INTRODUCTION

ZrO_2 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 ZrO_2, was presented after World War II [2]. A later, more detailed, edition put more emphasis on the properties of ZrO_2 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 ZrO_2 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 ZrO_2 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 ZrO_2 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 ZrO_2 materials described in the following.

SOLID ELECTROLYTES

Originally, stabilizing was only performed to prevent phase transformation. The side effects resulted in important products that were much more significant than the original high-temperature applications.

During stabilizing, Zr ions are replaced with stabilizer ions. As the latter have a smaller electrical charge than the zirconium ions, vacancies are produced in the partial lattice structure of the oxygen ions. At higher temperatures, oxygen ions diffuse through these vacancies creating new vacancies thus giving rise to a so-called solid electrolyte with oxygen ion conductivity. This effect helps when measuring concentrations of oxygen. Besides the alkaline-earth oxides (MgO and CaO) stabilizers mentioned above, the rare-earth oxide Y_2O_3 in particular has proven itself for this application. Y_2O_3 stabilized materials allow for applications at relatively low temperatures and under highly corrosive conditions. The highest electrical conductivity is obtained with fully stabilized materials, however, the drawback of low strength and resistance to temperature changes must be accepted. This maximum electrical conductivity is required only for special applications such as fuel cells. When measuring the oxygen concentration, little electrical conductivity is sufficient for the potential differences measured. Therefore it is almost always possible to work with partially stabilized materials which have better mechanical properties than fully stabilized materials.

Partially stabilized materials are achieved by adding less stabilizers than necessary to provide a consistent cubic structure. In structures produced in this way only part of the crystallites is in the stable cubic phase, the rest remain capable of transformation between monoclinic below and tetragonal above the transformation temperature. Compared to the fully stabilized materials, a drastically increased strength and/or resistance to temperature changes was measured with such partially stabilized materials, which were initially produced more or less by accident. Despite the increase in volume induced during transformation of the non-stabilized partial phase, manufacture of crack-free components was possible. The earlier much feared phase transformation in particular causes this increase in strength during cooling, under certain requirements as shown in the following chapter.

HIGH-STRENGTH MATERIALS THROUGH TRANSFORMATION TOUGHENING

The term "transformation toughening" was chosen for the mechanism allowing for customised ZrO_2 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 ZrO_2 raw material, the residual impurities and the temperature control during heating, sintering and cooling.

Table 1 compares selected properties of transformation toughened ZrO_2 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 ZrO_2 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	Hardness[1] Mohs	Bending strength[1] N/mm	E-Modulus[1] 10^5 N/mm	Thermal conductivity[1] 10^{-6} K	Thermal expansion[2] 10^{-6} K	Resistance to temperature changes
Porcelain, stoneware	7 - 8	50 - 150	1 - 2	1 - 5	4.5 - 6	medium to good
Oxide ceramics made of Al_2O_3	approx. 9	250 - 500	3.5 - 4	approx. 30	approx. 7,5	middle
Fully stabilized ZrO_2	approx. 7	100 - 200	approx. 2	approx. 3	approx. 9.5	bad
Partially stabilized ZrO_2	approx. 7	300 - 1500	approx. 2	approx. 3	approx. 11	good to very good
High-strength steel	6 - 8	1000 - 2000	ca. 2	approx. 50	approx. 16	very good

Table 1: Comparison of materials, range of properties

[1] at room temperature
[2] 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.
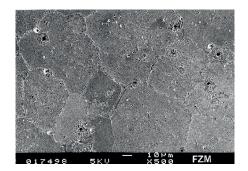

Figure 1: Structural conditions inside the material Mg-PSZ
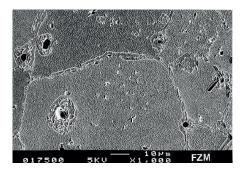

Figure 2: Enlarged area of figure 1

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 ZrO_2 materials containing a homogeneously distributed stabilizer (so far mostly Y_2O_3). 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.
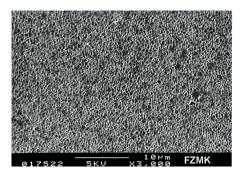

Figure 3:
An optimal structure, e.g. with Y-TZP

POSSIBILITIES AND LIMITS

Table 2 comprises the main differences between the PSZ and the TZP type, e. g. with MgO and Y_2O_3 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 Al_2O_3, SiC, Si_3N_4), 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.

Materials	Structure particularities	Significant application properties	Price
Mg-PSZ	Coarse crystalline		
A) tempered with regard to strength	Fine structure mainly tetragonal	Bending strength 400 - 800 N/mm² Resistance to temperature changes: medium	medium to high, depending on raw material, sintering and temperature conditions
B) tempered with regard to resistance to temperature changes	Fine structure with high monoclinic share	bending strength 300 – 500 N/mm² Resistance to temperature changes: good	
Y-TZP	Fine crystalline		
A) normal sintered	Density 96 – 98% of Theory	Bending strength 700 – 1100 N/mm² Resistance to temperature changes: good	Very high, expensive raw materials
B) pressed (HIP)	Density > 99% of theory	Bending strength 1200 – 1800 N/mm² Resistance to temperature changes: good	Particularly high

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.

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

Table 3: PSZ and TZP ceramics: Advantages and risks

APPLICATION EXAMPLES

Table 4 summarises ZrO_2 materials that can be used as solid electrolytes with oxygen ion conductivity for measuring of oxygen concentration.

Sample applications for O_2 probes	Applied materials
Gas pressure flow measuring devices for gas analyses with heated ceramics: measuring in optimal temperature range	Ca-FSZ, Mg-FSZ, Y-FSZ
Direct measuring of kiln atmosphere at different temperatures: Frequent stress induced by different temperature changes and corrosion	Ca-FSZ, Y-PSZ, Y-TZP
Monitoring air-fuel-ratio in cars (lambda probes) Measuring at low temperatures; stress induced by temperature changes and corrosion	Y-PSZ, Y-TZP
Immersion probes for measurements in steel melts: High temperatures, strong changes in temperature	Mg-PSZ

Table 4:   Electric applications as solid electrolytes
Fully stabilized ZrO_2 = FSZ
Partially stabilized ZrO_2 = 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	Resistance to wear and corrosion	Mg-PSZ, Y-TZP
Thread guides	Wear resistance low coefficient of friction	Mg-PSZ, Mg/Ca-PSZ
Knife blades	Particularly high resistance to rupture, wear and impact	Y-TZP

Table 5: Mechanical, thermal and chemical applications
(partially stabilized ZrO_2 = PSZ and TZP)

The following pictures show sample applications for O_2 probes described in table 4 as well as components for some of the applications mentioned in table 5:
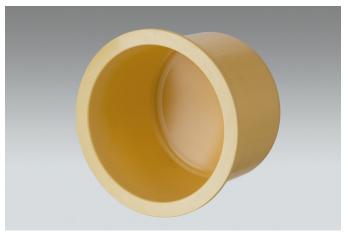

Figure 4: O_2 probes made of Y-PSZ

Figure 6: Spacer can made of Mg-PSZ for magnetically coupled pumps

Figure 5: Brazed O_2 probe made of Y-PSZ

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. 1000N/mm². As a consequence, even ZrO_2 based materials could be produced with extreme resistance to high temperatures. This trend and the superplastic materials mentioned previously allow for high expectations.

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The edited volumes of Conferences on Zirconia provide literature on recent developments in all fields of ZrO_2 ceramics.

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