

# Zirconia, un material extraordinar

## *Zirconia, a wonderful material*

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### ABSTRACT

*Titanium is a valuable biomaterial for implantology since 1952 and demonstrated its impressive clinical steadiness over time, but some studies also showed to be the cause of significant local reactions and chronic pain that may require its removal. Nowadays zirconia replaced titanium more often in orthopaedic and dental surgery because of its higher flexure strength and fracture resilience. Perhaps zirconia ceramics (zirconium oxide partially stabilized with yttrium) is the best solution for titanium failure. This work is a review as well as an overview of zirconia and its applications.*

**Keywords:** zirconia, osseointegration, biocompatibility, implantology

### ZIRCONIA'S SPECIAL PHYSICO-CHEMICAL FEATURES

Zirconium, the transitional metal found in the 5th period of group IV B in Mendeleev's table, with atomic number 40, was known since antiquity as being a precious metal. Its name originates from the Arabic word *Zargon* which means gold colour; even in natural condition, it has a bright white gray stone or a blue-black powder appearance (1).

Identification of zirconium oxide was a marvellous discovery of the year 1789, when German chemist Martin Heinrich Klaproth (1743-1817) obtained it as a reaction product upon heating a stone. Since the real value of the material was discovered, it was used as a pigment for ceramics in combination with other oxides

extracted from rare soils (2). Nowadays, it is considered one of the most important ceramic for many domains.

In nature, zirconia is found only in impure forms and is usually extracted chemically from two minerals: zircon ( $ZrO_2 - SiO_2$ ,  $ZrSiO_4$ ) and baddelyite ( $ZrO_2$ ). Although the zircon is more abundant, it has a low content of zirconia and requires a more laborious process compared to the baddelyite, which has a similar chemical structure and properties with partially stabilised zirconia, and may contain zirconium at concentrations between 96.5-98.5% and about 2%  $HfO_2$  (3).

To produce a qualitative ceramic, with high properties, it is essential to use only controlled pure powders that have particles of a certain size, and uniformly distributed so as to obtain a

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specific degree of agglomeration. By changing any conditions of temperature, pressure, vapours, particle size or concentration of the stabilizing oxides, may cause undesirable microstructural flaws, which affect the properties and reliability of the obtained material (3).

Over time several methods for zirconia powders preparation were tested – starting from the simple mechanical method, which involves a coarse grinding with many impurities and going up to complex procedures, like hydrothermal or chemical methods, that are more expensive than the former, but provide a strict control of powder characteristics (4). It is only by sintering performed in special ovens that ceramic powders acquire new improved properties, due to heating at high temperatures and compaction by pressing into a predesigned mould.

The electronic structure of zirconia studied by SEM represented an important step in understanding its structural, thermodynamic and spectroscopic properties and polymorphism of the three phases – monoclinic, cubic and tetragonal (5).

At room temperature, monoclinic phase prevails in pure zirconia, which remains stable up to 1170°C, and then passes into tetragonal phase and in cubic phase over 2370°C (1,2,3). In the range of 1150-1120°C, zirconia is found in a monoclinic – tetragonal phase while in the range of 900-1100 °C it acquires a tetragonal – monoclinic phase (6).

By cooling, pure zirconia retrogrades successively through the same phases. An interesting phenomenon was observed during the cooling process by transition from the tetragonal to monoclinic phase. In the range of 1000-850°C a volume expansion of the material by 3-5% was observed, therefore objects made of pure zirconia crack (2). Hence, pure zirconia in any of the three phases of crystallization is rarely used for technical applications (7). However, the transition from tetragonal to monoclinic phase can be used to prevent the cracking of the crystal. (3)

The polymorphism of the cubic phase of zirconium and its instability at room temperature was observed by Ruff *et al.*, who found also a solution to this drawback at the end of 1929 by adding a small amount of lime, as a stabilizer (1).

The use of stabilizers in the production of zirconium oxide developed a generation of multi-phase materials, stable at room temperature, consisting mainly of cubic phase and the monoclinic and tetragonal zirconia precipitates, which

are known as partially stabilized zirconia (PSZ) (53).

The addition of a small amount (less than 8 mol%) of CaO or Y<sub>2</sub>O<sub>3</sub> can stabilize the tetragonal phase to high temperatures and increase its mechanical strength, while to stabilize the cubic phase at room temperature more than 8 mol%, is required, but with the advantage of increasing ionic conductivity above the other ceramics (7).

Zirconia can be fully stabilized by adding 16 mol% of MgO, 16 mol% of CaO or 8 mol% of Y<sub>2</sub>O<sub>3</sub>. For industrial purposes however, multi-phase structures formed from a high part of cubic zirconia and a small part of monoclinic or tetragonal zirconia precipitates are usually designed (1), (3).

Spontaneous transformation of metastable tetragonal phase to monoclinic phase, a process known as „aging“, occurs gradually and has a maximum point in aqueous medium at 200-300 °C. The result of this process is a mechanical degradation of the material manifested by reducing resistance, hardness and density, which is shortening lifespan and performance. By reducing the grain size and/or increasing the amount of stabilizing oxide, the rate of aging and wear of the ceramic reduces significantly (8). According to chemical analysis the average aging tetragonal zirconia polycrystals ceramics is of at least 25 years at 37 °C and the process begins when the monoclinic phase exceeds 20% of its composition. (1)

Significant hardness, sometimes superior metal alloys can be improved by incorporating zirconia grain in ceramic matrix. By changing the variables during the manufacturing process, such as the rigidity of the ceramic matrix, the zirconia grain size, chemical composition of grain by the addition of oxides or melting temperature, give rise to a variety of materials with different qualities (6).

Few studies have shown that during hydrothermal transformation at a low temperature and high humidity, zirconia alloys degrade spontaneously, which is a real problem for implants insert in human body, even if the corrosive effect of water to yttrium tetragonal zirconia polycrystals is low (9).

Zirconium anodising at a constant potential of 3-30 V in H<sub>3</sub>PO<sub>4</sub> solution induces precipitation of the Ca and P compounds and increases formation of the zirconium apatite on the surface of the material, in a single step (10). Probably to maintain low corrosion parameters with-

out need for additional treatments, anodization is also the optimal solution for surface modification of zirconia.

Unlike other ceramics, zirconia is bioinert and does not break down by hydrolysis in acidic solution, does not dissolve in the alkaline pH greater than 8 and is extremely resistant to mechanical degradation (11).

The need of hard materials for industry purposes that can cope with extreme mechanical conditions for a long time at high temperatures made zirconia a leader because it fully demonstrated its electrical, thermal and mechanical performances.

In the last decade, aeronautical researchers have been devoted to improvement and optimization of zirconia coatings for anti-thermal shields of space shuttles and jet engine parts manufacturing. Ranging from 0.1-1 mm thick, depending on the application they are used in, these ceramic coatings can withstand temperatures of over 1500°C without changes (12). Therefore, they are also used to cover gas turbines parts, valves and gaskets for internal combustion engines, parts and valves for furnaces (1) (2).

Raised conductivity of stabilized cubic phase and increased melting temperature recommends it for pumps and oxygen sensors or batteries based on solid fuel manufacture (6) (7). Batteries based on solid zirconia are a strong candidate for the energy sector, which tend to replace AC generators. High conversion rate in high-energy emission and low waste polluting environment is a great advantage, but the actual cost of production is high enough to be used on an industrial scale or by home users. Using atmospheric plasma-spraying technique and sol-gel method could be the ideal solution to cheapen the cost of batteries and electrolytes production (13,14).

High chemical, thermal and pH stability of zircon oxide powders are desirable properties for many biotechnological applications, such as support surfaces for chromatographic separation of proteins and enzymes, investigation of the absorbent behaviour of the protein core, the protein ultrafiltration membranes or absorbent material ionic dyes (11).

Nanoparticles of tetragonal zirconia enriched with various earth ions have a high potential for photonic applications by producing a multicolour emission with an increased luminescence (15).

## ZIRCONIA IN CLINICS

In the vast medical field, this material demonstrated its extraordinary usefulness also, due to its high mechanical strength at low volume, resistance to torsion and bending, resistance to corrosion, electrically and chemically neutrality, opaqueness for imaging techniques etc.

Proving its ability to withstand the force of chewing while tested for dental implantology, zirconia has gradually replaced titanium in orthopaedic surgery. Its high fracture resistance ( $K_{IC}$ : 7–10MPa m<sup>1/2</sup>) and hardness (8.5 on the Mohs scale) were perfectly completed by a good biocompatibility with human tissue, demonstrated clinically and histologically (1).

Medical zirconia is a tetragonal zirconia polycrystal stabilized with yttrium, containing over 97% zirconium oxide, 3 mol% of yttrium oxide, hafnium oxide < 2%, aluminum oxide and silicon oxide < 1%. This ceramic has special physical properties (Table 1) which makes it to be preferred for dental crowns in visible areas (2,16,17).

**TABLE 1.** Physical properties of zirconia

Physical properties	Measure	Value
Colour	White	Good
Density	6 gcm <sup>-3</sup>	Good
Porosity	< 0.1%	Low
Bending strength	900-1200 MPa	High
Compressive strength	2000 MPa	High
Fracture resistance	$K_{IC}$ : 6-10 MPa m <sup>1/2</sup>	High
Young's modulus	200 GPa	Low
Thermal expansion coefficient	11×10 <sup>-6</sup> K <sup>-1</sup>	Low
Thermal conductivity	2 WmK <sup>-1</sup>	Low
Hardness	1200 HV 0.1	Very high

Zirconia (Figure 1) is an ivory-coloured, mat or translucent ceramic, which also may be coloured for a better imitation of natural teeth, tissue or hair (ex. potential use for Bone Anchored Hearing Aids implants), unlike the gray appearance of the titanium implant, which changes gingival mucosa when it is too thin or retracts (17). Using the new dentistry system of Computer Aided Design and Computer Aided Manufacturing, it can be easier to obtain more qualitative dental crowns with higher aspect margins that can satisfy the aesthetic needs of the most demanding patients (2).

Clinical studies have also shown a higher amount of metallic ions and corrosion products released from oral titanium implants that cause



**FIGURE 1.** Bone Anchored Hearing Aids implants – zirconia (handmade, left) and titanium (right)

an unpleasant metallic taste and accumulate in regional lymph nodes, thereby inducing negative effects on patient's health (17,18).

*In vivo* experiments on bacterial colonization involving zirconia versus titanium oral implants showed a decreased development of dental plaque and bacterial adhesion on the surface of the ceramic were bacteria arranged in small groups, compared to uniformly thin film coated of bacteria on the metal implant surface (19).

To obtain an enhanced biological response regarding the interaction with the human cells, an efficient osseointegration of the material surface, an increased resistance at the bone-implant interface for long time periods, various treatments can be performed to improve implant surface, such as hydroxyapatite aggregation, magnesium ions enriching, blasting or acid etching.

Laser modification of the surface material is a promising alternative since it can be performed automatically, it is reproducible, and in addition it does not cause contamination of the surfaces. Thus, increased roughness surfaces and stable characteristics can be obtained to as-

sure a long term efficient biointeraction. The surface roughness of the implant is correlated with a shorter period of healing abutments, ability to use shorter abutments, which do not affect the stability of the implant and enhance the success of osseointegration (18).

Several animal studies comparing titanium and zirconia, confirmed non-allergenic properties of zirconium oxide, its biocompatibility with the all tissues tested. Moreover, the process of its osseointegration knows a faster rate in the first three months, which recommended it as a valuable implant material (2,16).

*In vivo* studies regarding biocompatibility of zirconia with the soft tissues reported a complete encapsulation of the inserted implants inside subcutaneous tissues by a fibrous connective tissue with a discrete inflammatory infiltrate (20).

Hence, most of the comparative studies about the two materials performed in the last two decades showed that zirconia is ready to dethrone gradually the leading place in implantology held by titanium, for over half century. Zirconia is a material with great qualities, which may prove useful for many other domains.

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