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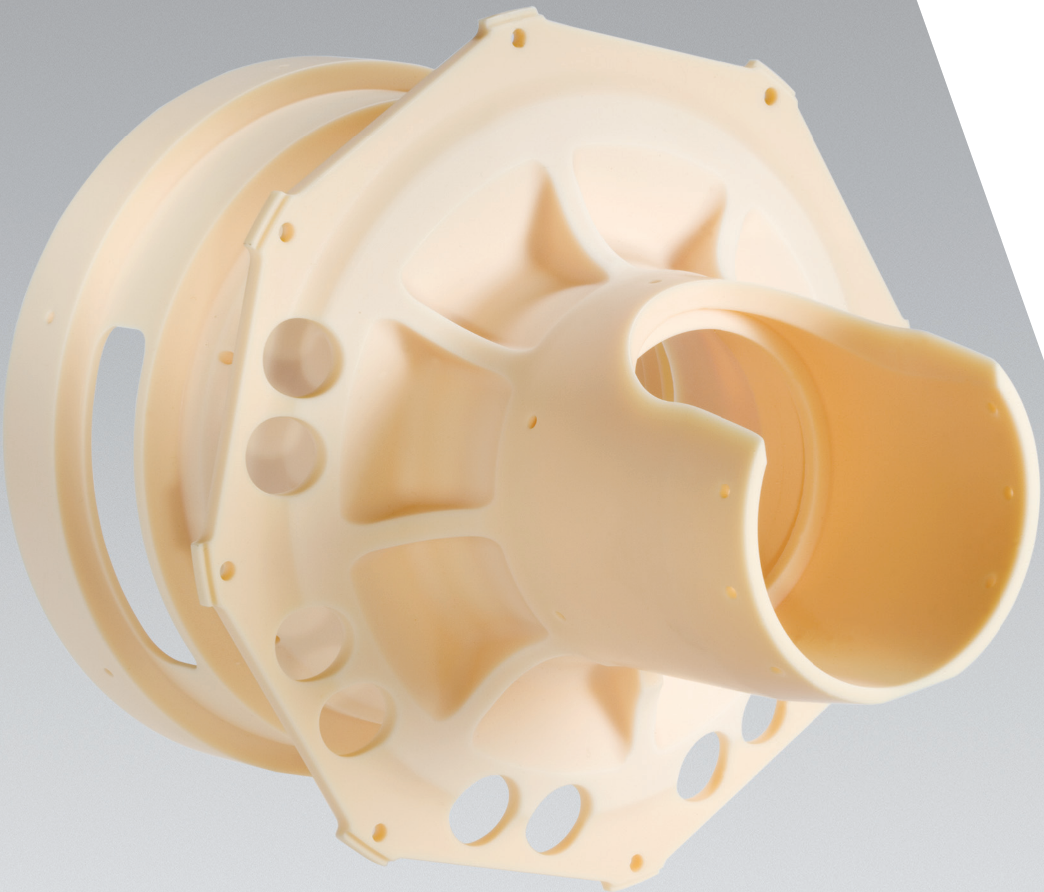

FRIATEC

WHITE PAPER
HIGH-PERFORMANCE CERAMICS

Key components for efficient improvement of
technical systems due to combination of specific properties

www.friatec.de

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1. INTRODUCTION

The requirements imposed on machine components, special purpose machines and mass produced articles are continually increasing with the development of technological concepts. Specific property profiles are often required but cannot be fulfilled by conventional materials. Alternatives are needed when optimisation potential of design and construction is exhausted and materials, such as metal and plastic, have reached their efficiency limits.

Technical ceramics reveals specific property profiles which often strongly influence the overall construction and provide completely new conceptional approaches.

In many cases ceramic components used in pumps, mechanical and thermal process engineering or measuring and sensor technology allow the efficiency of the complete systems to be significantly increased. The special properties of ceramic material solutions also allow process efficiency, process management precision or the general lifetime of technical systems to be improved.

Technical ceramics can therefore be the key to further enhancement of economic efficiency and durability of products and processes, thus contributing to the development of sustainable technology

2. TECHNICAL CERAMICS

2.1 MATERIAL OVERVIEW

The materials used in technical ceramics are basically grouped as follows:

- Silicate ceramics
- Oxide ceramics
- Non-oxide ceramics

Silicate ceramics are the oldest form of ceramics. Components are added to natural raw materials such as clay to create a specific impact on material properties. The natural origin explains the low price level of this group of materials, which includes porcelain, stoneware, earthenware, steatite, cordierite and mullite.

This document will not go into detail about this material group, even though the growth of FRIATEC AG at its site in Mannheim is based on stoneware. This type of ceramic has been the material of choice used in sewer systems and chemical plants for many decades.

Unlike silicate ceramics, **oxide ceramics** are predominantly materials with a single-phase structure (> 90%). The use of synthetic powders and extremely high sintering temperatures allows the creation of components with such powerful microstructures. Powder preparation, processing and use of energy exceed silicate ceramic materials significantly, which inevitably affects production costs. Important materials in this group are aluminium oxide, zirconium oxide, magnesium oxide and titanium oxide.

Non-oxide ceramics, like oxide ceramics, are manufactured from synthetic powders as single-phase materials. These are highly priced materials and their manufacture involves considerable expense and effort. Outstanding materials in this group are silicium carbide, silicium nitride, aluminium nitride as well as boron carbide and boron nitride.

The following focuses on oxide ceramics, the most important of which are aluminium oxide (Al_2O_3) and zirconium oxide (ZrO_2).

2.2 MATERIAL PROPERTIES OF HIGH-PERFORMANCE CERAMICS

When compared to traditional clay-based ceramics, oxide ceramics and non-oxide ceramics are generally referred to as high-performance ceramics. According to ISO 15165, these high-performance ceramics are defined as “sophisticated and highly efficient material which is mostly non-metallic and inorganic and which has several well-defined properties”.

Some outstanding properties of high-performance ceramics are:

- Resistance to wear
- Extraordinary hardness
- Low specific weight
- Very good corrosion resistance to acid and alkaline solutions
- Resistance to high temperatures up to 1950 °C

These exceptionally attractive material properties are accompanied by the economic parameter “cost”. Cost benefits resulting from the ceramic part should at least match this additional price. Sometimes it might be necessary to adjust the construction which might present a challenge for the engineer. For the ceramic manufacturer, the production facilities are extremely capital-intensive and the development of materials is complex. The required firing processes at temperatures of approx. 1800 °C are demanding and energy-intensive. Hardness and wear resistance of technical ceramics make further processing of the sintered products extremely time-consuming.

The higher price pays off if the application requires several outstanding properties from the component. In addition to good gliding properties, bearings often need to be resistant to additional corrosive attacks or lack of sufficient lubrication. Sometimes electric insulation might be necessary or the product must be protected from contact with nickel-containing metals. In such situations, conventional and economic materials reach their limits. Applications with extremely complex requirements imposed on their profiles often pave the way for an effective use of oxide ceramic components.

The following chapters provide more details of some of the main properties of high-performance ceramics.

2.2.1 CORROSION RESISTANCE

Compared to metallic materials, oxide ceramics are considered resistant to chemical attacks particularly with regard to acid and alkaline solutions. Products made from oxide ceramics are used in chemical plants for instance, as plastic coatings and metallic materials provide insufficient resistance to corrosion in these applications.

Fig. 1: Float bodies for flow monitoring made of aluminium oxide FRIALIT F99.7

Even if the pure basis oxide is exceptionally resistant to corrosion, under certain conditions highly pure ceramics with a purity of > 99.5% can also be subject to corrosion. The chemical composition as well as the phase distribution and structural conditions are decisive for the occurrence and degree of corrosion. Therefore, it is possible that even ceramics with nominally identical purities exhibit a completely different corrosive behaviour depending on their origin.

When examining the structures of densely sintered aluminium oxide ceramics, larger crystallites and a silicium oxide-rich phase can be seen running from inside to outside on the grain boundaries throughout the entire structure (fig. 2a). Silicium oxide is significantly less resistant to chemical attack than aluminium oxide particularly when additional impurities from alkalis or alkaline earth oxides are present in the glass.

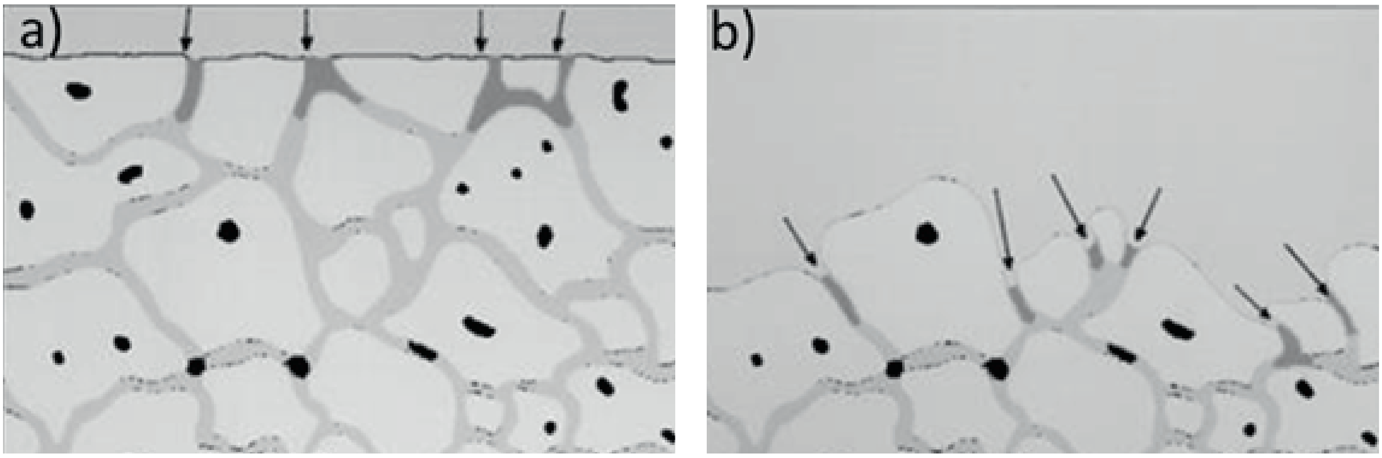

Fig. 2: Microstructure showing beginning corrosion (a) and extensive corrosion (b)

If a corrosive attack occurs at this glassy phase, it might not show initially because the width of these intergranular zones is mostly less than 1 µm. However, corrosion can migrate right into the ceramic body along the grain boundaries which ultimately leads to exposure of primary grains (fig. 2b). Over a longer period, this can lead to complete destruction of the material by dissolution of the glassy phase and dissolving of the crystallites. This process is described as intergranular corrosion; the higher the proportion of silicium oxide in the structure, the more intensive the corrosion.

Therefore FRIATEC produces highly pure and mostly silicium oxide-free materials. Internal test procedures ensure this high standard.

For more details concerning the corrosion resistance of FRIALIT-DEGUSSIT oxide-ceramic materials under different conditions, please visit www.friatec.de.

2.2.2 RESISTANCE TO HIGH TEMPERATURES

Ceramic materials play a decisive role in high-temperature applications with continuous operating temperatures ranging from 180 °C to well over 1200 °C. Due to these extreme temperatures, it is impossible to use plastic materials. Many materials are present as molten mass or even steam and when temperatures rise, metals lose their strength. This is a clear distinction between ceramic materials and metallic materials. The bending strength of silicium nitride and zirconia, for instance, can be compared to that of steel and remains almost unchanged at temperatures up to 1000 °C. However, depending on the alloy, the bending strength of steels already decreases at temperatures of 300 °C and over.

One of the oldest fields of application of ceramic is high-temperature measuring technology where it is used in thermocouple protective tubes at temperatures over 1900 °C (see fig. 3). The good high-temperature properties are based on the high melting point of pure oxides: 2050 °C for aluminium oxide and 2600 °C for zirconium oxide.

Fig. 3: Thermal protection tubes made of aluminium oxide DEGUSSIT AL24 for measuring and control technology

These properties can be found in the components only if a highly pure, high-quality base material is used. Electrical insulation properties, wear resistance and stability are maintained up to 1800 °C, especially for aluminium oxide. Improved stability is attainable through higher porosity.

However, if higher requirements for thermoshock resistance are imposed, silicium nitride or a porous aluminium oxide material with good resistance should be taken into consideration. Basically, large and thick-walled components are more sensitive to temperature changes than small and thin-walled shaped bodies.

Modern processing methods allow for a variety of geometries from these highly durable materials for plant and machine engineering.

2.2.3 HARDNESS AND WEAR RESISTANCE

Ceramic properties are determined by the choice of chemical elements, the type of bond and crystal structure. The metallic bond occurs in metals, having atomic cores surrounded by electron gas which explains their ductility and electrical conductivity, while ionic and covalent bonds occur in ceramics giving rise to strong bonding forces. This explains the high level of Young's Modulus, hardness and melting point, the low thermal expansion as well as the brittle fracture behaviour. There is an additional mechanism in ceramics based on zirconia in particular, which has a positive influence on ceramic properties when applied correctly. A phase transformation and the development of different phases may give rise to a transformation toughening resulting in an extremely high bending strength.

There are two basic mechanisms of tribological wear - impingement wear and friction wear. With impingement wear, particles impact and erode the surface. Friction occurs when two bodies rub against each other implying punctually high local stress and pressure which results in shear stress, fracture and high local temperatures. High temperatures may even lead to fusing or chemical reactions resulting in destruction of the surface. This occurs in such devices as rotating shafts, valve seats and metal extrusion and drawing dies, i.e. components which are well suited to the use of ceramic due to its high strength.

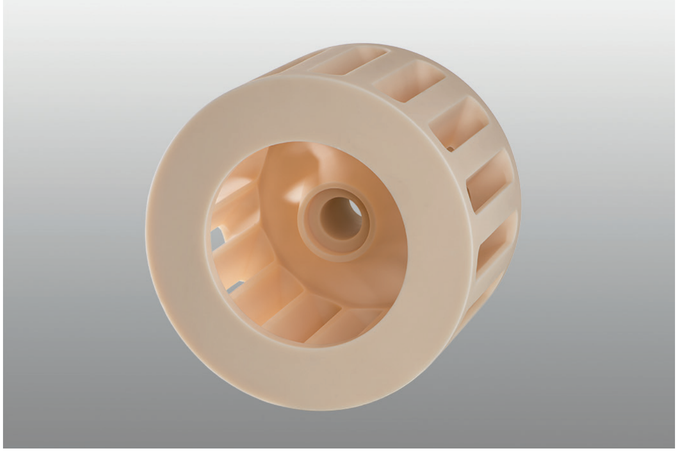

Fig. 4: Separator wheel made of aluminium oxide FRIALIT F99.7

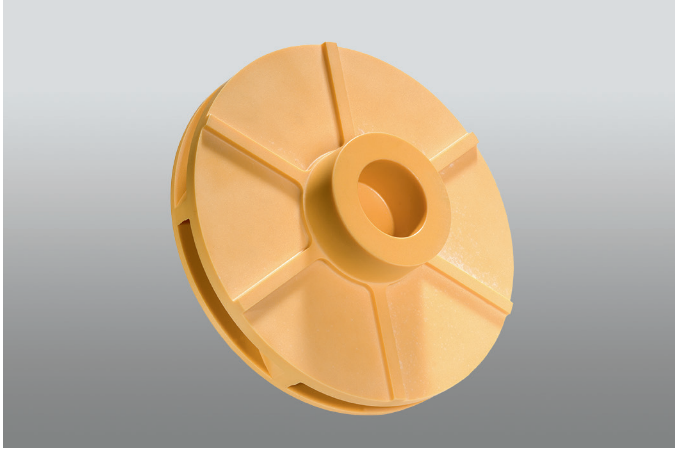

Fig. 5: Pump wheel made of zirconia FRIALIT FZM

2.2.4 ELECTRICAL INSULATION PROPERTIES

The electrical insulation property of components such as electrical feedthroughs and insulating parts is an important requirement for the functionality of many technical devices. The wide range of applications of such components meets a variety of variations of insulation materials attainable. Oxide ceramic materials are usually applied when property profiles are required that cannot be provided by cheaper materials.
One example is the requirement for high electrical resistance and high mechanical strength at operating temperatures above 500 °C and at the same time resistance to fast temperature changes, high mechanical strength and/or corrosive stress. Aluminium oxide ceramic is often the only insulation material meeting these requirements.

Fig. 6: Cable end plugs made of aluminium oxide FRIALIT F99.7

3. CERAMIC COMPOSITES

The successful use of ceramic components always depends on precise knowledge of application parameters and the installation situation. Besides thermal and mechanical stresses affecting the material, it is important to know how the ceramic is integrated into the overall construction.

3.1 POWER AND FORM BONDING METHODS

Methods such as the manufacture of shrunk ceramic-metal joints are applied whenever possible because they provide high reliability under operational conditions with relatively little technical effort.

The introduction of ductile intermediate layers between the ceramic and metal ensures firmly sealed joints in individual cases. As a typical example, fig. 7 shows a locking ring made of zirconium oxide (material type FRIALIT FZM) shrunk into steel.

Internal studies show that the extrusion of ceramic shrunk into a steel tube with a diameter of 19 mm and a length of 17 mm at room temperature requires a force of at least 25 kN.

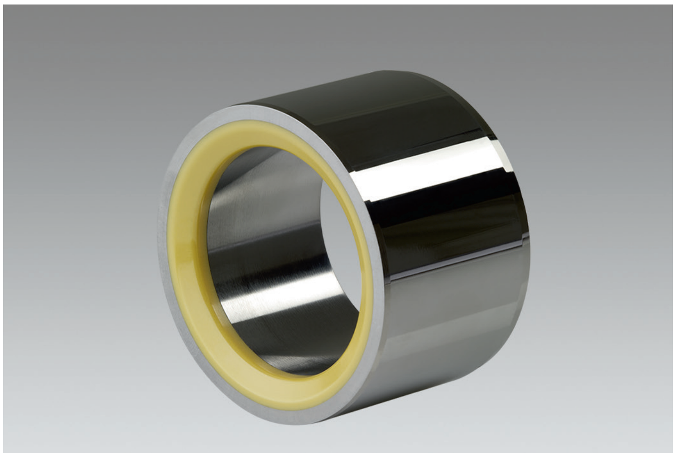

Fig. 7: Rings and sleeves made of zirconium oxide FRIALIT FZM, shrunk into steel

3.2 COHESIVE BONDING METHODS

3.2.1 ADHESIVE JOINING USING ORGANIC ADHESIVES

This joining technique is used mainly for applications requiring high joint strength at operating temperatures around 150°C and when shrunk joints cannot be used, for example, due to constructional reasons. The shear strength of these composites is 50 MPa at room temperature when specific inorganic adhesives are used in connection with a construction suitable for adhesion.

One typical product manufactured with adhesive joining is the pump piston made from Al_2O_3 ceramic (material type FRIALIT F99.7) as shown in fig. 8 combined with stainless steel.

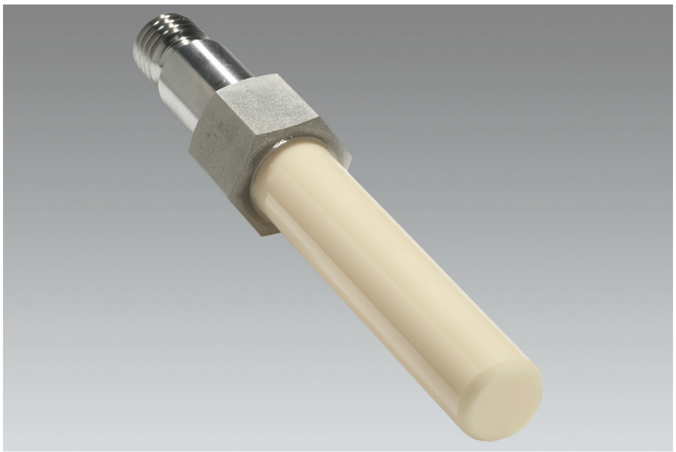

Fig. 8: Glued composite made of aluminium oxide FRIALIT F99.7 pump piston with stainless steel

3.2.2 BRAZING USING GLASS BRAZES

This joining technique is based mainly on the use of glass brazes with a thermal expansion matched to the ceramic as glass shows no metallic ductile properties. Strengths of 100 MPa can be easily achieved at room temperature with ceramic-ceramic-joints.

The current technology limits the maximum operating temperature of glass-brazed ceramic-ceramic-joints to 1100 °C in air. Fig. 9 shows an example of a construction that can be used at this temperature level.

Fig. 9: Glass-brazed ozone generator made of aluminium oxide FRIALIT F99.7

3.2.3 CO-FIRING AND DIFFUSION WELDING

The co-firing technique is used for example in the manufacture of measurement cells for magnetic-inductive flow meters. A Platinum-cermet electrode is joined with the ceramic to ensure high vacuum tightness.

When a pressure of 60 bar is applied to the inside of the tube, tubular measurement cells made of FRIALIT FZM with cermet electrodes arranged in the centre, leakage rates are $< 10^{-10}$ mbar·l/s for Helium as test gas.

A pressure of > 1000 bar must be applied for the measurement cell in fig. 10 to burst. Parts that burst in such tests do not show any predominant fracture in the cermet region indicating that low-stress conditions prevail there.

Sometimes pure ceramic components require structures which can only be manufactured using rather difficult and expensive methods due to their high degree of complexity.

If material of the same type is required, diffusion welding is the only practicable option for solid-bonded joining of components. The pump impeller made of FRIALIT F99.7 shown in fig. 11 was manufactured using this technique.

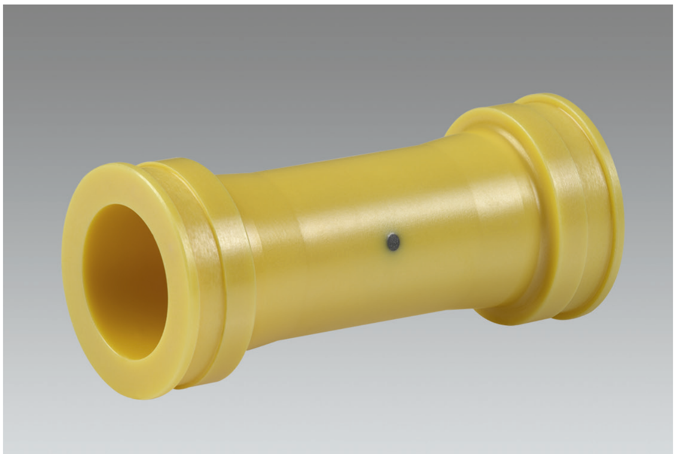

Fig. 10: Measurement cell made of zirconia FRIALIT FZM for magnetic-inductive flow measuring

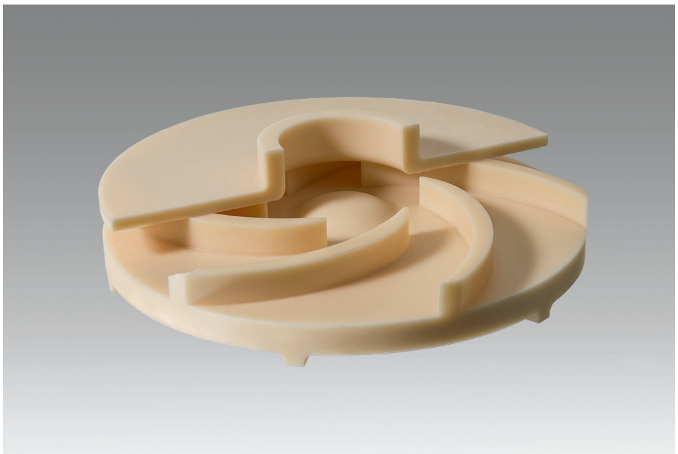

Fig. 11: Diffusion welded pump impeller made of aluminium oxide FRIALIT F99.7

3.2.4 BRAZING USING METALLIC BRAZES

For complex applications in electrical engineering equipment and plants, the requirements imposed on the ceramic-metal-joint is often a combination of high insulating capacity of the ceramic material, high vacuum tightness and high mechanical strength at temperatures above 500 °C. Al_2O_3 ceramics joined with various types of metal have now been established for decades.

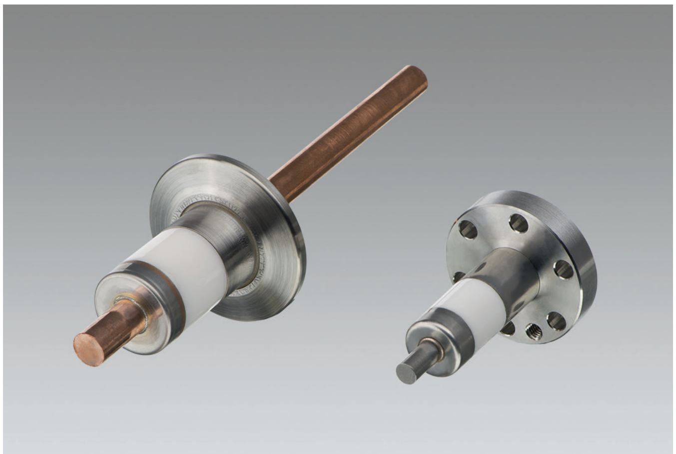

Fig. 12: Conventionally brazed UHV feedthrough made of aluminium oxide FRIALIT F99.7

3.2.5 BRAZING USING THE MoMn-METHOD

The classical production technology for electrical feedthroughs and insulating components with the properties described above is based on the molybdenum-manganese method, which was developed during the first half of the last century. The starting point for this process is a powder mixture composed of molybdenum, manganese and silicate additives, which are rendered into a pasty form by adding an organic binder. When the viscosity of this paste is adjusted, it can be applied to the Al_2O_3 substrate. The melt hardens as it cools down from the curing temperature resulting in a solid-bonded base layer on the surface of the ceramic.

As the majority of commercial flux-free vacuum brazes do not sufficiently wet this layer, it is generally coated with a few µm nickel using a galvanic method. This coating can be brazed to the metal parts e.g. in a inert gas atmosphere or in a vacuum with a sufficiently low residual pressure. Silver-copper-eutectic is the brazing material used.

Fig. 13 shows a cross-section through FRIALIT F99.7 ceramic brazed with material 1.3917 using the method described. Tensile tests show that this material combination results in strength values in excess of 100 MPa (according to DVS information sheet 3101).

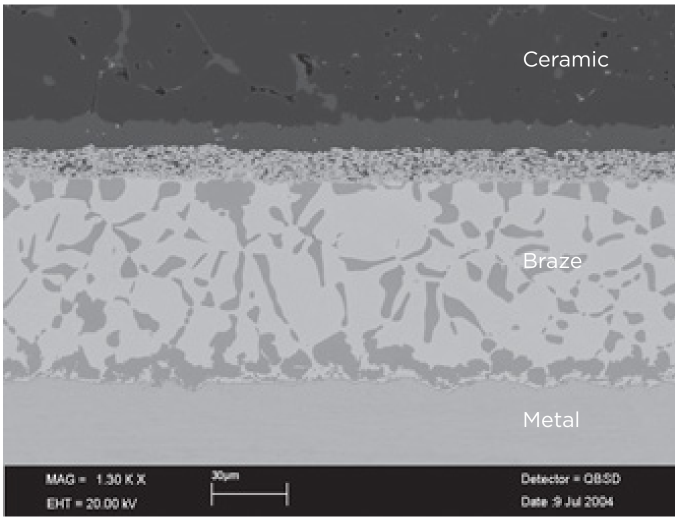

Fig. 13: Cross-section of a metallised and hard-brazed Al_2O_3 ceramic

3.2.6 ACTIVE BRAZING

For approx. 20 years, brazing materials with a content of < 5 % of a so-called active element such as Ti or Zr have been used for direct brazing of Al_2O_3 and ZrO_2 ceramics with a metal component without need for base metallisation.

However, brazing using active brazes can only be used effectively when carried out in an inert gas atmosphere or vacuum. Otherwise, the ceramic partner will not be sufficiently wetted by the braze due to the reaction of the active metal with the furnace atmosphere. Strength values of actively brazed composites match the level of hard-brazed, pre-metallized components. Active brazes, however, cannot be used as widely as standard vacuum hard brazes with classical MoMn-methods, because they remain inside the braze depot during the brazing process.

In order to achieve leakage rates of < 10^{-9} mbar·l/s for Helium in ceramic-metal joints, the brazing firing must be carefully controlled in order to avoid brittle phase formation.

Active brazing is necessary for brazing zirconium oxide as the classic metallisation method cannot be be applied in this case.

4. FRIALIT-DEGUSSIT HIGH-PERFORMANCE CERAMICS FOR YOUR APPLICATION

The shape and size of machine elements made of ceramic differs from its corresponding metallic element. The meticulous reproduction of a wooden bridge using concrete materials would no more meet the material-specific properties than the simple ceramic copy of a metal part. The construction has always significantly taken into consideration the chosen material and this also applies to ceramic materials.

Table 1 shows examples of the important material characteristics of some FRIALIT-DEGUSSIT high-performance ceramics.

Users often explore new ground when dimensioning constructions suitable for ceramics. This requires comprehensive support from the ceramic manufacturer to produce a construction that fulfils ceramic requirements and the required function, at the same time allowing cost-efficient manufacture of the component. Therefore, application engineers in the ceramic industry are often encouraged to carry out in-depth studies of the tasks imposed by the customer's construction design.

Tolerance settings, for instance, strongly influence hard machining required for a component. Fabrication tolerances ranging from ± 2–5 % can be realized without cost-intensive finishing. Consequently optimized constructions apply tolerances and surface requirements derived from a minimal effort in grinding. It is worthwhile carefully investigating saving potentials and grinding treatment of the construction. Grinding expenses can very often exceed the material costs for high-precision parts.

Quantity is an important consideration when choosing the manufacturing method. Automatic pressing and injection moulding are suitable for shaping processes for quantities of more than 800 pieces/batch. Set-up and tooling costs are not profitable for smaller batches. Shaping possibilities as well as constructive dimensioning and layout depend on the process used. A cast component also differs from a trimmed or turned part when it comes to metallic materials.

For this reason, it is important that the user and engineer know the production capabilities in order to successfully coordinate economic production methods with given requirements.

Properties	Unit	DEGUSSIT AL24	FRIALIT F99.7	FRIALIT FZT	FRIALIT FZM	DEGUSSIT FZY
Main components	-	α - Al_2O_3	α - Al_2O_3	α - Al_2O_3, ZrO_2	ZrO_2, MgO	ZrO_2, Y_2O_3, Al_2O_3
Purity	Weight-%	> 99.5	> 99.5	> 99.5	> 99.7	> 99.7
Density	g / cm³	> 3.4	≥ 3.90	≥ 4.05	≥ 5.7	≥ 5.5
Open porosity	Vol.-%	≤ 5	0	0	0	0
Average crystal size	µm	40	10	5	50	30
Bending strength σ_m	MPa	150	350	460	500	400
Compressive strength	MPa	1000	3500	3000	2000	2000
Maximum operating temperature in air	°C	1950	1950	1700	900	1700
Coefficient of linear thermal expansion (20 - 1000 °C)	10^{-6} / K	8.2	8.2	8.3	10.6 (20 - 900 °C)	10.9
Thermal conductivity	W / (m * K)	27.8	34.9	25 (100 °C)	3	2.5 (100 °C)

Table 1: Excerpts from FRIALIT-DEGUSSIT high-performance ceramics material data sheets. Basically, the preliminary observations in DIN 40680 apply to the property values indicated in the table, i.e. the values only refer to the samples for which these values had been measured. They can only be applied to a limited extent to other shapes. The values indicated are intended as reference values. They refer to temperatures of 20 °C unless otherwise indicated.

FRIALIT®-DEGUSSIT® HIGH-PERFORMANCE CERAMICS
CERAMIC INNOVATIONS SINCE 1863

FRIATEC manufactures components made of high-performance ceramics according to customer specifications, as well as a comprehensive standard program.

An experienced team of innovative application engineers and resourceful production specialists alongside painstaking quality control supports our customers in their choice of ceramic material, design and project execution. More than 150 years of experience in the field of ceramic manufacturing and our individual brand of materials, combined with innovative engineering, form the pillars of our company's successful development.

Our products, made of aluminium oxide, zirconium oxide, silicon carbide and silicon nitride, are used predominantly in the following areas:

ELECTRICAL ENGINEERING

- Single and multiple feedthroughs
- High-pressure feedthroughs for onshore/offshore technology
- Insulation tubes for liquids, gases and ultra-high vacuum - highly temperature resistant up to 1950 °C
- Standoffs
- Accelerator components
- Sensor components for pressure, temperature and oxygen levels, etc.

HIGH-TEMPERATURE TECHNOLOGY

- Tubes and insulating rods for the protection and insulation of thermocouples
- Tubes for gas inlet and outlet
- Grooved pipes and heating tubes for the construction of electric furnaces
- Diffusion tubes for the semiconductor industry
- Multiple capillaries
- Crucibles, boats, combustion trays and plates

MECHANICAL ENGINEERING

- Pistons for dosing pumps (fitted piston/cylinder units
- Plungers for high-pressure pumps
- Spacer cans for the chemical industry
- Glide rings, bearings, shaft protection sleeves
- Nozzles
- Shaped parts for heavy wear
- Drawing cones and guide elements for the wire industry

SURFACE FINISHING

- Fine grinding tools for surface finishing of ultra-hard materials in different shapes and dimensions

UTILITIES & INDUSTRY

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