Technical Paper | July 2013
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FRIALIT®DEGUSSIT®
Oxide Ceramics

Oxide-ceramic products for high-temperature technology

FRIATEC

Introduction

Products made of oxide-ceramic materials have for decades been the acknowledged standard for high-temperature technology in industry and research institutions. The classic oxide-ceramic material used in these areas of application, Al_2O_3, is virtually unrivalled due to its favourable price/performance ratio.

This results from the particular combination of high availability of suitable materials around the world at comparatively moderate prices, combined with a range of properties in the ensuing products that can fulfil even the most extreme and complex technical demands.

For this reason, the oxide-ceramic products used in technology today are generally made of Al_2O_3 ceramics.

For around 30 years there has been an ever-increasing demand for densely sintered Al_2O_3 ceramics for special applications in the high-temperature field as, due to their electrical properties, these materials have generated increasing interest, especially in the area of measurement and control technology.

This paper will present some special properties of these two material groups with regard to their implementation at high temperatures.

1. Process technology and quality assurance

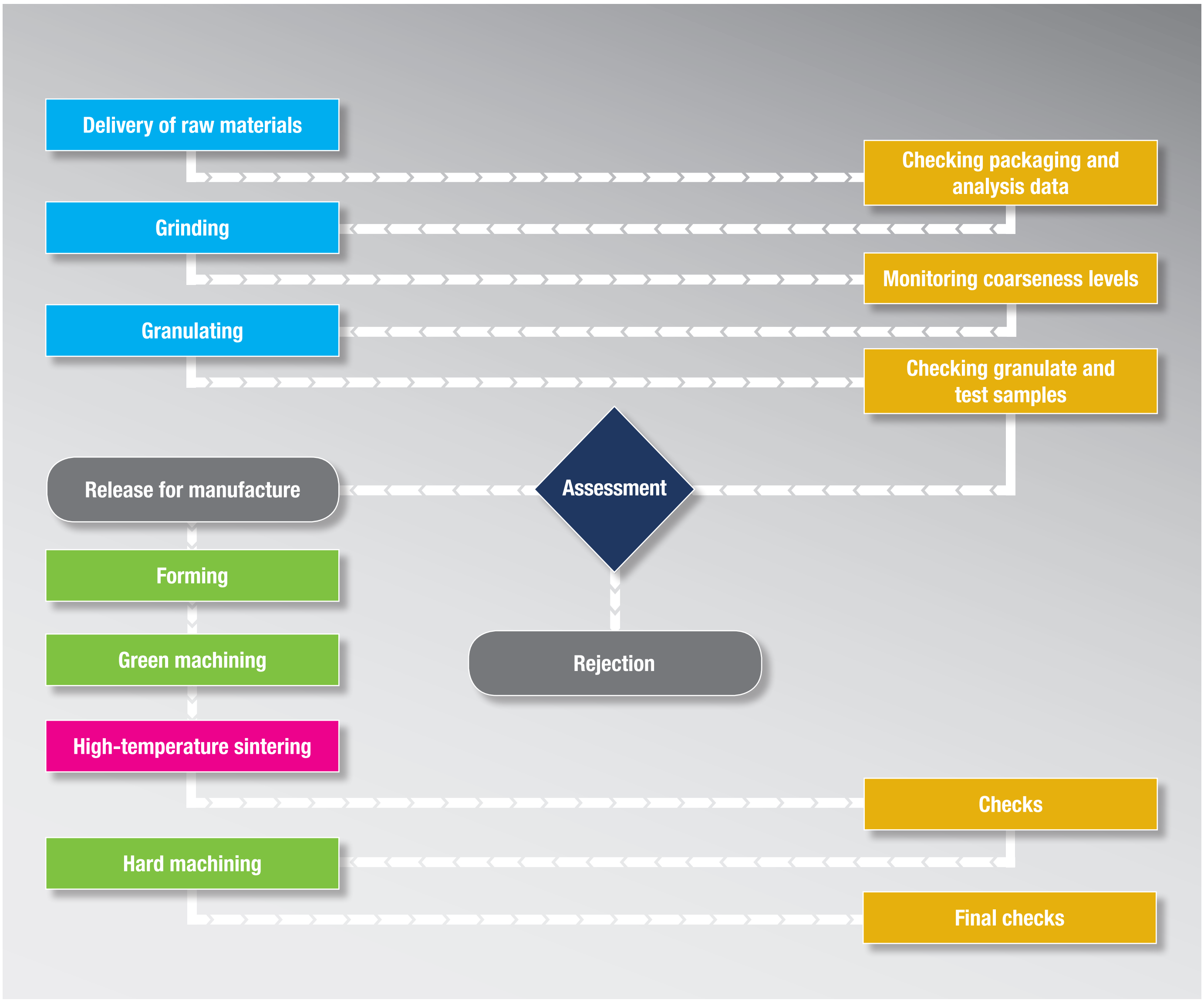


Figure 1: Process technology and laboratory checks

The manufacture of oxide-ceramic products for high-temperature technology follows the process technology illustrated in Figure 1. The diagram shows that processing, from the raw materials supplied to the final product, is necessarily connected with comprehensive, pre-production suitability testing.

It is only after concrete verification of the raw material as well as mass and material properties, obtained on the basis of laboratory test pieces manufactured under production conditions, that commencement of manufacturing is permitted. Furthermore, control routines are introduced at selected stages of manufacturing in order to also monitor the required properties on the concrete product.

These extreme efforts result in materials and products distinguished by consistently high levels of quality.

The stability of this level of quality is monitored by a control audit carried out on annually by an accredited Certification Office, and is re-audited every three years. The Ceramics Division of FRIATEC AG has been certified in accordance with DIN EN ISO 9001 since January 1996 and in accordance with DIN EN ISO 9001: 2000 since January 2001.

If required, special agreements are made with clients that go beyond standardised testing and manufacturing techniques in order to enable tracing of a product manufacturing path right back to the raw materials used.

2. Materials and their properties

Property	Range	Dimension	Al_2O_3			ZrO_2
			DEGUSSIT AL23	**DEGUSSIT AL24**	**DEGUSSIT AL25**	**DEGUSSIT FZY**
Content of main components in material	-	Weight %	≥ 99.8	≥ 99.7	≥ 99.7	≥ 99.7
Density	20 °C	g / cm^3	≥ 3.70	≥ 3.40	≥ 2.80	≥ 5.50
Open porosity	-	%	0	0 - 5	20 - 30	0
Average grain size	-	µm	10	40	70	50
Hardness (Knoop 100 g)	20 °C	GPa	20	-	-	17
Compressive strength	20 °C	MPa	3500	1000	300	2000
Bending strength (sm)	20 °C	MPa	300	150	70	350
E-module	20 °C	GPa	380	-	-	165
Relative thermal shock resistance [1]	-	-	2 - 3	2	1	2
Thermal application limit	-	°C	1950	1950	1950	1700
Specific heat	20 °C	J / (kg * K)	850	-	-	400
Thermal conductivity	25 °C	W / (m * K)	34.9	27.8	-	3.0
Thermal expansion	20 - 1000 °C	ppm / K	8.2	8.3	8.2	11.2
Dielectric strength	20 °C	kV / mm	≥ 30	-	-	-
Specific electrical resistance	20 °C	Ω * cm	10^{14}	-	-	10^{10}
Emission capability	-	%	21	-	-	-

[1] 1= high, 5 = low

A typical characteristic of oxide-ceramic products is their implementation in areas with complex and demanding requirements. The following core properties are essential in high-temperature applications:

- Thermal application limits
- Dimensional stability
- Thermal expansion
- Thermal conductivity
- Thermal shock resistance
- Electrical insulation properties
- Corrosion resistance

The table shows a summary of the main properties of high-temperature materials made by FRIALIT-DEGUSSIT.

The basis of these properties is to be found in the pure oxide properties and in the structure of the ceramics. While Al_2O_3 in the α form is not subject to any change in state up to its melting point of 2050°C, the pure ZrO_2 phase displays two reversible modification changes under normal pressure [1].

The limit between monoclinic (m) and tetragonal (t) phases is located in the range of 950 – 1200°C and the limit between the tetragonal and cubic (c) at approximately 2370°C. The melting point is reached at approximately 2370°C. As the t → m conversion is associated with a volume increase of the crystal lattice of approximately 4%, it has so far not been possible to manufacture crack-free ceramics with commercially available ZrO_2 raw materials. By doping with cations such as Y3+ the phase of the c structure is extended to ambient temperature. Doping with a minimum of 8 mol % Y_2O_3 is required for this fully stabilised zirconium oxide (Type FSZ).

DEGUSSIT FZY is doped with approximately 5 mol % Y_2O_3. This so-called partially stabilised zirconium oxide (Type PSZ) distinguishes itself in comparison with FSZ by higher strength and thermal shock resistance values. This results from the thermodynamically based separation of tetragonal nuclei in the cubic matrix, which starts during sintering in the cooling-down phase when the c → t phase limit is crossed. By means of special control of the sintering process, extension of the t phase can be limited to such an extent that t → m conversion is suppressed. This results in a type of structure subject to compressive stresses that, in comparison to FSZ, provides for higher strength and thermal shock resistance values.

2.1 Thermal and thermo-mechanical properties

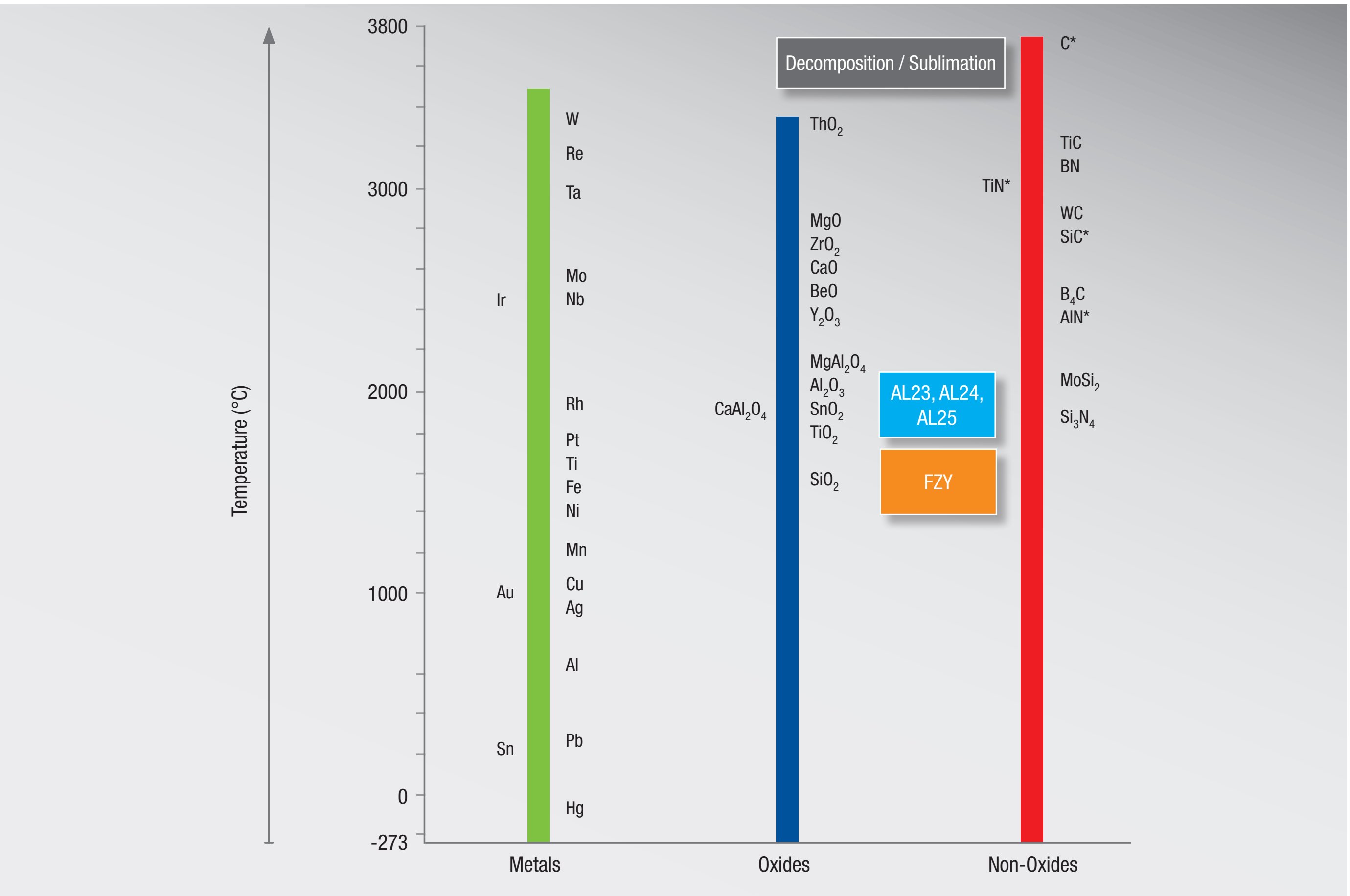


Figure 2: Melting, sublimation and decomposition points

Figure 2 shows the melting, sublimation and decomposition points of selected metals, oxides and non-oxides. The illustration shows that there are materials characterized by extremely high temperature resistance, not only among the oxides but also among the metals and non-oxides. With the exception of some metals belonging to the platinum group, these materials are, however, not permanently resistant in oxidizing atmospheres at temperatures exceeding 1500°C. In such conditions, ceramics made of Al_2O_3 and stabilised ZrO_2 are often the only suitable material.

The maximum application temperatures of oxide-ceramic materials are generally lower than those of pure oxides. This is due to the type of commercial raw materials used, which generally contain a proportion of other substances such as Ca, Mg, Si or Fe. In FRIALIT-DEGUSSIT high-purity materials, however, the total content of these substances does not exceed 0.2%.

If it does not dissolve in the crystal lattice, this accompanying substance is concentrated during sintering of the ceramics in the grain boundaries of the structure. The grain boundary material is frequently a silicate phase, the melting onset of which is below that of pure oxide. Thus, in the event of mechanical stresses, the material starts to deform through grain-boundary gliding already at temperatures below the melting point of pure oxide. At temperatures of below 1000°C, however, this creep tendency is negligibly low for practical applications [2].

By setting a coarser grain structure and by increasing porosity the dimensional stability of the ceramics can be improved as the number of possible glide planes in this way diminishes. DEGUSSIT AL24 and DEGUSSIT AL25 are typical of such materials.

The thermal application limits of the oxides are, in general, lowered by reducing conditions. Al2O3 ceramics, however, is also stable under such conditions up to temperatures of approximately 1700°C Al_2O_3 [3].

The installation environment for oxide-ceramic products in high-temperature plant often requires a compound construction with metal parts. In such circumstances the thermal fit of the materials that are in mechanical contact with each other is vital for the reliability of the construction.

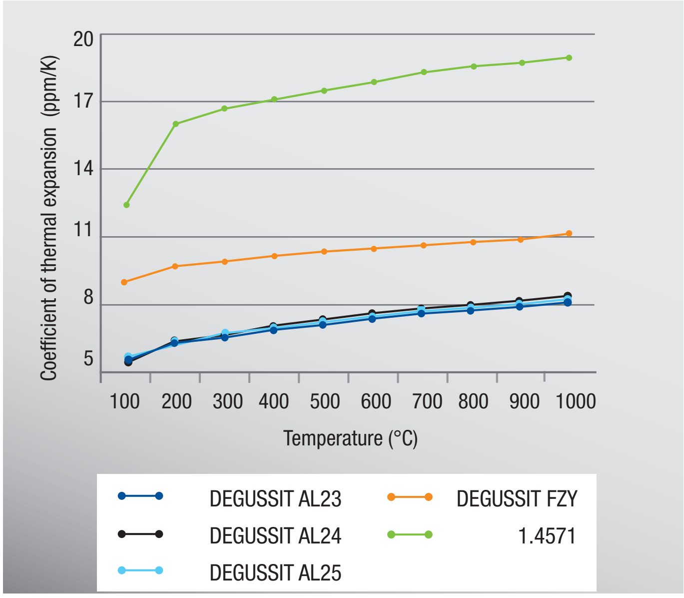


Figure 3: Thermal expansion of FRIALIT-DEGUSSIT materials and stainless steel

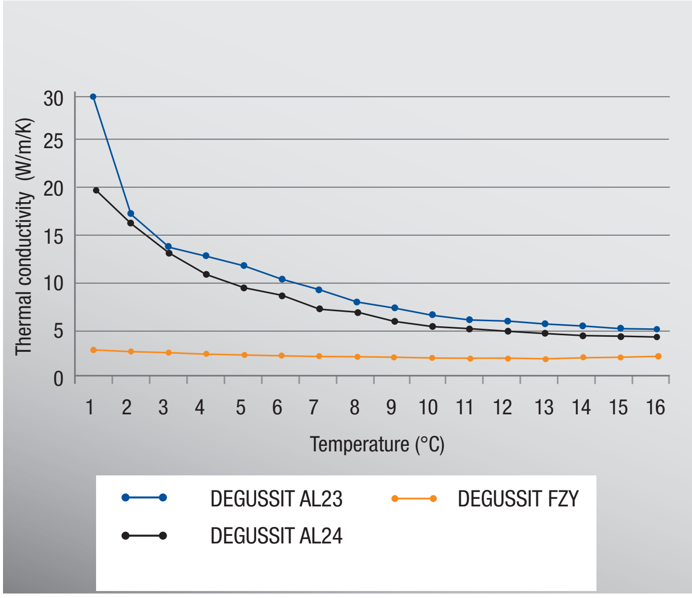


Figure 4: Thermal conductivity of FRIALIT-DEGUSSIT materials

Figure 3 shows the thermal expansion of DEGUSSIT AL23, AL24, AL25, FZY and that of stainless steel 1.4571, as a function of temperature. The chart depicts clear differences between Al_2O_3 and ZrO_2 ceramics, as well as between steel and ceramics in general. Due to the high compressive strength of the oxide-ceramic materials, reliable compound constructions with steel and other materials with high thermal expansion, such as Incoloy, should be designed in such a way that, under all operating conditions, only compressive stresses and, at the most, negligibly low tensile stresses have an effect on the ceramics. In Figure 3, for example, the ceramics in a tube-shaped compound is positioned within the metal tube.

As depicted in Figure 4, the thermal conductivity of Al_2O_3 and ZrO_2 varies. At ambient temperature, DEGUSSIT AL23, when compared to the majority of other ceramic materials, shows higher thermal conductivity, which considerably decreases, however, with increasing temperature. Due to its degree of porosity, DEGUSSIT AL24 is less thermally conductive, but basically behaves in a similar way to DEGUSSIT AL23. In contrast, the thermal conductivity of ZrO_2 ceramics is considerably lower, but this level is also maintained at higher temperatures. This type of material is therefore well suited for thermal insulation.

The degree of resistance of oxide-ceramic products to thermal shock is determined firstly by the type of material, and then by porosity and shape factors.

Under otherwise constant conditions ceramic materials are generally less sensitive to thermal shock than to quenching. As, in the case of finite heat flow, e.g. through a ceramic wall, the outer surface of the ceramics is subjected to compressive stresses under thermal shock and to tensile stresses when quenched, the basic behaviour of this material is based on the high compressive strength of oxide-ceramic materials.

The thermal shock resistance of a material can be increased significantly by a targeted inclusion of porosity in the structure. Due to the higher pore content, DEGUSSIT AL24 is thus more resilient to abrupt changes in temperature than DEGUSSIT AL23.

2.2 Electrical properties

DEGUSSIT AL23, as an electrically insulating material made of high-purity Al_2O_3 ceramics, belongs to Class C799 of DIN EN 60672 [4]. At ambient temperature it reaches a specific electrical resistance of 1014 Ω*cm. It decreases with increasing temperature, e.g. at 400°C to 1011 Ω*cm until, at over 1600°C, it reaches the threshold of electrical conductivity (106 Ω*cm). Products made of DEGUSSIT AL23 have thus been well-proven components for heat conductor supports and thermocouples for many decades.

The above-mentioned doping of ZrO_2 with trivalent cations, such as Y^{3+} in DEGUSSIT FZY, for example, requires a defect structure in the partial lattice of the oxygen ions for the electrical charge neutrality of the lattice. This is the prerequisite for the O^2 conductivity of the zirconium oxide and its use as a solid electrolyte in oxygen sensors [5]. Between temperatures of approximately 500 and 1000°C the material is a virtually ideal ion conductor. For this reason, DEGUSSIT FZY is frequently used as an electrolyte for oxygen sensors with external heating of between 700 und 800°C.

The specific electrical resistance of DEGUSSIT FZY at this temperature level amounts to approximately 80-40 Ω*cm. In addition, the ionic conduction component is accompanied by an electronic conductivity component at temperatures exceeding 1000°C, which, however, is subordinate. The viability of DEGUSSIT FZY as a component in oxygen sensors operated at temperatures above 1000°C is, however, not limited by this.

2.3 Corrosion resistance

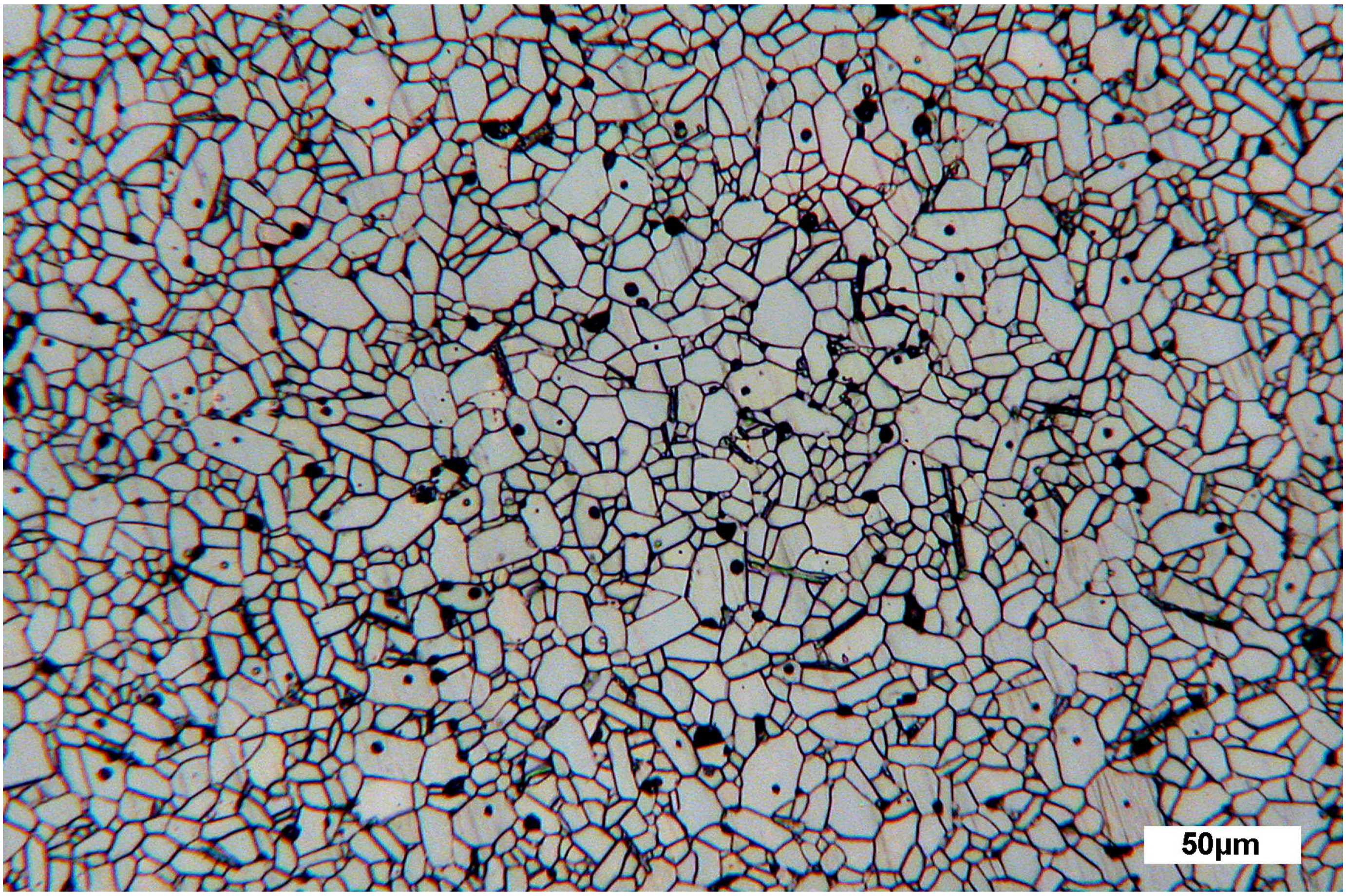


Figure 5: Microstructure of DEGUSSIT AL23 material

Oxide-ceramic materials are often subject to corrosive stresses caused by melting and gases, e.g. during glass processing. Apart from the two extremes – no corrosion attack and complete destruction of material in a very short time – selective attacks on the grain boundary phase must be emphasised. This is where the substance is found which, as mentioned above, does not dissolve in the basic crystal during sintering, or separate from the basic crystal during cooling down from the sintering temperature. As a result of its entirely different composition, this inter-crystalline phase also has different corrosion behaviour to that of the basic crystal itself. In so far as this phase is corrodible, the temporal sequence of these corrosion processes can be delayed by introducing a fine crystal structure, thus achieving a sufficiently long lifetime of the ceramics. By using ceramic materials of higher purity, such as 99.9 % Al_2O_3 ceramics (Type FRIALIT F99.9), it is partly possible to generate a considerable increase in corrosion resistance.

As a typical example of corrosion-resistant ceramics the structure of the DEGUSSIT AL23 material is illustrated in Figure 5. Ceramic products made of Al_2O_3 and stabilised ZrO_2 are resistant to most metals. Exceptions to this are some metals with high oxygen affinity, such as Ti und Zr, which can directly react with the ceramic base material. This property, disadvantageous as regards corrosion resistance, is today used to advantage in the manufacture of brazed, high-vacuum-tight products made of Al_2O_3 and ZrO_2 ceramics and metal by means of so-called active soldering [6].

Resistance to inactive metal melts can only then be assured if oxides cannot form under application conditions. Such melts must therefore be carried out in reduced or inert atmospheres. Porous oxide ceramics is also suitable for melting vessels, as the majority of pure, non-active metals are non-wetting.

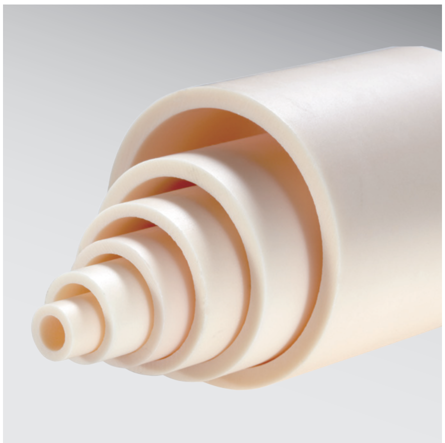
As a rule, oxide-ceramic materials are less resistant to oxide melts than to metal melts. As oxide melts always wet, porous vessels are hardly suitable. In general it should always be taken into account when using oxide-ceramic products that other factors, such as pressure, composition of the atmosphere, environmental location (melting room, gas room), as well as only minor changes in these parameters can significantly shorten, but also considerably extend, the useful lifetime of the ceramics affected.

3. Product examples

Rectangular tubes for the printing industry

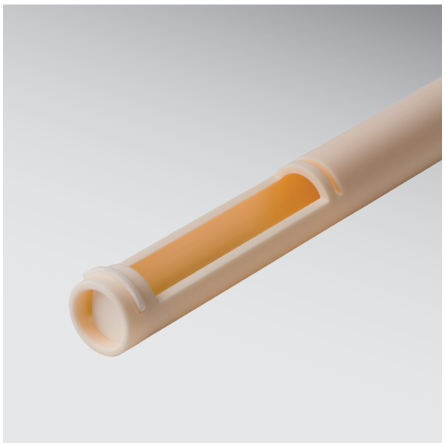
Thermal protection tubes for the glass and metallurgical industries

FZY sensors for oxygen measurement in gases



Thermal protection tubes for high-temperature applications

Thermocouple



Dilatometry tube

High-purity Al_2O_3 ceramics from FRIATEC are used in a multitude of areas due to their high application temperatures and dimensional stability, as well as their mechanical, electrical, chemical and other further thermal properties. The following examples from the field of high-temperature technology clearly illustrate this:

- Protection and capillary tubes for thermocouples
- Insulating beads
- Heat conductor supports
- Gas diffusion pipes
- Combustion liners (plates, capsules)
- Furnace components
- Vessels (crucibles, annealing boxes, boats) for melts, solubilisation and thermal analyses
- Components for dilatometers (tubes, plates, rods)

DEGUSSIT FZY is used as densely sintered partially stabilised ZrO_2 in high-temperature technology primarily due to its ion-conducting properties. Tubes made of DEGUSSIT FZY are today mainly used for the measurement and control of combustion processes in furnaces, for monitoring high-purity gas atmospheres and carbonization processes, but are also used as crucible material for the culture of mono-crystals and ceramic superconductors.

References

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