, depending on the application and structural shape of the later cable. In exceptional cases, different numbers of bore-holes are used – items of up to 20 bore-holes have already been produced. The corresponding wires are threaded into the bore-holes, then the ceramic tube with the wires inserted is pushed into a metallic cladding tube. This is then sealed at both ends and then drawn through a nozzle which will reduce the external diameter of the cladding tube.

In this process, the ceramic tube will be crushed completely into powder and will exert its own pressure on the wires in the bore-holes, leading to a reduction in their cross-section – the same will also happen to the insulation and the cladding tube. The length of the material will increase due to the reduction of the cross-section after the final density of the insulation has been reached – similar to wire drawing. The cladding material will become brittle due to the forming, the cable must therefore be soft-annealed via intermediate annealing. The next step to reduce the external diameter then takes place. The final diameter of the cable desired is achieved via step-by-step drawing and intermediate annealing of the cable (sheathed thermocouples, heating cables, fire-proof cables, etc.). Using the special grain sizes from Rauschert, even sheathed thermocouples with an external diameter as low as 0,25 mm can be produced.

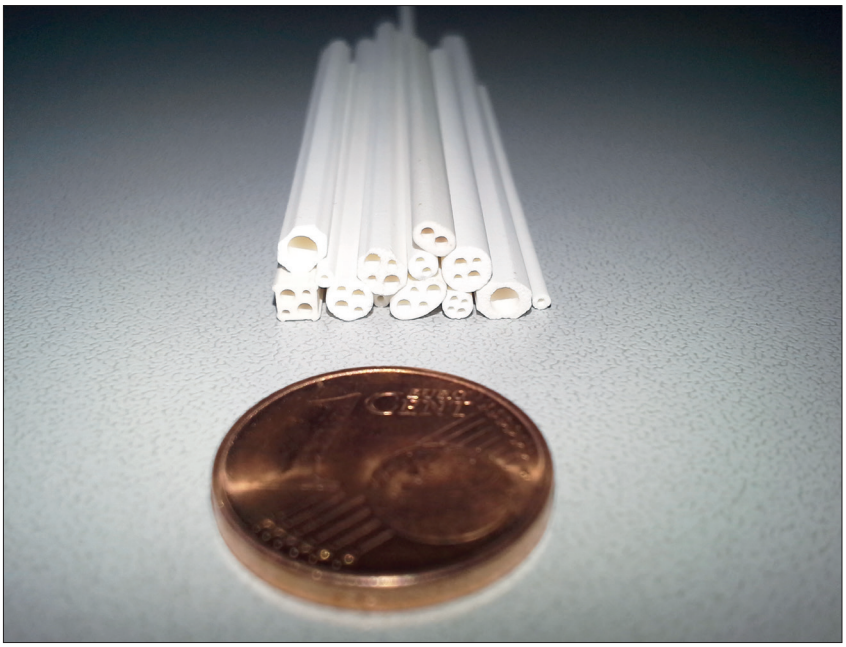

Fig. 8
Crushable tubes for micro-coiled heaters manufactured by Rauschert

Heating elements and coil cartridge heaters/tubular cartridge heaters as well as special thermocouples are compacted using hammers. The procedure is also known in cold forming under the term rotary swaging. To produce high performance heating elements, a thin heat conductor wire is first wound around a mandrel (Fig. 7). Metal rods are inserted through the larger boreholes in the centre of the mandrel via which the power is supplied. The heat conductor wire is connected to these rods. Targeted distribution of power can be set along the length of the heating element by varying the winding distances. The mandrel is then centred using a thin-walled tube or with the help of spacers in the cladding tube. Any remaining gaps are filled with a free-flowing MgO sand, the heating element is then sealed. The external diameter is reduced by approximately 20 % by the rotary swaging. During this process, the crushable ceramic in the inside breaks into the initial grain size and this seals the heat conductor and any thermocouple that has been installed. Electrical insulation is thus ensured and, at the same time, good heat transfer from the heat conductor through the ceramics to the metallic cladding tube of the heating element is ensured. During the reduction

of the external diameter, the parameters must be coordinated with each other such that a certain lengthening of the element occurs. It is then ensured that the maximum compaction of the crushable ceramic has taken place. To manufacture tubular cartridge heaters, a heating coil is first wound around a mandrel. This is then removed to separate the individual coils from each other. Small, thin-walled tubes with one or more boreholes are then pulled over the coils (Fig. 8) and then pushed into the metallic cladding tube. This cladding tube is then compacted using hammers, the MgO is thus moved between the heating coils and into the empty interior space. After this process has been completed, the heating coil is completely embedded in MgO. These tubular cartridge heaters can be bent into astoundingly tight radii, you can even make a knot with them. As long as these bends don't go below the certain bending radii specified by the manufacturer, the safe operation of the tubular cartridge heaters is still ensured even after they have been bent. The granulation of the MgO insulation is defined such that the maximum level of electrical insulation is ensured, but that bending of the cartridges is still permitted. The powder flows when the cladding tube is bent and ensures the dissipation of heat outwards and the electrical insulation between the heating coils themselves and between the heating coils and the cladding tube.

Tubular heating elements and other relatively long heating elements, e.g. panel radiators for point heating devices, are often compacted by rolling. The structure is similar to that of tubular cartridge heaters, only the diameter is larger. Often, crushable ceramics are dispensed with completely and the cladding tube is filled with free-flowing MgO sand when it is stood upright with heating coils centrally fixed via lances. After the sealing, the external diameter is reduced by using several profile rollers, where the space between the rollers becomes compressively smaller. The heating elements can also be bent after compacting here.

The highest levels of compaction are generally achieved by hammers, as is demonstrated in [5]. The density of insulation in sheathed thermocouples is there. Individual cases have demonstrated up to 90 % of the theoretical density. These densities are not achieved via drawing.

Applications

A majority of crushables are used in electric heating technology. MgO takes advantage of its high thermal conductivity and its good electrical insulation capacity at high temperatures. At lower temperatures, porous steatite C230 can also be used; alternatively, porous steatite C230 can also be used. Alternatively porous steatite C230 can also be used to thermally insulate certain areas of a heating element in a targeted manner, as its thermal conductivity is only approximately 1/20th of that of MgO. It should be noted here that porous steatite C230 is only suitable for compacting via swaging or rolling, it is not suitable for compacting via drawing. Steatite flows much more poorly than MgO during compaction by drawing. Furthermore, the annealing temperatures of many cladding materials are too high for steatite; steatite would sinter again during the annealing process and would thus harden.

Magnesium oxide is the standard material for sheathed thermocouples. For maximum temperature thermocouples, hafnium oxide is used in a similar manner, but such applications are somewhat rare. Cables with mineral insulation are also used for the manufacturing of signal cables for the transmission of measurement values in extremely rough environments (e.g. in steel works) or areas with particular safety requirements (e.g. fire-proof cables in tunnel structures).

Crushable ceramics that are based on magnesium oxide and fully stabilised zirconia are used in high temperature-high pressure experiments, for example in geology. The conditions in the earth's mantle are recreated, in order to determine the mineral phases under high pressure for example. Crushables are used in these cases for isostatic pressure transfer to the test sample, as these materials do not themselves melt (which would invalidate the results) due to their high melting points. The heat balance for the experiment is created by the combination of MgO with high thermal conductivity with zirconia which has a low thermal conductivity. MgO is used where heat has to be transferred and zirconia in locations that have to be insulated.

Detachable high temperature feedthroughs may be implemented by using compression fittings based on porous steatite C230, or even unfired steatite. Here, sheathed thermocouples are guided through the inside of a steatite tube and this tube is then inserted into a compression fitting. When the compression nut is tightened, the steatite is compacted and this ensures the hermetic closure of the feedthrough. If this feedthrough has to be opened again, then the compression nut is detached again, the thermocouple is removed and freed from the compacted steatite. A new steatite tube must always be used in order to be able to install the thermocouple again.

Incidentally, the lambda sensor is also sealed against the outside space using a mineral seal that is based on steatite – in this case however it is not intended that this connection should also be able to released again. Crushables represent a wide area of application but are a very specialised material group within the field of ceramics. We come into contact with them, directly or indirectly, almost every day without realising it.

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