TECHNICAL PAPER
PROPERTIES AND APPLICATIONS OF HIGH-PERFORMANCE CERAMICS MADE OF ZIRCONIA

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INTRODUCTION
ZrO₂ ceramics are among the oldest oxide-ceramic materials but were refined into a material with high-performance properties only fairly recently. Today, sophisticated materials with special electrical and mechanical properties are made from it.

This article describes this development and the most important types of material. It also explains the effect mechanisms and introduces modern applications.

THE BEGINNINGS
About 80 years ago, zirconia as well as alumina and magnesia oxide were involved when the first oxide-ceramic materials were produced. Even then, it was possible to avoid the particular disadvantages of zirconia in the production of dense, crack-free sintered materials (i.e. the reversible phase transformation from monoclinic to tetragonal at approx. 1100 °C that exhibits a volume increase during cooling down to below the transformation point and the reversion of the monoclinic phases) by adding specific additives, so-called stabilizers.

The first commercially produced materials of this type were launched in 1928 [1]. These materials were stabilized with MgO but only a relatively low sintered density was achieved. Among the first products were crucibles for metal melts for use in applications requiring temperatures so high, that the competing alumina could no longer be used. CaO was later successfully used as stabilizer as an alternative to MgO and its products, too, were limited to high-temperature applications for about 30 years.

A first summary of oxide-ceramic materials, also those made of ZrO₂, was presented after World War II [2]. A later, more detailed, edition put more emphasis on the properties of ZrO₂ materials [3]. Back then, the desired structure was described as fully stabilized i.e. adding as much stabilizer as necessary in order to have all ZrO₂ in stable cubic modification down to room temperature. This requires a content of 8-10 Mol% for conventional stabilizers. However, when compared to sintered alumina, there were some drawbacks with fully stabilized ZrO₂ materials, such as a much lower strength and resistance to temperature changes. Limited to certain high-temperature applications, these materials have lived in the shadow of alumina for a long time. Recently discovered properties, achieved partly by varying the type and amount of stabilizers, led to acceptance of these materials.

HIGH-PERFORMANCE PROPERTIES OF MODERN ZrO₂ CERAMICS
Today, high-performance ceramics refer to materials whose range of characteristic ceramic properties such as resistance to corrosion and high temperatures has been complemented by non-applicable properties such as high stability and toughness which so far have only been known from metals. Due to their specific electrical, magnetic and thermal properties, modern ceramics have also found their way into other applications. Depending on the main application, high-performance ceramics can be divided into functional ceramics (electrical or magnetic functions) and the so-called structural or engineering ceramics (mechanical function).

In many cases, a selected combination of customised properties can be offered today. Textbooks on ceramics provide detailed reports of these [4]. This applies particularly to modern ZrO₂ materials described in the following.
The term “transformation toughening” was chosen for the mechanism allowing for customised ZrO₂ materials with a strength that until now was considered out of reach for ceramics. Important knowledge has been gained through developments carried out at the MPI for metal research in Stuttgart [5, 6].

In simple terms, this mechanism can be described as follows: Tetragonal particles below a critical size (far below the critical size of 1 μm) can be maintained in this form in a densely sintered structure down to room temperature, however metastable. A micro crack growing under stress and its impact on the particle triggers the transformation into stable monoclinic modification. This transformation releases energy thus decelerating the crack growth or splitting the crack into smaller and less dangerous cracks. This is the reason for the increase in strength. The achievable strength dimension depends on the transformation potential of these metastable particles, i.e. their inner structure with the respective stabilizing atoms, their size and structure matrix, and is influenced by the type and amount of stabilizer, the particle size of the ZrO₂ raw material, the residual impurities and the temperature control during heating, sintering and cooling.

Table 1 compares selected properties of transformation toughened ZrO₂ high-performance ceramics and conventional ceramic materials, previously known as oxide ceramics and metallic construction materials. The wide ranging properties in this group of transformation toughened ZrO₂ high-performance ceramics is based on the numerous variations attainable. First, there is a difference between the two basic materials: the PSZ type and the TZP type. PSZ stands for Partially Stabilized Zirconia and TZP for Tetragonal Zirconia Polycrystals, and refers to fundamentally different structural conditions. Moreover, each basic material can be modified to provide certain property combinations.
### Materials with dense structure

<table>
<thead>
<tr>
<th>Materials</th>
<th>Hardness$^3$</th>
<th>Bending strength$^3$</th>
<th>E-Modulus$^3$</th>
<th>Thermal conductivity$^3$</th>
<th>Thermal expansion$^4$</th>
<th>Resistance to temperature changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porcelain, stoneware</td>
<td>7 - 8</td>
<td>50 - 150</td>
<td>1 - 2</td>
<td>1 - 5</td>
<td>4.5 - 6</td>
<td>medium to good</td>
</tr>
<tr>
<td>Oxide ceramics made of Al$_2$O$_3$</td>
<td>approx. 9</td>
<td>250 - 500</td>
<td>3.5 - 4</td>
<td>approx. 30</td>
<td>approx. 7.5</td>
<td>middle</td>
</tr>
<tr>
<td>Fully stabilized ZrO$_2$</td>
<td>approx. 7</td>
<td>100 - 200</td>
<td>approx. 2</td>
<td>approx. 3</td>
<td>approx. 9.5</td>
<td>bad</td>
</tr>
<tr>
<td>Partially stabilized ZrO$_2$</td>
<td>approx. 7</td>
<td>300 - 1500</td>
<td>approx. 2</td>
<td>approx. 3</td>
<td>approx. 11</td>
<td>good to very good</td>
</tr>
<tr>
<td>High-strength steel</td>
<td>6 - 8</td>
<td>1000 - 2000</td>
<td>ca. 2</td>
<td>approx. 50</td>
<td>approx. 16</td>
<td>very good</td>
</tr>
</tbody>
</table>

Table 1: Comparison of materials, range of properties

$^3$ at room temperature

$^4$ at room temperature range up to approx. 600 °C

### THE PSZ TYPE

Originally, PSZ was generally used for partially stabilized ZrO$_2$ and is still being used to some extent for all non-fully stabilized materials. However, this article applies the term only to the conventional partially stabilized material, as is usually found in literature.

These conventional materials contain the metastable transformable particles in the form of fine-crystalline precipitations ≤ 0.1 µm within cubic crystals approx. 50 µm in size. This type of material had already been produced empirically using different stabilizing processes before clarification of special effect mechanisms. The production methods are well known from theory and practice: Sintering at a temperature range that allows only the cubic phase to exist (requiring temperatures >17000 °C and allowing the formation of the coarse crystalline structure), defined cooling or quenching and subsequent tempering at selected temperature ranges, resulting in the precipitation of metastable particles in the cubic crystals. The technical know-how from manufacturers sets out the conditions required to form these particles in the optimal size and maximum number. Depending on the type of temperature treatment, it is possible to produce materials with the best possible strength or materials that have a particularly high resistance to temperature changes at low strength. This type of material was optimized by an Australian research team in particular with regard to maximal strength and resistance to temperature changes [7, 8, 9].

Figure 1 shows the structural conditions inside a material stabilized in this way with MgO, referred to as Mg-PSZ. Figure 2 shows an enlarged area of figure 1. The surface of the large crystals clearly shows the fine structure resulting from the above mentioned ultra-fine precipitations.
**THE TZP TYPE**

These materials were designed in accordance with the information gathered on the mechanisms of transformation toughening. The fundamental idea was based on the perception that it should be possible to build a dense structure using only very small tetragonal crystallites which are kept metastable up to room temperature at least inside the material and are thus available for transformation toughening (hence, the name TZP). This idea was realized using extremely fine-crystalline chemically precipitated ZrO₂ materials containing a homogeneously distributed stabilizer (so far mostly Y₂O₃). This allows for sintering a highly dense structure with each single crystallite below the critical size, which would not be able to maintain the tetragonal particles metastable at room temperature, if the crystallites were above the critical size. After successfully producing TZP materials from almost 100% metastable tetragonal crystallites, it became clear that this allowed for a significant increase in the strength of PSZ types (only part of the structure can adopt the form of metastable tetragonal precipitations). Figure 3 shows an optimal structure, e.g. with a so-called Y-TZP type. The proof-of-principle studies for this type of material were first carried out by American research teams [10, 11, 12]. However, Japanese researchers were the first to begin practical applications.

![Figure 3: An optimal structure, e.g. with Y-TZP](image)

**POSSIBILITIES AND LIMITS**

Table 2 comprises the main differences between the PSZ and the TZP type, e.g. with MgO and Y₂O₃ stabilized materials referred to as Mg-PSZ and Y-TZP. It is recognised that more variations with selected target properties were developed for both groups. This allows the optimization of either strength or resistance to temperature changes of Mg-PSZ during the sintering process. Compared to Mg-PSZ, Y-TZP already has a higher strength, which can be increased by hot isostatic pressing (HIP). It is remarkable that best strength enhancement is achieved in both cases after grinding the sintered probes. This allows the tetragonal particles to transform into their monoclinic form in the surface layers. The resulting volume increase induces compressive stress on the surface adding to strength enhancement. Unlike other modern ceramic materials (e.g. based on Al₂O₃, SiC, Si₃N₄), the strength is enhanced by a subsequent treatment which is always required in practice for the manufacture of close tolerances of many components. This strength enhancing effect is particularly distinct with the TZP type. In contrast, the PSZ type has another particular advantage. Its optimized structure provides strength values with particularly narrow distribution.
Properties and applications of high-performance ceramics made of zirconia

<table>
<thead>
<tr>
<th>Materials</th>
<th>Structure particularities</th>
<th>Significant application properties</th>
<th>Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-PSZ</td>
<td>Coarse crystalline</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A) tempered with regard to strength</td>
<td>Fine structure mainly tetragonal</td>
<td>medium to high, depending on raw material, sintering and temperature conditions</td>
</tr>
<tr>
<td></td>
<td>B) tempered with regard to resistance to temperature changes</td>
<td>Fine structure with high monoclinic share</td>
<td>bending strength 300 – 500 N/mm² Resistance to temperature changes: good</td>
</tr>
<tr>
<td>Y-TZP</td>
<td>Fine crystalline</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A) normal sintered</td>
<td>Density 96 – 98% of Theory</td>
<td>Bending strength 700 – 1100 N/mm² Resistance to temperature changes: good</td>
<td>Very high, expensive raw materials</td>
</tr>
<tr>
<td>B) pressed (HIP)</td>
<td>Density &gt; 99% of theory</td>
<td>Bending strength 1200 – 1800 N/mm² Resistance to temperature changes: good</td>
<td>Particularly high</td>
</tr>
</tbody>
</table>

Table 2: PSZ and TZP ceramics: Properties of most important variations

Using the example of important application properties, table 3 indicates the risks when using these materials. The advantage of transformation toughening offsets the disadvantage that the transformation pressure of metastable-tetragonal particles diminishes as the temperature increases and as a consequence also the strength enhancement. Thus, there is no transformation toughening above the transformation temperature. Therefore, if particular importance is attached to resistance to high temperatures, it should be said that the PSZ and TZP types described here are not high-temperature materials.

In addition, when comparing Mg-PSZ and Y-TZP, the following differences are found: Mg-PSZ is subject to gradual decomposition above 900 °C. Y-TZP has a critical temperature range between 200 and 400 °C at which it can also decompose if exposed to unfavourable structure formation (i.e. failure due to impurities, unequal distribution of the stabilizer, exceeding sintering temperatures). Y-TZP remains stable at higher temperatures.

There is a clear advantage with the PSZ type with regard to chemical resistance to acid and alkaline solutions especially at higher temperatures. When using pure raw materials, the result is an outstanding resistance to corrosion. Y-TZP in its previously developed variations is more sensitive to impacts from corrosion. The structure anomalies already mentioned which cause the material's instability at temperatures between 200 and 400 °C, lead to a drastic reduction in the chemical resistance at temperatures starting below 100 °C when acid or alkaline solutions are present. This could lead to micro cracks spreading through the material and destroying it according to a mechanism which, analogous to certain metals, can be referred to as stress corrosion cracking.

Thus, compared to other high-performance ceramics, PSZ and TZP type materials require even more specialized know-how when it comes to optimizing their properties. Only experienced manufacturers have this knowledge.
Properties and applications of high-performance ceramics made of zirconia

### Materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Behaviour at higher temperatures</th>
<th>Chemical resistance to acid and alkaline solutions up to 150 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-PSZ</td>
<td>Strength reduction: Reaches approx. 80% of room temperature strength at 500 °C Decomposition above 900 °C</td>
<td>Mostly good, depends on purity of raw materials</td>
</tr>
<tr>
<td>Y-TZP</td>
<td>Critical temperature range at 200 - 400 °C: danger of decomposition depends on structural conditions No decomposition at higher temperatures, increasing plastic deformability</td>
<td>Mostly problematic, depends on structural conditions: danger of stress corrosion cracking</td>
</tr>
</tbody>
</table>

Table 3: PSZ and TZP ceramics: Advantages and risks

### APPLICATION EXAMPLES

Table 4 summarises ZrO₂ materials that can be used as solid electrolytes with oxygen ion conductivity for measuring of oxygen concentration.

<table>
<thead>
<tr>
<th>Sample applications for O₂ probes</th>
<th>Applied materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas pressure flow measuring devices for gas analyses with heated ceramics: measuring in optimal temperature range</td>
<td>Ca-FSZ, Mg-FSZ, Y-FSZ</td>
</tr>
<tr>
<td>Direct measuring of kiln atmosphere at different temperatures: Frequent stress induced by different temperature changes and corrosion</td>
<td>Ca-FSZ, Y-PSZ, Y-TZP</td>
</tr>
<tr>
<td>Monitoring air-fuel-ratio in cars (lambda probes) Measuring at low temperatures; stress induced by temperature changes and corrosion</td>
<td>Y-PSZ, Y-TZP</td>
</tr>
<tr>
<td>Immersion probes for measurements in steel melts: High temperatures, strong changes in temperature</td>
<td>Mg-PSZ</td>
</tr>
</tbody>
</table>

Table 4: Electric applications as solid electrolytes  
Fully stabilized ZrO₂ = FSZ  
Partially stabilized ZrO₂ = PSZ and TZP

Table 5 shows possible applications for PSZ and TZP high-performance materials requiring ceramic material resistant to abrasion, breaking and/or corrosion.
### Sample applications | Special requirements | Applied materials
---|---|---
Grinding bodies, grinding vessels | Resistance to wear | Mg-PSZ, Mg/Ca-PSZ, Y-TZP
Forming tools for cold and hot forming | Breaking strength, wear resistance, low coefficient of friction, resistance to temperature changes | Mg-PSZ, Mg/Ca-PSZ

#### Pump components
- **Special requirements:** Resistance to wear and corrosion
- **Applied materials:** Mg-PSZ, Y-TZP

#### Thread guides
- **Special requirements:** Wear resistance, low coefficient of friction
- **Applied materials:** Mg-PSZ, Mg/Ca-PSZ

#### Knife blades
- **Special requirements:** Particularly high resistance to rupture, wear and impact
- **Applied materials:** Y-TZP

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Table 5: Mechanical, thermal and chemical applications (partially stabilized $\text{ZrO}_2 = \text{PSZ}$ and TZP)

The following pictures show sample applications for $\text{O}_2$ probes described in table 4 as well as components for some of the applications mentioned in table 5:

- **Figure 4:** $\text{O}_2$ probes made of Y-PSZ
- **Figure 5:** Brazed $\text{O}_2$ probe made of Y-PSZ
- **Figure 6:** Spacer can made of Mg-PSZ for magnetically coupled pumps
- **Figure 7:** Forming tool made of Mg-PSZ
RECENT DEVELOPMENTS

While the development status of the conventional PSZ type has matured to a large extent, TZP materials require further development particularly with regard to a reproducible structure stabilization. Recent papers have attempted to create an intermediate type that combines the positive properties of the PSZ and TZP type into a single material. Based on the TZP type, special concepts developed in Japan offer variations of material properties in different directions such as increase of hydrothermal resistance when alumina is added. Among these are so-called superplastic materials which allow plastic shaping at high temperatures. Existing reports suggest that it is a highly microcrystalline Y-TZP. The future will reveal whether these developments will result in ductile ceramics, which have until now been unattainable. Of course, a superplastic ceramic material cannot be suitable for high temperatures.

Again, recent Japanese papers [15, 15, 16] show that the inevitable strength reduction at higher temperatures as a consequence of reduced impact of transformation toughening can be compensated for by adding certain additives to the TZP structure. Such variations have resulted in a bending strength of up to 2500 N/mm² at room temperature. When subjected to an increased temperature of up to 1000 °C, this drops to approx. 1000 N/mm². As a consequence, even ZrO₂ based materials could be produced with extreme resistance to high temperatures. This trend and the superplastic materials mentioned previously allow for high expectations.

References


The edited volumes of Conferences on Zirconia provide literature on recent developments in all fields of ZrO₂ ceramics.

