One Plus One Equals Three? Alumina Plus Zirconia Equals ZTA

Technical high-performance ceramics can be roughly divided into two groups: oxide ceramics and non-oxide ceramics. Non-oxides, for example, include carbides (e.g. silicon carbide SiC) and nitrides (e.g. silicon nitride Si_3N_4). The best-known representatives of oxide ceramics are alumina (Al_2O_3) and zirconia (ZrO_2).

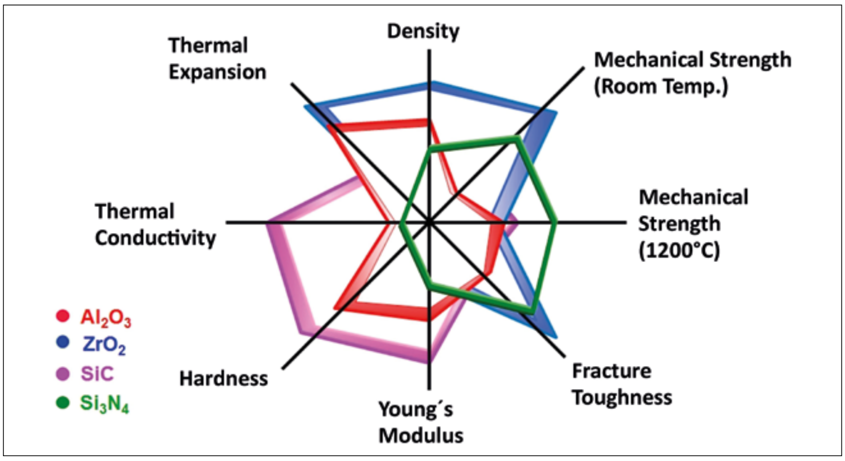

Fig. 1
Material properties of typical high-performance ceramics

$$\text{monoclinic} \underset{950\ ^\circ C}{\overset{1170\ ^\circ C}{\longleftrightarrow}} \text{tetragonal} \overset{2370\ ^\circ C}{\longleftrightarrow} \text{cubic} \overset{2680\ ^\circ C}{\longleftrightarrow} \text{melt}$$

Eq. 1
Phase transitions in zirconia [2]

Introduction

The materials alumina and zirconia differ in terms of their physical properties (Fig. 1).

The main differences are physical in nature and relate to strength and fracture toughness and, from a commercial perspective, also to price. In the world of ceramics, zirconia is the strongest material and also demonstrates a very high degree of fracture toughness. These properties can only be achieved with a raw material which, compared to standard alumina, can be up to 20 times more expensive.

Keywords
alumina, zirconia,
Zirconia Toughened Alumina (ZTA)

The advantages of alumina lie in its good mechanical properties combined with its moderate price.

A further difference can be seen in terms of the crystallographic properties. Unlike Al_2O_3, ZrO_2 goes through phase transitions. Depending on the temperature, this material has three phases which are partly reversible (Eq. 1).

Since the typical sintering temperatures for this material are around 1500 °C, during cooling the material changes from the tetragonal phase back to the monoclinic phase and increases in volume by some 3–5 %. As a result, cracks form and the component is damaged. To prevent this, 3 mol-% yttrium oxide (Y_2O_3) is added to the zirconium oxide. This addition keeps the tetragonal phase stable so that it is also maintained at room temperature. This version of zirconium oxide is also known as TZP ceramic (Y-TZP, Tetragonal Zirconia Polycrystal) and boasts impressive physical properties, especially with regard to strength and fracture toughness.

Zirconia Toughened Alumina (ZTA)

In order to improve the properties of the more cost-effective alumina, particularly in terms of strength, a lot of money and effort has been invested in developing this material over the past few years. With monolithic ceramics such as Al_2O_3, the strength level is determined by the structural properties. With Al_2O_3, this is essentially a product of the particle size and the imperfections. In the case of a material with two phases, the different properties of both phases interact. Changes to the expansion behaviour or elasticity (elasticity modulus) can result in internal tension which does not always have a negative impact. As such, the addition of zirconium oxide to alumina can lead to new material properties which can be additionally influenced by modification of the zirconium oxide. This type of composite material comprising ZrO_2 and Al_2O_3 is also known as ZTA ceramic (Zirconia Toughened Alumina).

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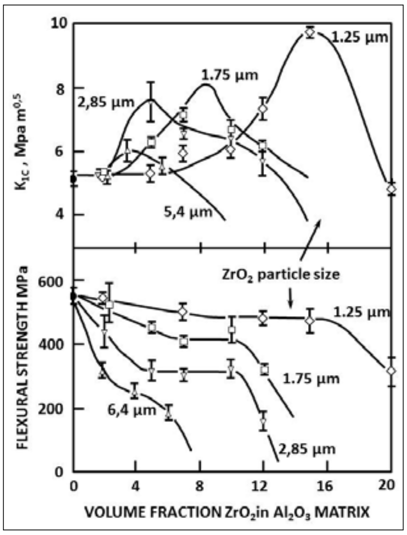


Fig. 2
Influence of the ZrO$_2$ content and particle size on strength and fracture toughness [3]

Initial tests from the 1970s performed by Claussen [3] involving non-stabilised zirconia in alumina have shown that the strength and fracture toughness of a composite material is influenced by the amount and size of the zirconium oxide particles (Fig. 2).

Here, the maximum fracture toughness is achieved with fine-grained ZrO$_2$ with 16 vol-%. Toughness drops again with higher volume fractions. The amount and particle size of the zirconium oxide in the alumina matrix has a negative impact on strength.

These effects can be explained by the modification changes of the zirconia. After the sintering process, during the cooling phase, non-stabilised zirconia converts to the monoclinic phase whilst increasing in volume. This leads to the formation of microcracks in the structure which, on the one hand, reduces the strength yet, on the other hand, increases the fracture toughness. Further tests have shown that there is a critical zirconium oxide particle size for this conversion between 0,4–0,8 µm. Larger particles are converted during cooling, whereas smaller particles remain in the tetragonal phase as these remain under tension due to the sintering process of the alumina. Subsequent conversion only results from an external influence, e.g., a crack running in the structure. The energy of the crack is abated by the modification change and the associated change in volume, hence the progression of the crack is stopped.

As such, the alumina with zirconia is strengthened by microcracks or also by a stress-induced conversion.

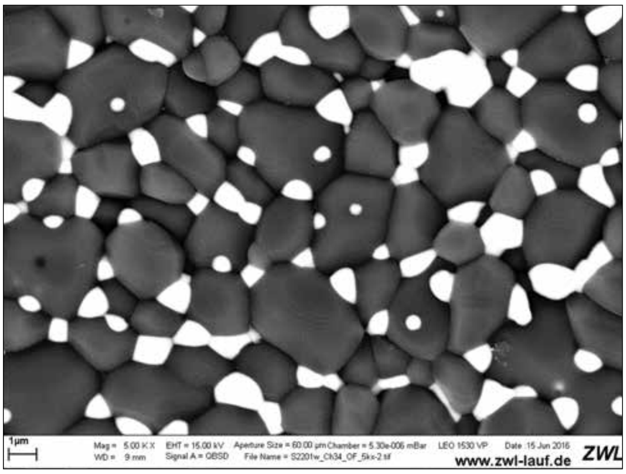


Fig. 3
ZTA 85/15 standard

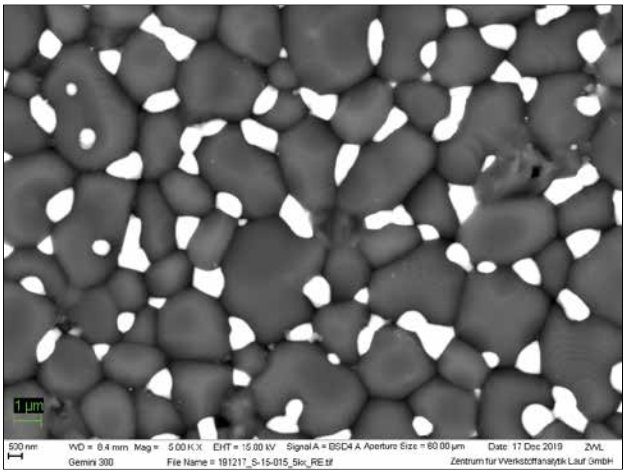


Fig. 4
ZTA 90/10 coarse-grained

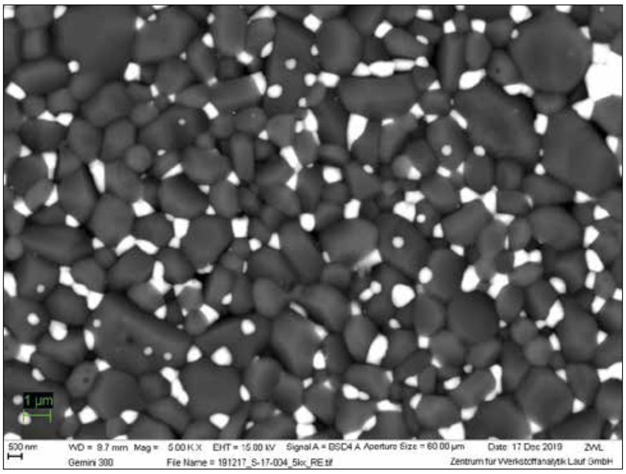


Fig. 5
ZTA 90/10 fine-grained

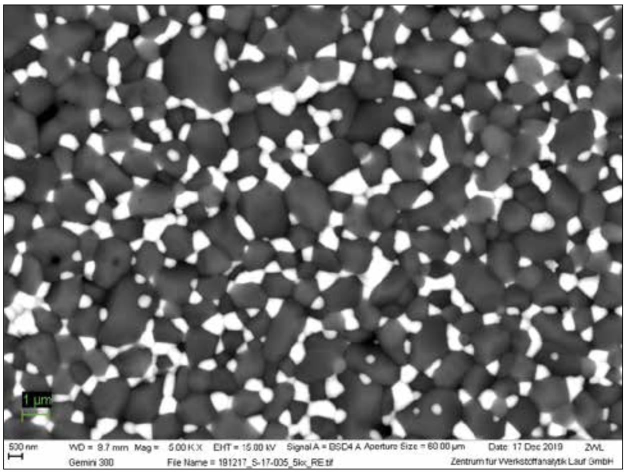


Fig. 6
ZTA 80/20 fine-grained

Today, it is common practice to use Y_2O_3-stabilised zirconia. This has the advantage that the amount of ZrO_2 can be anywhere from 0–100 % and that particle growth remains below the critical range during sintering. As a consequence, not only is the fracture toughness of the composite material Al_2O_3/ZrO_2 increased, but also its strength. Ratios from 90/10–80/20 are commonplace. A ratio of 20/80 results in a new material class which is known as ATZ ceramic (Alumina Toughened Zirconia) and which represents the inversion of ZTA ceramic 80/20.

Material properties

Today, Rauschert offers ZTA ceramics with ratios from 90/10–80/20. A standard material with 85/15 is offered under the name

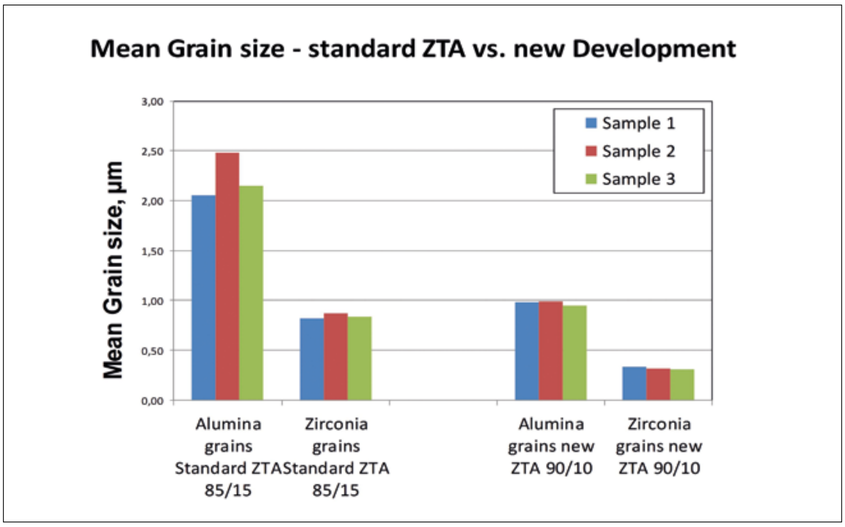


Fig. 7
Graphic comparing grain sizes – standard ZTA 85/15 vs. new fine grained ZTA 90/10

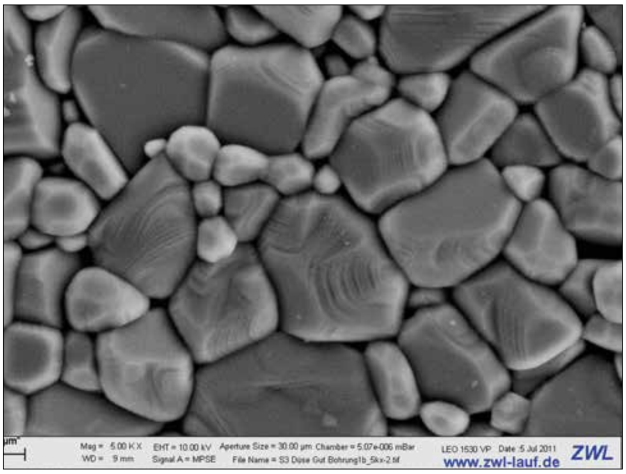


Fig. 8
Alumina coarse-grained

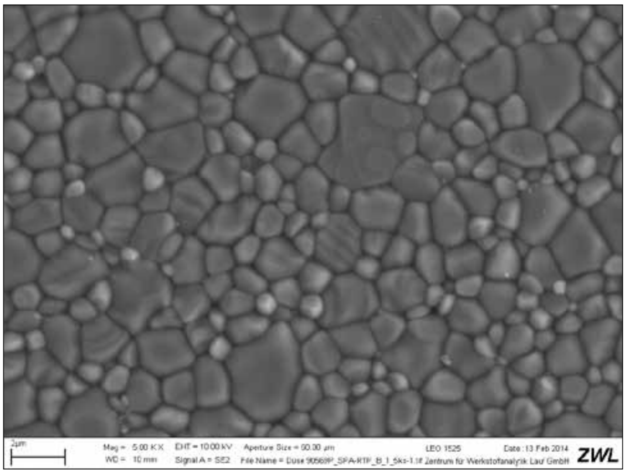


Fig. 9
Alumina fine-grained

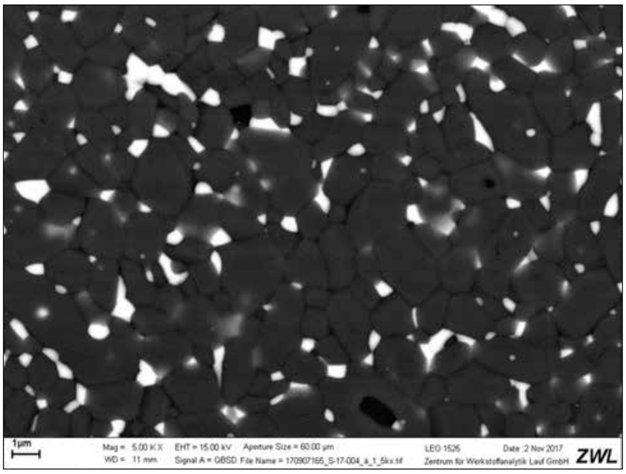


Fig. 10
ZTA 90/10 fine-grained

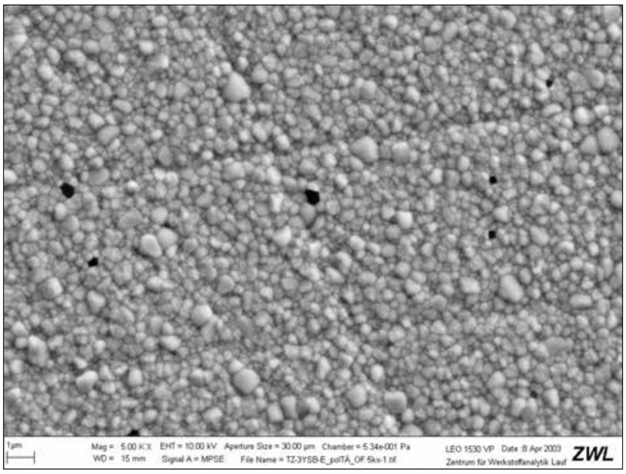


Fig. 11
Y-TZP (Y-stabilised ZrO_2)

Rapal®200 AZ. Two goals were important to improve this material:

1. Setting of the particle size of zirconium oxide to below the critical range after sintering.
2. Minimising of the particle size of the aluminium oxide matrix.

Fig. 3–6 show the surfaces of the different materials.

Fig. 7 shows that both goals were successfully achieved on the basis of three samples. With the standard ZTA, the ZrO_2 particle size was in the border area, whereas a significant reduction was achieved with the new development. This manifested itself in a considerable increase in strength as described in the literature.

It can be assumed that with the standard material, the particle size of the zirconium oxide is within the critical range (around 0,8 µm) and, as such, a partial transformation from tetragonal to monoclinic cannot fully prevent the strength being negatively affected. With the new development, the particle sizes are below the critical range which, in turn, has a positive effect on strength. A further positive factor is the reduction of the particle size of the alumina, which also contributes to increased strength.

The influence of the structure on the strength values is illustrated in Fig. 10–12.

On request, different mixtures of Al_2O_3/ZrO_2 can be produced, such as 60/40 and 40/60 in Fig. 13–14, for special applications.

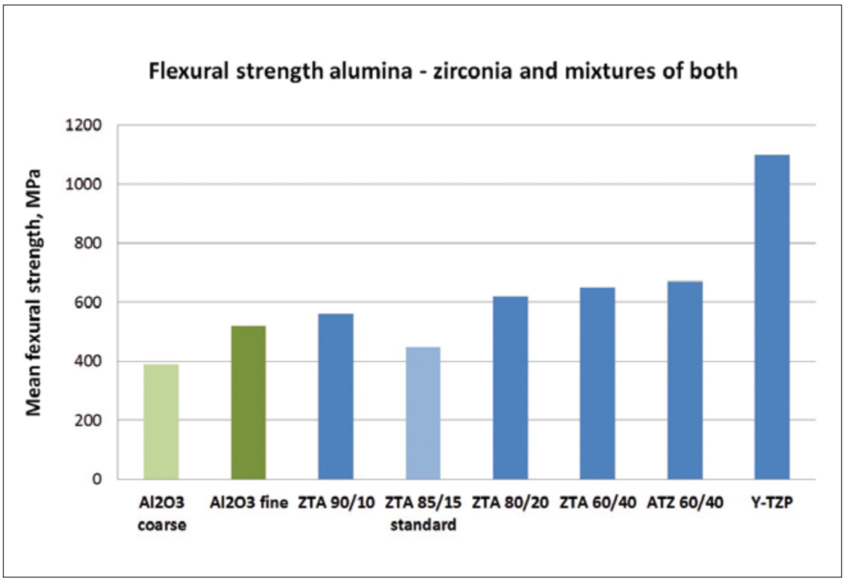


Fig. 12
Comparison of the flexural strength by 4-point bending strength of different materials from the field alumina–zirconia

Applications for ZTA materials

Today, ZTA materials have filled numerous application niches, especially where pure alumina is no longer sufficient due to its mechanical properties and where zirconia is not necessary due to mechanical requirements and also cannot be financially justified. Furthermore, ZTA materials achieve a better polishing quality than pure alumina materials and therefore ZTA has established itself for applications which require good and extremely smooth surfaces.

Another application field is components which, in addition to the mechanical requirements, also demand a relatively high degree of thermal conductivity: in the range from 30–100 °C, zirconium oxide materials have a thermal conductivity of 1,5–3 W/m·K, alumina materials with a Al_2O_3 content of > 99 % have a thermal conductivity of 19–30 W/m·K. The thermal conductivity of ZTA materials in the stated temperature range is given as 15 W/m·K. The higher thermal conductivity of ZTA can mean that it is favoured over zirconium oxide materials for certain applications.

Given their property profile, ZTA materials have become established for the following typical applications:

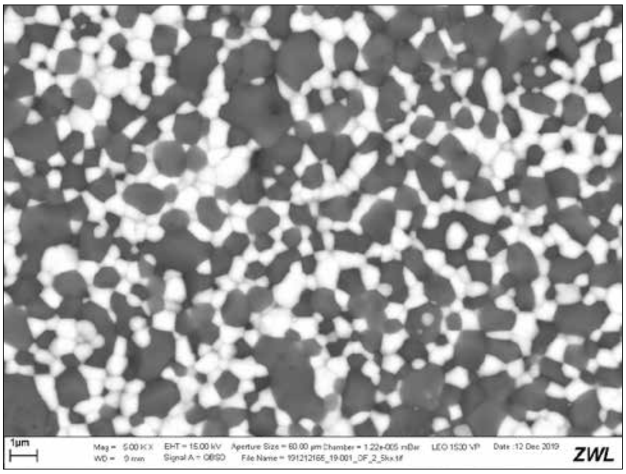


Fig. 13
Al_2O_3/ZrO_2 – 60/40

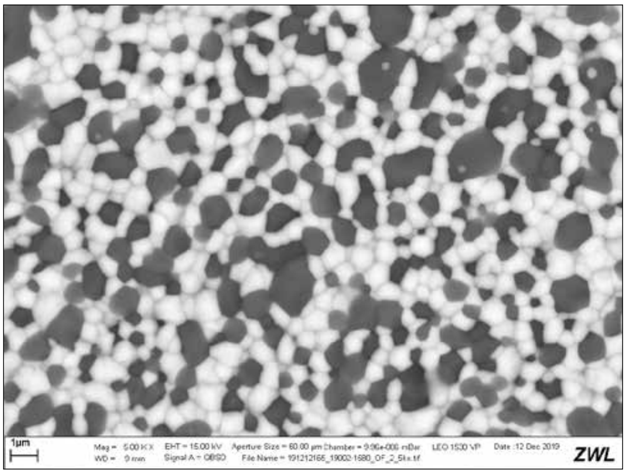


Fig. 14
Al_2O_3/ZrO_2 – 40/60

- pump plungers and components for managing liquids;
- thread guides for the textile industry;
- components for surgical instruments;
- implants (dental and joint replacement);
- cutting tools;
- etc.

Below, only the applications which Rauschert provides are discussed.

Pump plungers and components for managing liquids

For pump plungers and other components for managing liquids (sliding rings, valve components, etc.), very smooth and flat ceramic surfaces are generally required to prevent leakages. If these surfaces run against an elastomer seal during use, then smooth and defect-free surfaces are important to limit wear on the softer elastomer and to extend the service life of the assembly for as long as possible. Y-TZP is required to meet the highest demands in this field, however, a ZTA material is also often sufficient. The necessary surface qualities can be achieved with ZTA materials with less production effort than for alumina materials.

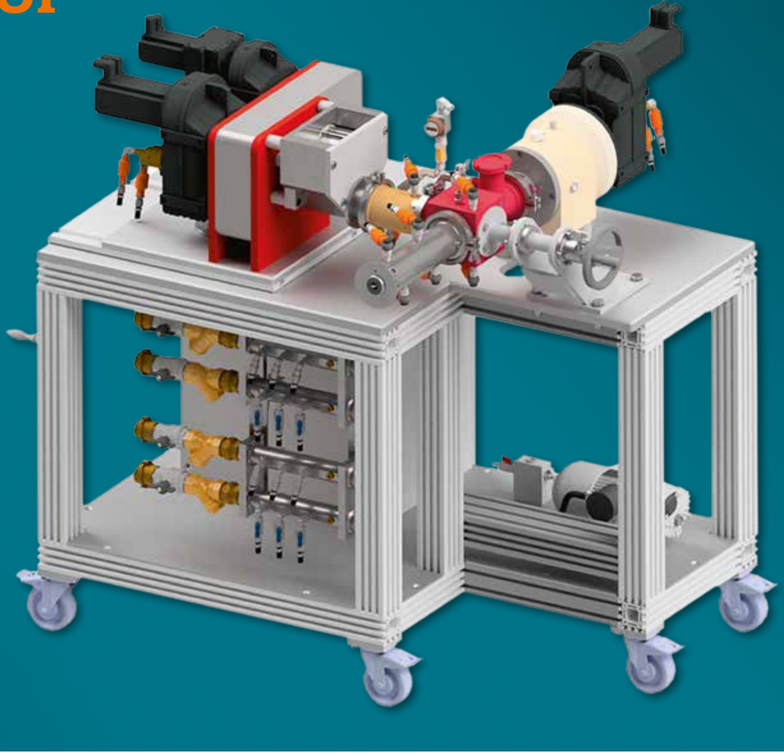
In some application cases, ceramic/ceramic pairs are used which make great demands of both partners. Here, the leakage rate must then be weighed up against the breakaway force/torque required in order to put two valve components which run against each other into motion: the smoother and flatter the surfaces, the greater the cohesion and thus also the breakaway force/torque. On the other hand, smoother surfaces also have naturally lower leakage rates. This must be adapted to the specific case in consultation with the customer.

Thread guides for the textile industry

Thread guide elements made of ceramic have been used as standard in the textile industry for decades. If, during the textile production process, very smooth surfaces or certain running properties for yarn/ceramic are desired, or if impact or shock loads can occur on the ceramic at certain points which could result in breakage, then the use of ZTA materials is favoured. The considerably more expensive zirconium oxide materials only make economic sense in the case of very high impact and shock loads. An advantage of ZTA materials over zirconium oxide materials in such applications is the high thermal conductivity of the ZTA which is almost level with that of alumina. This means that frictional heat can be dissipated more effectively through such materials than through zirconium oxide materials.

However, it must be mentioned that ZTA materials are used in far fewer applications in textile ceramics than zirconium oxide, or even the far more widespread alumina materials. Nevertheless, attractive niches for this material group are opening up all the time.

Typical applications are: navels for staple fibre spinning, components for winders (rotor tips, ceramic plates for take-up



winder guides, templates, etc.), or impact-stressed components in weaving machines which process bands into bags and big bags.

Components for surgical instruments

High-frequency current and even plasmas are used in minimally invasive surgery and also, in part, in classic open surgery in order to occlude bleeding vessels. To this end, various parts of the instruments must be electrically insulated against each other and also against the surrounding tissue within a very compact area. In such cases, ZTA materials are often used, as their strength is not reduced by repeated steam sterilisation, in contrast to zirconium oxide.

However, it should be stressed here that great progress has been made in reducing the loss of strength of zirconium oxide materials under hydrothermal conditions. In addition, one should also note the economic advantages of ZTA materials compared to zirconium oxide materials, assuming that zirconium oxide materials are not absolutely essential due to mechanical reasons. ZTA 90/10, particularly with a fine particle size, is widespread as it has a high mechanical strength and is standardised.

Further applications for ZTA include components for analytical technology and electrical insulators with high mechanical requirements. Indeed, there are also reports of porous ZTA applications in medical technology. The authors are also aware of fuse bodies made of a porous ZTA material for micro fuses which have been used in the SMD technology for many years now.

Summary

The properties of ZTA materials can be customised within certain limits by varying the ratio of zirconium oxide to alumina. As such, the material can be adapted to the specific application. Even if the application fields for this material group are, perhaps, still rather small, maybe these materials deserve more attention than they currently get.

Acknowledgement

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