Chapter 1: Zirconia-toughened Alumina for biomedical applications

1.1 Ceramics for biomedical applications

A biomaterial is a material (natural or man-made) used in a medical device intended to interact with a biological system. The field of biomaterials has continuously evolved during the last decades: from the 1930s, when the first engineering metal alloys became more widely used to make bone plates for fracture fixation, the scenario of available biomaterials is drastically changed, including today many different materials from all the main categories, such as polymers (polyamides, silicones, polymethylmethacrilate, polyethylene, polyglycolic acid), metals (titanium alloys, stainless steel, Co-Cr alloys), ceramics (alumina, zirconia, carbon, hydroxyapatite), composites (carbon-carbon), used in several types of complex prosthetic devices.

The uses of biomaterials include replacement of a body part that has lost function due to disease or trauma (artificial hip joint), they can be used to help healing (sutures, bone plates and screws), to improve function (cardiac pacemaker, contact lens) or correct congenital defects (spinal rod)\(^1\).

In order to properly assess the performance of a biomaterial or of an implant, researches must be focused on different aspects, concerning both the intrinsic properties of the materials and the responses of the human body to the introduced devices. First, the mechanical, physical, and chemical behaviour of the material in the biological environment must be studied, i.e. its resistance to fracture, fatigue, wear, corrosion. Then, its biocompatibility must be investigated and verified, by the analysis and identification of the reactions which occur at the interface between the material and live tissue, for example at the interface between the bone and the prosthesis or the graft. Thus, the success of an implant in the body depends on several factors, such as the materials properties, the design, the biocompatibility as well as other factors out of engineer control, including the technique used by the surgeon, the health of the patient, and his activities.

The research for upgraded or new biomaterials is related to the crucial topic of the enhancement of life conditions, and there is a continuous input from bioengineering for reaching a high level of comfort, improving reliability, finding new applications. This development is also a response to the growing number of patients afflicted with traumatic or non-traumatic conditions: as the average age of population grows, the need for medical devices to replace damaged or worn tissues increases. Particularly, an important biomedical research sector concerns orthopaedic field, also because the number of implants is continuously growing, due to the increase in persons who suffer from arthritis and joint problems. Steady growth in the number of joint replacements is observed since the ‘70s, and it is expected over the next decade. Besides, also the number of younger middle-age patients who undertake arthroplasty is increasing.

Ceramics have a great potential in the biomedical field, thanks to their compatibility with the physiological environment, their strength and wear resistance. Ceramics are also very
attractive for dental applications, because of their chemical inertness and their aesthetics. Thus, bioceramics are mainly used in the musculo-skeletal system, for orthopaedic and dental devices: the main applications include replacement for hip, knee, teeth, as bone gaps filler. A first distinction can be made between bioinert (as alumina or zirconia), bioactive (as hydroxyapatite, bioactive glasses, glass-ceramics), resorbable (as tricalcium phosphate). This distinction is based on the interaction between the material and the living tissue. In the first case the material is biologically inactive, having a minimal interaction with the surrounding tissue, and a nonadherent fibrous capsule of variable thickness is formed at the interface with the device. Movement at the bioinert material-tissue interface can occur, often leading to aseptic implant loosening. Instead, bioactivity refers to a material, which, being placed in the human body interacts with the surrounding bone through an ion exchange reaction between the implant and the surrounding body fluids. This leads to the formation of a biologically active carbonate apatite layer on the implant surface. This phenomenon is exploited in microporous ceramics, thought to promote ingrowth of living tissue into the porosity of implant materials, in order to obtain a “biological fixation”; thanks to the ability to elicit a specific biological response which results in a bond between the tissue and the material. Good results are also achieved using bioactive ceramics such as hydroxyapatite coating on a metal surface. Finally, resorbable bioceramics are able to degrade gradually, being replaced by the natural tissue. For resorbable bioceramics, the difficulties are the maintenance of strength and stability of interface during the dissolution and replacement period, and the matching between the resorption and repair rates, that depends on several variables, such as health and age of the patient.

This broad spectrum of biological interaction, from inactivity to biodegradation, leads to a corresponding range of engineering design strategies. In fact, bioactive materials such as tricalcium phosphate and hydroxyapatite have poor mechanical properties, so their applicability is confined to implants which do not have to sustain significant loading, and the main requirement is to provide favourable surfaces for biological bonding and bone ingrowth. Otherwise, the harsh conditions in joint replacement restrict the materials choice to the harder and stronger ones, such as alumina or zirconia, thanks to the good strength and wear resistance, even if they are not able to create a bone-material interface, and they cannot be successfully used as bone filler. Besides, bioceramics are characterized by brittleness and low crack resistance, thus, in some applications they cannot compete with metals or composites.

1.2 Case of total hip replacement

The hip and shoulder joints have a ball-and-socket articulation, while others, such as the knee and elbow, have hinge type articulation. However the main and common characteristic is the presence of two opposing smooth cartilaginous surfaces that are lubricated by viscous synovial fluid.

The joints prostheses induce some additional problems when compared to other implants, such as long bone fracture repairs; problems about wear and corrosion and their products, as well as complicated load transfer dynamics, must be taken into account. Arthroplasty devices have been developed since the early 1900s. The introduction of the total hip replacement (THR) by Dr. J. Charnley in 1960 represented a great advantage of efficiency of the hip prosthesis, the device consisted of a metal femoral prosthesis fixed to the bone by a cement, for instance PMMA, and of the acetabular component made of Ultra High Molecular Weight Polyethylene (UHMWPE).
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Materials for THR should satisfy several requirements, among which biocompatibility, wear resistance, low risk of failure in vivo, lastingness, reliability. More precisely, the desirable characteristics for materials used as the articulating surfaces in THR are the following:

- high strength, high elastic modulus, high fracture toughness and fatigue resistance for mechanical reliability, that elicit to a low risk of failure. The materials must resist, without deformation, when subjected to the load in the body, which can vary from three times (~3 kN) for normal walking to eight times the body weight (~ 8 kN) for jogging;
- high corrosion resistance and biocompatibility in vivo;
- good wetting (low contact angle) between the bearing surface and the synovial fluids, for good lubrication of the joint.

The materials, already in use or just investigated for this application, belong in three main classes. First, the metal alloys, such as Co-Cr alloys, or stainless steel, are used for femoral heads and acetabular cups. The second class contains monolithic oxides ceramics, alumina and zirconia and more recently alumina-zirconia composites for femoral heads and acetabular cups. The most common material used for the acetabular component is UHMWPE, inserted into a stiff metal cup.

The modular design currently used for the hip joint prosthesis is shown in Figure 1. The ball head is commonly made either of alumina, as specified by ISO 6474, or of Co-Cr alloys. Owing to standardized taper-fit connection, the surgeon can choose the type of ball to be implanted. The socket are modular, consisting of two components: the external span of the socket, made of metal bioalloy, that can accept the inlay, made of alumina or polyethylene. Besides, the external socket and the stem may be cemented to the bone with PMMA, or coated with bioactive hydroxyapatite, to promote bone integration.

The fixation of the implant is one of the main difficult problems of the joint replacement, and particularly of the hip joint. The cement allows attaching the implant with the bone, it also acts as a shock absorber and it helps to spread the load more evenly over a large area, reducing the stress concentration on the bone. Anyway the cement can give rise to some problems, for example the exothermic polymerization reaction can cause a local temperature increase, which can result in cells necrosis. The problem of the bone-cement interface may be solved by utilizing the concept of bone ingrowth. The performance of 92 components made of titanium alloy with a plasma-sprayed hydroxyapatite coating, having a minimum thickness of 150 µm, with a 28-mm alumina modular head was followed up for ten years by Gabbar et al., and they concluded that the systems is a good prosthesis for patients younger than 65 years: after 10 to 12 years, the cumulative survival rate was 94.29%.

The traditional bearing coupling for THR consists of a metal, typically a Co-Cr alloy, articulating against UHMWPE acetabular cup (see Figure 2 a). This kind of device has an average lifetime of about 10-15 years, while 25% of the total hip prosthetic joints fail prematurely by aseptic loosening. The life of these devices is limited by corrosion, wear, and/or ion release. The cause of aseptic loosening is debated, but the final explanation might be sought in a combination of multiple factors, such as prosthesis stiffness, particulate reaction and stress shielding.
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Figure 1 Modular design for bearing used in total hip replacement

Figure 2 Prosthetic hip implants with metal-on-UHMWPE (a) and ceramic-on-ceramic bearing (b) couples (titanium alloy stems)
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The problem of the stress shielding comes from an uneven stress distribution in the bone. It can be caused by the stress concentrations at the points of sharp contact, or it can be directly dependent by the prosthesis design and biomaterial stiffness. The bone stress in the distal region to the stem is higher than normal; in contrast the bone stress in the proximal region is reduced by the presence of the stiffer implant, as shown in Figure 3, where it is possible to appreciate the stress distribution on the medial and lateral side of the femur, before and after the implant. In the position 1, in the proximal region, the bone does not bear any load after the prosthesis implantation, and this stress shielding effect causes bone resorption, which in turn, leads to loosening or fracture.

The other cause of loosening is the wear of bearing surface: the microscopic debris can lead to periprosthetic inflammation and implant loosening. The need of materials with lower wear rate becomes crucial today, since THR is used on younger patients, who require devices that last longer and endure a more active lifestyle.

In this perspective, ceramics have been introduced as an alternative to Co-Cr/UHMWPE-bearing couples, thanks to the attractive tribological properties, the low friction coefficient and low wear rate. The exploited bearing coupling consists of alumina femoral head articulating against polyethylene, or against alumina monolithic sockets (see Figure 2 b). The advantages of ceramic surfaces, in reducing the wear particle volume in THR, have been extensively documented \(^5,6,7,8,9\), nevertheless fracture remains a rare but catastrophic complication \(^10,11,12\). Alumina was introduced in the orthopaedic field as a candidate for bearing surfaces in the 1970s, and stabilized zirconia in the 1980s, the first being the most widely used in THR. Anyway, the limitation for the use of ceramics in orthopaedic prostheses concerns their inherent brittleness, which can lead to catastrophic failure \textit{in vivo}, even if recently improvements in material quality, manufacturing process, implant design, have resulted in a reduction of failure. Therefore, the reduction of wear rate in THR, to avoid aseptic loosening of stem or socket, and the minimization of failure rate of ceramic component are the main targets for the research in biomaterials for hip joint replacement.

\textit{Figure 3} Stress on the surface of a femoral before and after the prosthesis implantation. Note that there is no stress in the position 1 after insertion of the implant \(^1\)
1.2.1 Monolithic ceramics

1.2.1.1 Alumina

Alumina as an alternative to metal-UHMWPE bearing system was first introduced in the 1970s, but early clinical applications showed a high fracture rate of 13% \(^1\). Failure in this first generation of ceramics was due to the fact that they could not be processed to full final density. A second improved generation of ceramics, developed in the late 1980s, resulted in higher density and smaller grains. The fracture rate associated to the second generation of alumina decreased to less than 5%. Finally, today a third generation of ceramic components is available, characterized by high purity, full density and finer microstructure, mainly thanks to the doping with MgO to control the grain growth and to the full sintering by hot isostatic pressing at about 1250°C. For this new alumina bearing, a lower fracture rate of about 0.004-0.015% is reported. Considering the data in Table I, supplied by the producer of Biolox® alumina \(^1\), the influence of the material characteristics on the mechanical properties is clearly stated: the mechanical strength is closely related to density, that must be maximized, to the mean grain size, kept small, as well as to the presence of glassy phase at the grain boundaries, that must be avoided by using a high-purity alumina. The flexural strength is higher than 550 MPa, and the Vickers Hardness is 1800-2000 HV, about four times the hardness of common orthopaedic metals such as Co-Cr or Ti alloys \(^4\). As mentioned before, the high hardness of alumina, and of ceramics in general, provides a minimum wear of the femoral heads and of the cups, also because it allows a superior surface quality. Besides, the capability of adsorbing polar molecules (as water, body fluid) promotes the formation of a liquid film which provides the lubrication between the ceramic head and the socket.

Table I Properties of various alumina ceramics (standard values)

<table>
<thead>
<tr>
<th>Property/Characteristic</th>
<th>Alumina ceramics as specified by ISO 6474</th>
<th>1(^{\text{st}}) and 2(^{\text{nd}}) generation Alumina</th>
<th>3(^{\text{rd}}) generation HIPed alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-point bending strength</td>
<td>400 MPa</td>
<td>500 MPa</td>
<td>580 MPa</td>
</tr>
<tr>
<td>Mean grain size</td>
<td>&lt; 4.5 µm</td>
<td>&lt; 3.2 µm</td>
<td>&lt; 1.8 µm</td>
</tr>
<tr>
<td>Density</td>
<td>3.94 g/cm(^3)</td>
<td>3.96 g/cm(^3)</td>
<td>3.98 g/cm(^3)</td>
</tr>
</tbody>
</table>

Definition: alumina ceramics was sintered in air (Biolox®). 1\(^{\text{st}}\) generation was manufactured until 1992, 2\(^{\text{nd}}\) generation until 1995. Hipped alumina (Biolox Forte®) was conforming to ISO 6747. 3\(^{\text{rd}}\) generation manufacturing started in 1995 \(^1\)

Despite the mentioned good properties of alumina, such as high mechanical strength, elastic modulus, high compression resistance, optimal chemical properties, its brittleness must not be forgotten: its fracture toughness is only \(\sim 4 \text{ MPa} \cdot \text{m}^{1/2}\) and it is also sensitive to slow crack propagation under a stress intensity factor \(K_I\) lower than the critical value \(K_{IC}\).

Ceramic materials are highly sensitive towards stress concentration, so uneven load distribution must be avoided. The design of the metal stems and tapers is important: Morse tapers must be properly designed for optimal load transfer, avoiding stress intensification in the ceramic-metal interface. The metal tapers have a specific surface roughness: the
microscopic pattern consists of peaks and valleys on the surface that flatten when the ceramic ball is applied on the taper. This approach provides a homogeneous load transfer. The failing load of alumina balls, achieved with this concept, corresponds to a safety factor of 10-50 times the body weight, as reported by Willmann.

1.2.1.2 Zirconia

Biomedical grade zirconia was developed in the 1990s, to solve the problems of alumina brittleness, since it showed the best mechanical properties among oxide ceramics, mainly thanks to phase transformation toughening. Particularly, yttria-stabilized zirconia (Y-TZP) became a popular alternative to alumina, because of the higher fracture toughness and strength. Yttria acts as phase-stabilizer, allowing the retention, at room temperature, of high-temperature tetragonal phase. The stress activated phase transformation of metastable tetragonal grains to the monoclinic phase in front of the crack tip is responsible of the increase of the crack propagation resistance. The enhancement of toughness is due to different mechanisms. The volume change associated to the transformation creates a compressive field at the crack tip able to contrast the crack propagation, and the strain energy associated with the transformation contributes to increase the fracture energy. Additional contributes to toughness may result from microcracking, associated to the accommodation of the transformation strain, and from crack deflection.

Otherwise, due to metastability of tetragonal phase at room temperature, zirconia is susceptible to low temperature degradation (LTD), because ageing phenomena can occur in the presence of water. Loss of strength and microcracking have been widely testified in TZP, placed in moist atmosphere, particularly at temperature of 200-300°C, or also under hydrothermal condition used during steam sterilization, due to slow transformation of tetragonal grains into monoclinic phase. Moreover, this detrimental phenomenon has been observed also under less severe conditions, for example at lower temperature, and can continue in the aqueous environment in the human body. It was widely observed that transformation proceeds from the surface to the bulk of zirconia materials, which results in surface roughening and microcracking, as shown in the Figure 4.

This material degradation has two important consequences in the use of Y-TZP in hip prostheses. First, roughening invalids the optimal surface finishing and impacts the wear performance of femoral heads: as the surface quality worsens, the wear rate of the acetabular insert increases, leading to osteolysis and implant loosening. Second, the pull-out of zirconia grains occurs due to the coupled effect of microcracking and wear, creating defects that may grow and lead to delayed fracture. The LTD is the more serious limitation to the use of Y-TZP, even if the manufacturers considered this problem as a minor issue until 2001 when hundred of failures of Y-TZP heads occurred in a very short period. This episode is now associated with the accelerated ageing in two particular batches of the leader Prozyr® product, caused by an uncontrolled process, that resulted in the withdrawal of this product. Anyway, owing to this, the use of zirconia for femoral heads drastically decreased. Moreover, some clinical reports show that Y-TZP can exhibit ageing even under “normal” conditions, and their behaviour in vivo has been found to be complex and unpredictable, mainly in the body environment, at 37°C, where frictional heating or localized high loads on the bearing surface can act as trigger for ageing, playing a role in the tetragonal to monoclinic transformation. More precisely, Brown et al. carried out a study on retrieved Zirconia balls at 1-15 years, they found that most retrieved heads showed high transformation percentages (30-85% monoclinic content) but someone showed no transformation. Moreover they observed that the
areas with major phase changes corresponded to PE contacts, suggesting that tribological
conditions under the cup were the trigger for transformation.

![Figure 4](image)

**Figure 4** Schematic explanation of ageing mechanism occurring in a cross section of zirconia
material, showing the transformation from a grain to the neighbour ones: (a) nucleation on a
surface grain (grey coloured grain) leading to microcracking (red path) and shear stress to the
neighbours grains, (b) growth of the transformed zone, (c) extensive microcracking and
surface roughening

### 1.2.2 Alumina-Zirconia composites

To overcome the low toughness of alumina and the ageing sensitivity of zirconia, alumina-
zirconia composites have been proposed for biomedical applications. The idea supporting the
development of these materials is the belief that they represent a way to benefit from the good
mechanical properties of alumina, especially hardness, at the same time improving the
toughness of the composite by means the zirconia transformation toughening, without the
major drawback of the ageing under steam or body fluid. Recently, CeramTec AG
(Plochingen, Germany) has commercialised BIOLOX® delta, a composite material consisting
of 80 vol. % Al₂O₃, approximately 18.5 vol.% ZrO₂ and 1.5 vol. % of mixed oxides (Cr₂O₃,
Y₂O₃ and SrO), characterized by a strength higher than 1150 MPa and a toughness of 8.5
MPa·m¹/² (as declared by the supplier). This material belongs to the class of Zirconia
toughened Alumina composites (ZTA), i.e. a two-phase material consisting of fine ZrO₂
particles, dispersed in a dense Al₂O₃ matrix. The presence of tetragonal ZrO₂ can induce
improvements in fracture toughness and strength, anyway the materials composition and fabrication conditions must be carefully controlled to optimize the transformation toughening, as it will be better explained in the following.

Rahaman et al. have reported a comparison of the mechanical properties of some ceramic materials to the Co-Cr alloy, and the natural bone (see Table II), and they have underlined the attractive properties of ceramics, and in particular of the ZTA composites, the latter exhibiting a coupling of the main advantages of the monolithic ceramic materials.

Table II Material properties (at Room Temperature) of dense Al₂O₃ and ZrO₂–based ceramics, compared to those of Co-Cr alloy and bone

<table>
<thead>
<tr>
<th>Property/Characteristic</th>
<th>Al₂O₃</th>
<th>Y.TZP</th>
<th>ZTA</th>
<th>Co-Cr</th>
<th>Bone (cortical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>99.9% Al₂O₃</td>
<td>ZrO₂ –3% mol Y₂O₃</td>
<td>Al₂O₃-20 vol. % ZrO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>&gt;3.97</td>
<td>6.05</td>
<td>4.40</td>
<td>~8.5</td>
<td>1.7-2.0</td>
</tr>
<tr>
<td>Grain size (µm)</td>
<td>1-5</td>
<td>0.1-1.0</td>
<td>1-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strength (MPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile</td>
<td>250-300</td>
<td></td>
<td></td>
<td>700-1800</td>
<td></td>
</tr>
<tr>
<td>Compressive</td>
<td>2000-3000</td>
<td>3000-4000</td>
<td>700-1000</td>
<td>130-180</td>
<td></td>
</tr>
<tr>
<td>Flexural</td>
<td>300-500</td>
<td>1000-1500</td>
<td>700-1000</td>
<td>60-160</td>
<td></td>
</tr>
<tr>
<td>Fracture toughness, Kₘ (MPa⋅m⁰.₅)</td>
<td>4-5</td>
<td>6-12</td>
<td>6-10</td>
<td>50-100</td>
<td>2-12</td>
</tr>
<tr>
<td>Fracture threshold, K₁₀ (MPa⋅m⁰.₅)</td>
<td>2.0-2.2</td>
<td>3.0-3.5</td>
<td>4⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vicker Hardness (HV)</td>
<td>1800-2000</td>
<td>1200</td>
<td>1600-1800</td>
<td>300-400</td>
<td></td>
</tr>
<tr>
<td>Thermal expansion coefficient (10⁻⁶K⁻¹)</td>
<td>8</td>
<td>11</td>
<td>8.5</td>
<td>~14</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity (Wm⁻¹K⁻¹)</td>
<td>30</td>
<td>2</td>
<td>17</td>
<td>~100</td>
<td></td>
</tr>
</tbody>
</table>

*Data referred to a ZTA material containing 10 vol.% ZrO₂.
1.3 Zirconia-Toughened Alumina: mechanical and technological properties

Since the aim of this thesis is the development and the characterization of zirconia-toughened alumina micro- nano composite for the production of femoral heads, in this section the characteristics of ZTA materials will be widely presented and discussed.

Particularly the mechanical properties such as strength, crack propagation resistance, wear resistance will be compared to the respective monolithic ceramics.

1.3.1 Theoretical background: fast failure and subcritical crack growth in ceramics

1.3.1.1 Fast crack propagation

Ceramics are brittle solids, so they are particularly sensitive to stress concentration around pre-existing small flaws, such as pores, scratches or cracks. When a tensile stress $\sigma$ is applied, the stress at the tip of the flaw, for instance a crack, can be described by the stress intensity factor $K_I$:

$$K_I = Y \sigma \sqrt{a}$$

where $a$ is the surface crack length, and $Y$ is a geometry factor, related to the defect geometry. Fast failure occurs when the above mentioned $K_I$ reaches a critical value for the material, namely the fracture toughness $K_{IC}$. The fracture strength $\sigma_R$ for a brittle material will be given by:

$$\sigma_R = \frac{K_{IC}}{Y \sqrt{a}}$$

According to the Eq. (2), the fracture strength of a ceramic is determined by its fracture toughness and the flaw size. Owing to this, two approaches to the problem of brittle failure are possible: the first concerns the increase of toughness by exploiting the use of composite materials, the latter is the improvement of the reliability by a refinement of the ceramic processing, in order to have fewer and smaller flaws in the material.

1.3.1.2 Subcritical crack growth

It is now well recognized that brittle materials are susceptible to slow crack growth (SCG): even if the stress intensity factor $K_I$ is kept below the critical $K_{IC}$, failure of ceramics can sometimes occur. Indeed, as mentioned above, $K_{IC}$ and $\sigma_R$ are related to fast crack growth. This phenomenon is also referred as “subcritical crack propagation”, because the crack propagates even if the factor is lower than the critical value $K_{IC}$.

The SCG depends on the applied loads, as well as on the environmental characteristics, such as the presence of water or steam. Thus, under specific conditions, the crack grows and when it reaches the critical length for failure at that stress level, according to the Eq. (2), the ceramic fails by fast fracture.
Slow crack growth in bioceramics is often associated to a stress-corrosion mechanism, consisting in the combined effects of high stress at the crack tip, and the reaction of water with the material that reduces the surface energy at the crack tip, inducing the propagation.

As a general trend, SCG is expressed by the relation between the crack velocity and the stress intensity factor. Experimentally, three stages are observed, as schematized in Figure 5, during the SCG.\textsuperscript{24,25}

During the first stage, the propagation depends on the reaction kinetics between water molecules at the crack tip and the material.

In the second stage, the controlling mechanism is the transport of the species along the crack interface, because in this branch the reaction that leads to a new surface creation is faster than the water molecules transport.

Finally, in the third region, at high velocity, the failure is insensitive to the environment, and it occurs as well as under vacuum.

A fundamental aspect of the $V$-$K_1$ curve is the presence of a threshold, below which no crack propagation occurs, this region is sometimes referred as region 0. The threshold corresponds to a condition of equilibrium with a zero crack velocity. This is fundamental for ceramic joint prostheses, because it determines a safety operative range. The higher the threshold, the higher the reliability, and consequently the lifetime. Thus, the advantage in establishing the presence of such a threshold is clear; however this is not easy, owing to the difficulty in following cracks growth at very low velocity, typically below 1 nm s$^{-1}$.  

\textit{Figure 5} Schematic representation of the three regions observed during the Slow Crack Propagation, expressed by the crack velocity ($V$) versus the stress intensity factor ($K_1$) plot.\textsuperscript{25}
The process involved in SCG can be clarified by an idealized representation proposed by De Aza et al. 25, showing the reaction between the water molecules in a humid environment and a strained Zr-O bond at the crack tip (see Figure 6). The reaction steps involve the adsorption of water to Zr-O bond, the transfer of protons and electrons, and the formation of surface hydroxyls.

![Figure 6](image)

*Figure 6* Schematic representation of the proposed reaction between water and strained Zr-O-Zr bond at the crack tip 25

Chevalier et al. 26 studied the SCG in zirconia-based composites, for different environments, as reported in Figure 7. The overall curve in air presented three different stages; in the curve obtained in water only one stage was observed, similar to the first stage in air; finally in silicon oil or under vacuum, where no water molecules are present, the V-K curve had a much higher slope and the SCG occurred only for a stress intensity factor close to $K_{IC}$. These results demonstrated that a stress corrosion mechanism also operated for the investigated ceramics. Moreover, they demonstrated that the addition of 5 vol.% zirconia to alumina increased the crack resistance, decreasing the crack velocity of several orders of magnitude. This was explained by the contribution of the transformation toughening. In terms of stress intensity factor, the stress-induced transformation leads to a contribution $K_{Ish}$ (in compression) that opposes to the crack propagation.

$$K_I = K_{tip} - K_{Ish}$$  \hspace{1cm} (3)

where the $K_{tip}$ is the local crack tip stress intensity factor and the $K_I$ is the applied stress intensity factor. Moreover, the $K_{Ish}$ is proportional to the applied one:

$$K_{Ish} = C_{sh} \cdot K_I$$ \hspace{1cm} (4)
being:

$$C_{sh} = \frac{0.214 \cdot E \cdot V_f \cdot e^T \cdot (1 + \nu) \left( \frac{\sqrt{3}}{12\pi} \right)^{1/2}}{(1 - \nu) \cdot \sigma_m^c}$$

(4)

where $E$ is the Young Modulus, $V_f$ is the volume fraction of transformed particles, $e^T$ is the volume dilatation associated with the transformation, $\nu$ is the Poisson Ratio, $\sigma_m^c$ is the local stress for phase transformation and $K_I$ is the applied stress intensity factor.

In the Eq. (4), $\sigma_m^c$ is at the denominator, and it is the needed stress to promote $t \rightarrow m$ transformation, which is greater for smaller grains. Consequently, as the grain size decreases, the toughening effect becomes less important.

![Figure 7 V-K diagram for 3Y-TZP ceramics under different environments](image)

*Figure 7* $V$-$K_I$ diagram for 3Y-TZP ceramics under different environments (○: air at 25°C, ▲: distilled water at 25°C, △: distilled water at 75°C, □: silicon oil at 25°C, ◆: secondary vacuum at 25°C)\(^{26}\)

### 1.3.2 Reinforcing mechanisms in ZTA

Zirconia-Toughened Alumina (ZTA) composites have been developed with the aim of coupling the best properties of the two constituents. In fact ZTA materials are the main investigated zirconia dispersed systems, receiving great attention in the last three decades thanks to hardness, strength and especially to the potential fracture toughness enhancement. The latter characteristic is due to several phenomena, such as the stress-induced phase transformation\(^{17,27,28}\), that occurs with a volume expansion of about 4%, or interaction of the crack front with microcracks\(^{29}\). Particularly, transformation toughening was recognized as the most important toughening mechanism\(^{27,30}\).
Claussen \(^{29}\) reported about the toughness enhancement due to microcracking in ZTA containing unstabilized zirconia. In that study the toughness increased as the amount of zirconia in the composite increased, reaching a maximum, and then decreased due to the reciprocal interactions of microcracks. Instead, the fracture strength diminished continuously with the increase in zirconia fraction, as shown in Figure 8 for two ZTA composites, in which the mean zirconia size in the material I was larger than in material II. Therefore, the microcracking phenomenon can lead either to an additional toughening or to a net reduction of toughening, depending on its extension. On the contrary, the effect of transformation toughening is different: both the strength and the fracture toughness increase with the zirconia content, when the zirconia size is below the critical value for spontaneous transformation, and no microcracking occurs.

The reciprocal contribution of transformation toughening and microcracking on the overall toughness enhancement was also investigated by Rühle et al. \(^{31,32}\), who studied the mechanical behaviour of ZTA composites, containing a fixed amount (15 vol.\%) of ZrO\(_2\), and a variable tetragonal zirconia fraction from 23\% to 86\%. All the tested samples had a toughness of about 6 MPa-m\(^{1/2}\), higher than that of pure alumina (assumed \(\sim 3.5\) MPa-m\(^{1/2}\)). Those results suggested that the ratio of monoclinic to tetragonal zirconia had a minimal effect in toughness, even if the toughening mechanism changed depending on the amount and the size distribution of the of tetragonal and monoclinic ZrO\(_2\). The material containing the highest fraction of \(t\)-ZrO\(_2\) presented a mean zirconia particle size of 0.4 \(\mu\)m, while the composite containing only 23\% \(t\)-ZrO\(_2\) showed a coarser zirconia size distribution, with large \(m\)-ZrO\(_2\) particles having a diameter of \(\sim 7\) \(\mu\)m. In the former material, toughening was mainly due to the \(t \rightarrow m\) transformation, while in the latter microcraking was mainly responsible for the \(K_{IC}\) enhancement. Moreover, the flexural strength decreased from \(\sim 1200\) MPa to \(\sim 700\) MPa, for the composites containing the highest and the lower \(t\)-ZrO\(_2\) amount, respectively.

\[\text{Figure 8 Fracture toughness and flexural strength as a function of zirconia volume fraction}^{29}\]
Lange described the transformation toughening mechanism in composites containing stabilized or unstabilized zirconia. In fact, tetragonal zirconia can be retained at room temperature, even if no phase-stabilizer is added, because of the action of the stiffer alumina matrix, whose elastic modulus is higher than that of zirconia. This study indicated that the increment of toughness was proportional to the amount of tetragonal zirconia.

Szutkowska investigated the role of unstabilized or Y$_2$O$_3$-stabilized zirconia in the Al$_2$O$_3$-10 vol.% ZrO$_2$ system, examining the R-curves of the two composites. The ZTA material containing unstabilized zirconia exhibited the highest $K_{IC}$, while the other system was comparable to pure alumina, that is, any toughness enhancement was produced. He noticed different behaviours in crack propagation into the two materials: an intergranular crack path was observed in the Al$_2$O$_3$-10 vol.% unstabilized ZrO$_2$, while in the Al$_2$O$_3$-10 vol.% stabilized ZrO$_2$ the crack path was linear and transgranular, demonstrating that a different fracture behaviour was exploited by the two materials. So, the comparison between ZTA composites containing unstabilized zirconia or Y$_2$O$_3$-stabilized zirconia has shown that best results can be achieved with the first type of system, since, when tetragonal phase is stabilized by doping, the stress to induce transformation at the crack tip raises, and consequently a lower amount of zirconia contributes to the toughness enhancement through $t \rightarrow m$ transformation.

The relative contribution of different toughening mechanisms to $K_{IC}$ enhancement in the ZTA materials, as well as the increase of mechanical properties and reliability, depends on specific microstructure features, such as zirconia distribution and grain size, homogeneity and lack of aggregates. Regarding the grain size influence, Shin et al. studied the relative contribution, on toughening, of the stress induced $t \rightarrow m$ transformation and microcracking, in three types of Al$_2$O$_3$-15 vol.% ZrO$_2$, prepared without additives, or using Y$_2$O$_3$ and MoO$_2$ as stabilisers for tetragonal or monoclinic phase, respectively. They assumed that the toughness enhancement due to the $t \rightarrow m$ transformation was proportional to the volume fraction of $m$-ZrO$_2$ transformed during fracture, and the increase caused by microcracking was proportional to the pre-existing $m$-ZrO$_2$ content, before fracture. The composite containing pure ZrO$_2$ grains showed the highest fracture toughness and the composite with Y$_2$O$_3$-doped ZrO$_2$ grains had the lowest one, in fact in that material no monoclinic zirconia was observed after fracture so that no toughening mechanism seemed to be active, being the $t \rightarrow m$ transformation hindered by Y$_2$O$_3$. According to the Authors, the contribution of transformation toughening was much more pronounced in the studied size range of zirconia grains, i.e. 0.3-1.4 µm, however a change in the size range has expected to elicit a change in the relative contribution of the two mechanisms. In fact, an increase in ZrO$_2$ grain size would increase the contribution to toughening of microcracking, because of the enhancement in microcrack density and the decreased amount of $t$-ZrO$_2$ transformable in $m$-ZrO$_2$.

To conclude, it appears that the toughening mechanism and the toughness-strength relation depend on the microstructure, including the amount and the type of zirconia, grains size of both alumina and zirconia, position of zirconia particles (intergranular or intragranular).

In Table III, some mechanical properties evaluated for ZTA by the previously cited Authors are reported.
Table III Mechanical properties of ZTA, as reported by different Authors

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fracture toughness $K_{IC}$ (MPa-m$^{1/2}$)</th>
<th>Flexural strength (MPa)</th>
<th>Toughening mechanism</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$-15 vol.% m-ZrO$_2$ (unstabilised ZrO$_2$)</td>
<td>$\sim$10</td>
<td>$\sim$450</td>
<td>microcracking</td>
<td>[29]</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$-10 vol.% t-ZrO$_2$ (3%mol Y$_2$O$_3$ stabilised ZrO$_2$)</td>
<td>$3.77 \pm 0.04$</td>
<td>_</td>
<td>No active toughening mechanics</td>
<td>[34]</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$-10 vol.% m-ZrO$_2$ (unstabilised ZrO$_2$)</td>
<td>$4.81 \pm 0.04$</td>
<td>_</td>
<td>$t \rightarrow m$ transformation</td>
<td>[34]</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$-15 vol.% t+m-ZrO$_2$ (unstabilised ZrO$_2$)</td>
<td>$4.92 \pm 0.26$</td>
<td>$870 \pm 81$</td>
<td>microcraking $t \rightarrow m$ transformation</td>
<td>[35]</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$-15 vol.% m-ZrO$_2$ (MoO$_2$ - stabilised ZrO$_2$)</td>
<td>$4.50 \pm 0.16$</td>
<td>$673 \pm 98$</td>
<td>microcracking</td>
<td>[35]</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$-10 vol.% t-ZrO$_2$ (unstabilised ZrO$_2$ colloidal processing route)</td>
<td>$5.90 \pm 0.2$</td>
<td>_</td>
<td>$t \rightarrow m$ transformation</td>
<td>[25]</td>
</tr>
</tbody>
</table>

Tailoring the zirconia size in the composite is a crucial issue, because the dimensions must range between two critical values, the $D_c'$ below which the transformation is completely hindered, being the tetragonal phase stabilised thanks to small grain dimensions, and $D_c$, above which spontaneous transformation occurs during cooling from the sintering temperature.

These critical size limits depend on the zirconia amount in the composite. Values between 0.6 and 2 $\mu$m for the upper limit, and between 0.1 and 0.4 $\mu$m for the lower limit, have been found.

### 1.3.3 Subcritical crack propagation in ZTA

Crack velocity curves have been recently determined for three medical-grade ceramics: $\text{Al}_2\text{O}_3$, Y-TZP and ZTA (alumina containing 10 vol. % of unstabilized zirconia)\textsuperscript{25}. The results obtained by De Aza et al. are reported in Figure 9, which shows the crack velocity diagram, plotting $V$ as a function of $K_I$. In these curves the presence of a threshold $K_{I0}$ can be noted, below which an abrupt decrease of the crack velocity propagation can be observed. Alumina has a lower susceptibility to water and stress-corrosion; this is demonstrated by the higher slope of its curve respect to zirconia one. Since in the composite the crack propagation occurs through the alumina matrix, it is possible to keep the benefit of the low susceptibility to stress corrosion of alumina. In fact, the curve obtained for the composite has a similar slope.
of that of alumina. Moreover in the composite material the shift of the diagram $V-K_I$ towards higher values of stress intensity factor is due to the reinforcing effect of zirconia.

The enhancement in the threshold allows a higher reliability than in the monoliths, and the hardness and stability of alumina are kept in the composite, thanks to the limited amount of zirconia (10 vol.%).

![Figure 9 V-K\textsubscript{I} diagram for biomedical-grade of Alumina, Zirconia (3Y-TZP) and Al\textsubscript{2}O\textsubscript{3}-10 vol.% ZrO\textsubscript{2}]

The influence of zirconia aggregates has been studied by De Aza et al. They studied the mechanical behaviour, particularly the slow crack propagation of ZTA composites obtained by different elaboration methods, for instance by a conventional powder mixing technique and by a colloidal route. The results, in terms of zirconia size distribution and crack propagation, are shown in Figure 10. This investigation demonstrated that a colloidal route may lead to a narrower and more controlled distribution of zirconia particles with respect to a conventional process, such as powder mixing (Figure 10 a). Moreover, when the zirconia size distribution ranges between the aforementioned critical values $D_c$ and $D_c'$, so that the main zirconia particle can undergo to stress induced transformation, the mechanical properties are effectively improved (Figure 10 b).
1.3.4 Ageing in ZTA

Few studies about the ageing behaviour of zirconia-toughened alumina have been published. Recently, Deville et al.\textsuperscript{38} studied the changes in crystalline phases due to low-temperature ageing of different yttria doped and non-doped zirconia-toughened alumina composites, under controlled humidity and temperature conditions in autoclave. Moreover, in this study the role of processing route was evaluated, by comparing the behaviour of composites obtained by powder mixing or colloidal route. In this investigation, the Authors observed a rapid ageing in the materials containing stabilized zirconia, in fact all the samples exhibited an increase of about 10% of monoclinic zirconia content after 2 h of ageing (Figure 11 a). All these samples were obtained by powder mixing, and this process led to some zirconia aggregates in the composites, in which an easier degradation was observed, in fact the higher strain energy barrier induced by alumina was missed in the aggregates. This first stage was observed in all
the samples, while a further ageing was only observed in samples containing more than 20 wt% zirconia (corresponding to ∼16 vol.%). This phenomenon is related to the ageing propagation mechanism. Considering that the $t \rightarrow m$ transformation is accompanied by the creation of microcracks, and, if the zirconia content is equal or higher than the percolation value, the microcracks provide a continuous path for water diffusion to one grain to the neighbouring, and also ageing propagates. This explains also why no substantial degradation was observed in samples with lower zirconia content.

Figure 11 Ageing of ZTA composites at 140°C for systems containing 3 mol% $Y_2O_3$ stabilized zirconia (a) and unstabilised zirconia (b)
Concerning the systems containing unstabilised zirconia, two different behaviours were observed as a function of zirconia contents: up to 10 wt% of zirconia, no degradation occurred, as already observed for the second stage in ageing of stabilized systems, because the zirconia amount is lower than the percolation threshold (Figure 11 b). Anyway, ageing occurred when the zirconia content was higher than 16 vol.%, thanks to the possibility for water to diffuse through the microcracks into the volume of the samples. The influence of the processing methods can be appreciated by comparing the ageing behaviour of the samples containing 10 vol.% unstabilised ZrO$_2$, obtained by powder mixing and colloidal route. In the former case, a monoclinic zirconia content of about 65% was constant during the ageing test, being the overall zirconia content below the percolation value, while in the latter a lower monoclinic zirconia content was measured, of about 50 vol.%, thanks to a narrower zirconia size distribution.

An interesting preliminary investigation of the surface degradation of a ZTA femoral heads was carried out by Pezzotti at al. They studied the ageing behaviour of a commercially available femoral head, Biolox Delta, manufactured by CeramTec, which was made of Al$_2$O$_3$-18 vol.% ZrO$_2$, showing that tetragonal-to-monoclinic transformation occurs in the femoral head, because of environmentally assisted processes. They observed that in the initial stage of phase transformation of zirconia grains, a release of compressive residual stresses in the alumina matrix occurred, and with progressing transformation (after medium and long term exposure in water vapour) the alumina phase underwent an increasingly tensile stress state, which ultimately led to grain detachment from the surface.

1.3.5 Wear of ZTA

As aforementioned, the wear of bearing in the THR is a major issue, because the prostheses are prone to failure due to the late aseptic loosening, caused by the osteolytic response to wear debris. In the currently used hip prostheses, wear occurs at the articulating contact areas. Multiple factors influence wear rate in a THR implant, including type of material, contact stress, surface hardness and roughness.

Wear can be measured as volumetric wear, that is the volume of material detached from the bearing surfaces, or as linear wear or penetration, that is the displacement of one bearing surface relative to another. The former type of wear is a result of the articulation, while the latter depends on the contact geometry. For example, for a given set of conditions, the penetration is greater in socket articulating against smaller head prostheses than for the larger one.

In laboratory studies, the wear of the component is often measured through gravimetry, by weighting the device and then converting these values into a volume loss. In vivo wear measurement is usually undertaken by measuring the penetration of the head with respect to the socket, from radiographs, by comparing the post-surgical radiograph and the latest one available.

Data in Table IV compare the wear response for different coupling systems.
Table IV Data for the linear wear rate in sliding wear of bearing couples used in THR

<table>
<thead>
<tr>
<th>Material combination</th>
<th>Linear wear (µm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Cr/UHMWPE</td>
<td>200</td>
</tr>
<tr>
<td>Alumina/ UHMWPE</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Y-TZP/ UHMWPE</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Alumina/Alumina</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Y-TZP/Y-TZP</td>
<td>Disastrous</td>
</tr>
</tbody>
</table>

Screening tests for wear and corrosion, to evaluate materials for hip prostheses, are performed using simplified geometries and methods, as illustrated in Figure 12. The most widely used tests are the pin-on-flat (Figure 12 a) and the annulus-on-flat (Figure 12 b) tests, carried out in the presence of lubricating fluids, such as simulated body fluids or protein containing solutions. Regarding these simplified configurations, the hip simulator can replicate more precisely the in vivo conditions, for instance the motion and load transfer, choosing the angular position of the femoral head and the force components over the cycle, in order to simulate the physiological walking.

Figure 12 Screening tests for the evaluation of wear and corrosion: pin-on-flat (a), annulus-on-flat (b), hip joint simulator (c)
Regarding the behaviour of ceramic-ceramic bearing, the alumina-alumina bearing systems exhibit a very low friction coefficient and linear wear is at least one order of magnitude less than for metal on UHMWPE prostheses, being the wear particles themselves more inert. On the contrary, zirconia-zirconia bearing pairs show the worst results: the high friction coefficient, coupled to the low thermal conductivity (about ten times less than the alumina one) can lead to a local increase of temperature, and this can affect the efficiency of lubrication and promote ageing.

The wear behaviour of ZTA/ZTA bearing couples has been recently studied: Affatato et al. compared the wear in $\text{Al}_2\text{O}_3$-60 vol.% $\text{ZrO}_2$ and $\text{Al}_2\text{O}_3$-80 vol.% $\text{ZrO}_2$ to the pure commercial alumina, finding comparable results for the monolithic and the composite systems.

Similar results have been obtained by Gutknecht, who extensively compared the wear response of the common bearing couples to the wear performance of the $\text{Al}_2\text{O}_3$-10 vol.% $\text{ZrO}_2$ composite. The measured frictional coefficient for the ZTA composite was 0.06, comparable to the $\text{Al}_2\text{O}_3$ one (0.05 ± 0.01). In Figure 13 SEM observations of ZTA and zirconia surfaces, after the wear test, are shown: a visible surface damage can be observed on the zirconia surface, while the ZTA material presents negligible wear.

![Figure 13 SEM observations of ZTA material (a) and Y-TZP (b)](image)

### 1.4 Elaboration of alumina-zirconia composites

In the previous sections, it was discussed about the importance of microstructure features, for a real improvement in the mechanical properties of the alumina-zirconia composites. In fact, the content and the distribution of zirconia grains inside the alumina matrix have a strong impact on the ZTA strength, resistance to crack growth, as well as on the ageing behaviour. For instance, micro-nano composites in which nano zirconia particles are embedded in micron-sized alumina matrix exploited slow crack growth resistance and stability. To achieve the control of microstructural features at different scales, each step of the process, from powder synthesis to sintering, must be carefully set up.

In 1989, Lange discussed about the issue concerning powder processing science and technology for increasing reliability of ceramics. In this paper he supported the need of improving ceramic processing, which, in his opinion, still lacked a clear approach for
controlling microstructure heterogeneity. The powder processing involves some basic steps: powder manufacture, powder preparation for consolidation, consolidation to an engineering shape and, finally, densification —microstructural development. Lange individuated in each step the potential for introducing detrimental heterogeneities, which will persist during further processing and act as stress concentrators and fracture origins. In Figure 14, different heterogeneity typologies are presented as flaw population which limit the material strength.

![Figure 14 Schematic plot of frequency versus potential strength of different flaw population, potentially present in a ceramic material](image)

Figure 14 Schematic plot of frequency versus potential strength of different flaw population, potentially present in a ceramic material

Agglomerates are the major heterogeneity present in powders, induced by forces, such as Van der Waals and capillary forces, responsible for free particle agglomeration. Another problem raises in the common consolidation technology based on dry pressing, where flowable powder are required to uniformly fill a die cavity. To promote powder flowability, ceramic slurries containing polymeric additions are spray dried to obtain large granules, in which the repulsive forces overcome the attractive ones. Lange illustrated as several changes in processing significantly increased the mean strength of ceramics, either by the elimination of flaw or by the reduction of their size, as depicted in Figure 15.
Figure 15 Changes in processing for avoiding stress concentrating heterogeneities and increasing the mean strength of three transformation-toughened ceramics \(^{43}\)

Regarding the specific case of ceramic femoral heads, the manufacturing process, commonly adopted for producing these devices, is schematised in Figure 16, including the following main steps:

1) The selected powder is atomized;
2) The granules are cold pressed, in spherical or cylinder shape, in the latter case the green body undergoes a further shaping step to achieve the final configuration;
3) The green body can be sintered in air;
4) The sintered body undergoes a post-hot-isostatic treatment;
5) The bore is machined, if not done before sintering;
6) The surfaces are ground and polished;
7) The head is marked by laser, for identification;
8) Finally, the product undergoes the inspection.

Current procedures include tightly controlled ceramic processing methods for homogeneous mixing and consolidation of the powders, and processing environments, to minimize inclusions and impurities in the product. The first generation of alumina bearings was produced by natural sintering, while today hot isostatic pressing is commonly used to guarantee the production of fully dense material with a fine grain size.
In order to produce femoral heads made of zirconia-toughened alumina, the choice of the powder elaboration results a major issue. There are two possible approaches: the first is the powder mixing elaboration, that involves the mixing of two commercial powders, and a second way is the \textit{in situ} synthesis of a composite powder. In the following section the most common routes for producing alumina-zirconia composite powders will be described.

Depending on the selected former methods, the composite powder can be optimized for pressing or dispersed in a slip to cast. As aforementioned, the femoral head elaboration provides the isostatic pressing of the powder to form the green body. In this perspective the composite powder must be optimized for flowing and compaction. As a consequence, the powder is generally dispersed and spray dried to obtain granules, suitable for pressing. In the following sections the different requirements for suspensions in view of casting or spray drying and pressing are described.

\subsection*{1.4.1 Composite powder elaboration}

The powder characteristics have a pronounced effect on subsequent processing. Powder synthesis is the first important step in the overall fabrication of ceramics. Since advanced ceramics must meet very specific properties requirements and reliability, the quality of the starting powder must be carefully controlled, in terms of size, size distribution, shape, state of agglomeration, phase composition and surface properties \cite{44}. The characteristics influence the
powder consolidation step and the microstructure of sintered body, for example the use of powder having a particle size greater than 5 µm precludes the colloidal consolidation methods because of the setting time of the particles is too short, or in the case of very fine powders, the densification rate strongly increases with the decrease of particle size, thanks to the higher specific surface. Regarding the size distribution of the powder, even if a wide distribution generally leads to a higher packing density in the green body, the control of the microstructure during sintering can be difficult because the larger grains can rapidly coarsen including the smaller ones. On the other side, the homogeneous packing of a narrow size distribution powder allows a better microstructural control. Also the agglomerates lead to heterogeneous packing in the green bodies, which gives rise to differential sintering rates.

In the case composite materials, the homogeneous powder mixing is required to ensure an even distribution of the reinforcing phase into the matrix in the final material. In fact, a strict control of microstructure, in term of size and distribution of the second phase, is necessary to assure good mechanical properties.

In the case of ZTA different elaboration methods have been exploited, such as powder mixing, sol-gel, co-precipitation, powder-alkoxide mixture, soft solution preparation methods involving the mix of aqueous solutions of inorganic salts. Sophisticated powder processing techniques have been exploited in the last two decades, with the aim of synthesizing more homogeneous powders with controlled specifications.

### 1.4.1.1 Powder mixing

Several papers have shown the role of the second phase dispersion optimization and of a close control of the zirconia particle size, which must be maintained close to the critical transformation size to promote the maximum strengthening and toughening. When powder mixing is performed for producing ZTA composites, microstructural defects, such as zirconia aggregates, or uneven second phase distribution, can arise from the non-optimized or unstable mixed suspension. Therefore, a crucial aspect of the powder mixing process, common to several other ceramic processing, is the optimization of the suspension in terms of dispersion, homogeneity and rheological properties.

The particles suspended in a liquid are subject to electrostatic potential ($V_{\text{elec}}$) due to the electrical double layer around their surface, which can be attractive or repulsive depending upon the charge of the surfaces, and attractive potential ($V_{\text{vdW}}$) due to Van der Waals forces: the total interaction energy ($V_{\text{tot}}$) is given by:

$$V_{\text{tot}} = V_{\text{elec}} + V_{\text{vdW}}$$

where, for two spherical particles, of radius $a$ at a distance $h$, $V_{\text{vdW}}$ can be expressed by:

$$V_{\text{vdW}} = -rac{A}{6} \left( \frac{2a^2}{H^2 - 4a^2} + \frac{2a^2}{H^2} + \ln \left( \frac{H^2 - 4a^2}{H^2} \right) \right) \quad \text{being: } H = h + 2a$$

where $A$ is the Hamaker constant.

$V_{\text{elec}}$ is given approximately by:

$$V_{\text{elec}} = 2\pi \epsilon_0 \epsilon \kappa^2 \ln \left( 1 + e^{-\kappa h} \right)$$
where $\phi$ is the surface potential of the particles, $\varepsilon$ is the dielectric constant of the liquid medium, $\varepsilon_0$ is the permittivity of the vacuum, and $K$ is the Debye parameter, $1/K$, usually referred as Debye length, may be considered the thickness of the double layer and it depends on several experimental parameters, such as ions charge and concentration in the liquid medium.

By electrophoretic technique, the potential of the first compact charged layer on the particle surface, called $\xi$ potential, can be measured and it is an important guide to the stability of colloidal suspensions: greater the absolute value of the $\xi$ potential, more stable is the suspension, otherwise if this value is close to the isoelectric point (IEP) the suspension may rapidly flocculate because the repulsion between particles may not be sufficient to overcome the Van de Waals attraction.

A general trend for $V_{tot}$ as a function of particle separation, for a typical colloid suspension containing ceramic particles showing the same surface charge, is reported in Figure 17.

![Figure 17](image)

Figure 17 Potential energy between two particles in a liquid, resulting from the effect of the Van der Waals attraction and the electrostatic repulsion, due to the electric double layer.

The resultant curve for $V_{tot}$ depends on the relative magnitudes of $V_{elec}$ and $V_{VdW}$. While $V_{VdW}$ is almost constant, $V_{elec}$ can be changed significantly by changing the ions concentration and valence in solution. Moreover, the curve in Figure 17 exhibits a maximum which is the energy barrier that particles have to overpass before coagulating. Some systems may also show a secondary minimum which gives rise to a soft agglomeration.

From the above considerations, it follows that the stabilization of a colloidal suspension can be achieved by three commonly methods:
Electrostatic stabilization, in which the repulsion between particles is based on electrostatic charge on their surfaces;

Steric stabilization, in which the repulsion is produced by an uncharged polymer adsorbed onto the particle surfaces;

Electrosteric stabilization, consisting of a combination of electric and steric repulsion, when a polyelectrolyte (a charged polymer) is adsorbed on the particle surfaces.

The stabilization and homogenization of mixed suspension containing alumina and zirconia powders are concerns of great importance, since often the worsening of mechanical performance has been correlated to the microstructural unhomogeneities, caused by improper powders dispersion. For instance, Deville et al.\textsuperscript{38} observed the presence of a significant amount of very large aggregates, their size was up to 10 µm and they represented roughly 30 vol. % of the total zirconia amount (see Figure 18). In that case, aqueous suspensions of the two powders were obtained, by adding 0.5 or 1 wt.% of an alkali-free organic polyelectrolyte. Moreover, they observed that the zirconia aggregates caused additional degradation, compared to the materials obtained by colloidal route, which were aggregates-free.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ZTA_composite.jpg}
\caption{Microstructure of a ZTA composite containing 10 vol.% 3Y-TZP, obtained by powder mixing technique, the suspension was electrosterically stabilized.\textsuperscript{38}}
\end{figure}

The influence of the dispersant nature was also investigated by Gutknecht\textsuperscript{42}, who found that the electrosteric stabilization could lead to the same rheological properties than electrostatic stabilized suspensions, but in the final ZTA materials a marked dishomogeneity was observed when the polyelectrolyte was used for deflocculating. Examples of the microstructures obtained by Gutknecht, in the case of electrosterically and electrostatically stabilized suspensions, are reported in Figure 19. Moreover, he demonstrated the effectiveness of electrostatic stabilization for the elaboration of ZTA composites, obtained by powder mixing. On the basis of the $\xi$ potential measurements on both the $\text{Al}_2\text{O}_3$ and the $\text{ZrO}_2$ powders (see Figure 20), he optimized the pH of the mixed slurry, operating at pH equal to 4.5, in order to achieve a good dispersion of both the constituents.\textsuperscript{42}
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Figure 19 Microstructure of a ZTA composite containing 10 vol.% 3Y-TZP, obtained by powder mixing technique; the suspension was stabilized electrosterically (a) and electrostatically (b) 42

Figure 20 Zeta potential of 35 wt.% alumina and zirconia slurries as a function of the pH of the slurries 47

A good electrostatic stabilization was achieved also by Leriche et al. 45,46, who developed a processing method to produce high-performance ZTA materials by powder mixing. Particularly, they stabilised each suspension electrostatically, by changing the pH, and just after deflocculation Al₂O₃, ZrO₂ and Y₂O₃ slurries were mixed together, in order to obtain the desired compositions.

1.4.1.2 Chemical methods for the synthesis of ZTA composite powder

Several wet chemical routes for the synthesis of ZTA composite powders were developed, with the aim of improving the control on the size and distribution of both alumina and zirconia grains, and to avoid the possibility of aggregation as shown in the previous section.

Among the several powder processing techniques investigated to synthesize homogeneous composite powders, the precipitation and the sol-gel methods are maybe the most known, already used, for example, in the production of commercial zirconia nano-powders.
The starting precursors used in sol-gel method, for the sol preparation, are inorganic salts or metal-organic compounds, among which the metal alkoxides are the most widely used. Thus, the sol is converted into a highly viscous mass (the gel), by hydrolysis and condensation reactions. These chemical reactions have a significant influence on the homogeneity of the gel. Therefore a basic problem is to understand which parameters, for instance precursor chemical composition, reactant concentration, solution pH, temperature control the reaction rate.

The gel, obtained by the conversion of the precursor sol, contains a large amount of liquid, so it must be dried. The dried gel is referred to as xerogel. Most gels have an amorphous structure after drying and contain rather uniform and fine pores, yielding powders characterized by a high specific surface area. When a dense ceramic is required as final product, a reduction of the sintering temperature is reported as an advantage of the sol-gel route, compared to the production of similar products by the traditional processing routes. The sol-gel processing can provide substantial benefits, in fact it allows to obtain the product in various special shapes directly from the gel state, such as monoliths, films, fibers and particles, to control the homogeneity of chemical composition and to lower the processing temperatures. However, there are also some disadvantages, among which the high cost of metal alkoxides, and the care needed in handling these chemical products, often sensitive to moisture.

For the production of simple oxides, the sol-gel procedure yields to a gel containing one type of metal cation. In the case of complex oxides, the gels contain more than one metal cation, and the primary concern is the prevention of individual component segregation, matching the conditions for hydrolysis and condensation for all the components, to achieve a uniform mixing.
Regarding to the synthesis of Al₂O₃-ZrO₂ composite powders, eventually containing Y₂O₃ to stabilize the zirconia tetragonal phase, the sol-gel method has been used by several Authors, because of the advantages previously reported, primarily the possibility to obtain homogeneous distribution and finer size for the constituents. Lee et al. ⁵¹ reported about the elaboration of Al₂O₃- 50 vol.% ZrO₂(Y₂O₃) nano-composites: the sol-gel composite powder, obtained from the aluminium and zirconium alkoxides, was calcined at 400°C for 1h and pressureless sintered at 1200°C for 2 h, retaining the nano-crystalline phases (less than 20 nm) and reaching 96.2% Theoretical Density (TD). The Authors investigated the thermal evolution of the powder by DTA-TG analyses and X-Ray Diffraction, and they observed that the powder was amorphous after synthesis and cubic zirconia crystallized at 980°C and it transforms into tetragonal at 1200°C, while α-alumina was detected only at 1200°C.

Otherwise, Sarkar et al. ⁴⁹ started from inorganic salts to produce Al₂O₃-5 vol.% ZrO₂ composite powders, via sol-gel. The dried gel was calcined at 900°C for 4 h, the particles size distribution is in the range of 20-200 nm (see Figure 22 a), showing that agglomeration of some primary particles occurred during the thermal treatment. The densification behaviour of this powder is reported in Figure 22 b: high densities were achieved for high sintering temperatures, for example, sintering at 1550°C for 4 h a density of 98.4 % TD was achieved, with very fine zirconia particle in a micron-sized alumina matrix (see Figure 22 c).

![Figure 22](image-url)  
*Figure 22 Al₂O₃-5 vol.% ZrO₂ composite powders, obtained by sol-gel technique, after calcination at 900°C for 4h: TEM image (a), densification behaviour as a function of sintering temperature (b) and SEM micrograph of the final composite material sintered at 1550°C for 4 h (c), the white particles are zirconia, and the arrows indicate residual pores.*
Another important chemical route for the production of powders is the precipitation from a solution. This technique consists in the preparation of an aqueous solution containing the desired cations, than the precipitation in the solution is promoted or by evaporation of the liquid, or by adding a chemical reactant. In both the cases, the solubility product of the species in solution is exceeded, inducing the precipitation of metal hydroxides. The precipitation of particles from the solution occurs by nucleation and growth, and the control of powder characteristics is achieved by controlling the reaction parameters, for instance the temperature, the concentration of metal salts, their chemical composition, the pH of the solution, the presence of anions in the solution. The metal ions are generally hydrated in an aqueous solution: they form soluble hydroxylated complexes by hydrolysis reaction, which are the precursors of the particle nuclei. Uniform particles can be generated from these nuclei, by adjusting the temperature and the pH of the solution; these parameters influence the nucleation and growth mechanisms and consequently the morphology of the particles. Complex oxides are obtained by coprecipitation from a solution of mixed salts. A common problem for coprecipitation is the achievement of a suitable condition for the simultaneous precipitation of all the species present in solution.

Matsumoto et al. \(52\) prepared \(\text{Al}_2\text{O}_3\)-\(\text{ZrO}_2\) composite powders with 5-30 mol% \(\text{ZrO}_2\) by adding ammonia to the mixed solution of aqueous aluminium sulphate and zirconium alkoxide containing 2-propanol. They obtained an amorphous powders by coprecipitation, and followed up the phase evolution during thermal treatments. After calcination at 1200°C for 1 h, the powders were isostatically hot pressed at 1400°C, reaching a mean grain size of 1.5-2.5 \(\mu\)m for alumina and of 0.2-0.7 \(\mu\)m for zirconia, depending on the composite composition.

Some procedures for the production of ZTA starting from a commercial alumina powder and a synthesized zirconia precursor, have been developed. These methods represent a compromise between the powder mixing technique and the chemical ones, often they involve the surface modification of the starting powder, whose particles are coated by the second phase precursor. These techniques allow to limit the inhomogeneity coming from the powder mixing method, and to achieve a deeper control of the final microstructure, by exploiting a simpler procedure, if compared to the sol-gel or coprecipitation ones.

Schehl et al. \(53\) developed a powder processing technique which involved mixture of zirconium alkoxide and a dispersed alumina slurry. This process involved the substitution reaction between the metal alkoxide and the hydroxyls adsorbed on the surface of the alumina particles, as schematized in the Figure 23. Thus, the particle surface is coated with the metal alkoxide. They observed that zirconia crystallized as tetragonal phase at 700°C. The powder was calcined at 850°C for 2 h in order to remove organic residues, and attrition-milled. Finally, the powder was cold isostatically pressed and sintered in air at 1600°C for 2 h. They measured a tetragonal zirconia content of about 91 vol.% in the sintered composites containing an overall zirconia content of 5 vol. %. The mean grain size of alumina was 1.6 \(\mu\)m, while zirconia grains were about 200 nm (see Figure 24).
A similar procedure developed by Rao and Cannon involved the precipitation of hydrate zirconia from zirconium chloride onto a commercial alumina powder. The precipitation of zirconia was carried out as follows: first, the alumina slip was prepared in an aqueous solution containing zirconium chloride, then the complete precipitation of the metal hydroxide was induced by adding NH₄OH. In that study, the influence of the calcination treatment of the composite powder was underlined, in terms of zirconia phase evolution. In fact when the uncalcined powders were slip cast into green bodies, after sintering a low overall percentage of zirconia (both monoclinic and tetragonal) was detected by X-Ray Diffraction, together with very fine zirconia particles that induced to a broad peak at low 2θ° values in the diffraction pattern. Instead, in samples obtained from the same powder calcined at 500°C, pressed and sintered at the same temperature, a higher crystallised zirconia amount was detected. Anyway, no information is reported in this paper about the phase composition and content of crystalline zirconia in the differently calcined composite powders, so it is difficult to clearly explain the mechanism that led to a higher crystallinity degree and to a coarsening of the zirconia grains when the powder was calcined before forming.

Soft solution preparation were investigated by Kikka et al for the production of zirconia in the presence of alumina, from mixed aqueous solution of zirconium and aluminium...
chlorides. This procedure consisted in the preparation of an aqueous solution of zirconium and aluminium species (ratio Al/Zr=0.39) and citric acid. Then, the solution was heated at 80°C under stirring, inducing gelation. A homogeneous mixing of zirconium and aluminium species in the citric gel was achieved. The Authors exploited the same procedure to obtain a composite powder for producing ZTA materials. In that case the aqueous solution containing zirconium, yttrium and aluminium species, with citric acid, was added to a suspension containing α-alumina; the total chemical composition was adjusted to obtain Al₂O₃-5 vol.% 3Y-ZrO₂. They produced large alumina particles covered with zirconia, whose size was about of 10 nm, as shown in Figure 25.

Figure 25 TEM micrograph of alumina powder homogeneously coated by ZrO₂ fine particles, prepared by the citric acid route.

1.4.2 Forming methods

Two common methods for forming ceramic powders into green bodies are described in this section. The desired goal of the forming step is the production of green bodies with homogeneous particle packing having a high density.

The colloidal techniques provide considerable benefits for the control of the packing homogeneity in the green body. The most common forming methods which exploit fully stabilized colloidal suspensions are slip casting and tape casting.

Otherwise, mechanical compaction of dry powder in a die is one of the most widely used operations in the ceramic industry.

1.4.2.1 Slip casting

In slip casting, a slurry is poured into a permeable mould, which has microporous walls to draw the liquid from the slurry into the mould, thanks to the capillarity suction pressure.
The suspension characteristics have the strongest influence on the microstructure of the cast. Generally, the higher the slurries concentration, the higher the green density. Moreover, flocculated slurry leads to a cast with high porosity, while a well-dispersed and stabilized slip containing no agglomerates leads to the formation of a cast with high packing density and homogeneous microstructure. To avoid flocculation, electrostatic and/or steric dispersion is needed, in order to enhance repulsion between particles.

In the case of binary particulate systems, the dispersion degree must be more closely controlled to enhance both the particle packing in the green bodies and the phase distribution. When a dispersant is used, its amount has to be chosen to assure the optimal dispersion of the two constituent in the slurry, taking into account that the powders could have different tendency to adsorb the dispersant, and this could lead to a different dispersing efficiency.

Olhero et al.\(^{58}\) have observed the rheological behaviour of alumina-zirconia slurries, containing different amount of the two powders. They used a polycarboxylic acid as dispersant (Dolapix CE 64) and they measured a higher viscosity in the slurries containing larger amount of zirconia. They explained the observed rheological behaviour taking into account the use of an anionic dispersant, that is a polycarboxylic acid, which has a higher tendency to be adsorbed onto the alumina particle surfaces rather than the zirconia ones. Therefore, they expected a better dispersing efficiency, and consequently a lower viscosity, in the mixture $\text{Al}_2\text{O}_3$-30 wt.% $\text{ZrO}_2$, respect to the $\text{Al}_2\text{O}_3$-60 wt.% $\text{ZrO}_2$ slurry. Such a difficulty regarding the simultaneous dispersion of the powders in the slip, can cause at least a dishomogeneity in the final microstructure, if preferential coagulation of one species occurs.

Galassi et al.\(^{59}\) investigated the correlation between casting parameters and mechanical properties of a ZTA composite, containing 30 wt.% $\text{ZrO}_2$. Particularly, they studied the influence of the solid content and pH of the suspension, keeping constant the others parameters, such as chemical composition and dispersant amount. They found a complex relationship existing between the several parameters. For instance, the higher solid load seemed to promote a higher density both in green and fired bodies, but higher suspension concentration increased the possibility of coagulation, and some aggregates and large pores were present in the sintered parts, which mainly affected the flexural strength.

Suitable suspensions for slip casting could exhibit a compromise between high solid loading, low viscosity and homogeneous dispersion of all the constituent.

### 1.4.2.2 Pressing

Isostatic pressing is the forming technique commonly used in the femoral heads processing. It involves the application of a uniform hydrostatic pressure to the powder contained in a flexible rubber mould. Anyway, as in the case of uniaxial pressing, one of the major issues concerns the optimization of the powder, and particularly its flow behaviour. Fine powders do not flow easily, and are difficult to compact homogeneously. Often, a granulation step is necessary to improve powder quality for pressing; it is performed by spray drying the ceramic slurry.
Spray Drying procedure

During the spray drying procedure, the ceramic suspension is atomized into droplets, which are introduced in a drying chamber where they circulate and consequently are fast dried, finally the granules are separated from the air stream. The granule characteristics depend on several parameters, such as the particle size distribution of the starting powder, the degree of flocculation of the slurry, its rheological features, the nature of additives, and the spray drying conditions. Droplets’ drying occurs in the following stages:

- **Constant drying rate period**: steady drying proceeds as long as the droplet surface remains saturated with liquid. In this stage the droplet shrinkage occurs and the liquid moves from the bulk to the droplet surface, where evaporation takes place. The drying rate remains constant until the particles into the droplet come in contact: at this moment also the shrinkage stops. Often, the moisture content into the droplet, corresponding to the change from constant to decreasing drying rate, is referred as critical.

- **Falling drying rate period**: the drying rate decreases as the liquid-vapour interface recedes into the porous materials until all the liquid evaporates. During this stage any further shrinkage cannot occur.

The key characteristics for granules have been individuated:

1) **Size, size distribution and shape**: granules prepared by spray drying have a nearly spherical shape and size in the range 50-400 µm, with the average size of ∼100 µm.

2) **Particle packing**: the particle packing density in the granule depends on the particle size distribution of the powder, as well as the concentration of the suspension, and its stability.

3) **Hardness**: the granule hardness is controlled by the particle packing density and by the nature of the binder. A high particle density or a hard binder (characterized by a high glass transition temperature) leads to the formation of hard granules which can induce difficulties during pressing.

One common problem that occurs with ceramics slurries is the formation of granules with large craters.

Walker et al. performed a systematic study to determine how the characteristics of spray dried granules are influenced by processing parameters, such as the binder type, the deflocculant level, and the spray dryer type. Particularly, the influence of the rheological characteristics of the suspensions on the granules quality was emphasized. The slurry viscosity was described using the Casson equation:

\[
\tau^{1/2} = \tau_y^{1/2} + \eta_w^{1/2} \dot{\gamma}^{1/2}
\]

where \(\tau\) is the shear stress, \(\dot{\gamma}\) is the shear rate, \(\tau_y\) is the yield stress, and \(\eta_w\) is the viscosity limit for infinite shear rate. The parameters \(\tau_y\) and \(\eta_w\) have a clear physical significance for a flocculated slurry. Interparticle attractive forces cause a network of weakly bonded particles, which makes more difficult the flow of the suspension. A finite \(\tau_y\) is required to initiate flow;
as the slurry is sheared, the floc structure breaks down and at high shear rate the viscosity approaches $\eta_\infty$. Thus, the yield stress $\tau_y$ is influenced by the degree of suspension flocculation, and, consequently, by the presence and the amount of the dispersant: generally an optimal dispersant concentration can be individuated to minimize $\tau_y$. Instead, the $\eta_\infty$ is independent of deflocculant level, which means that the flocculated structure is broken at high shear rates. $\eta_\infty$ is mainly influenced by the binder type and solid content.

Moreover, Walker found that the granule size distribution was influenced by the suspension solid content, while the mean granule size increased with the increase of the slurry $\eta_\infty$.

Regarding the granule shape, granules with a large central void have been commonly observed, and this characteristic is related to the flocculation level of the suspension. Mahdjoub et al. observed that granules prepared from a dispersed Y-TZP slurry resulted in hollow shapes characterized by the presence of a single large open pore, while granules obtained from a flocculated suspension resulted in full or solid granules, i.e. without a central void.

Similar results are reported by Walker et al. for an alumina suspension. In that case, the suspension was electrosterically stabilized, and $\tau_y$ was found to be the fundamental parameter influencing both the granule density and shape. They proposed a mechanism for the granules formation, which is described in Figure 28. As the slurry is atomized, droplets form at high shear rate, but once the droplets leave the atomizer, the shear rate quickly decreases to zero, and the rheological behaviour is dominated by the slurry yield stress. The yield stress increases with temperature, therefore a gelation of the slurry occurs as the droplet temperature rises. In addition, both $\tau_y$ and $\eta_\infty$ increase as the liquid evaporates. Drying continues until the critical moisture content is reached, when the shrinkage stops and the diameter of the granule is established. If the yield stress of the suspension is weak (Figure 28 a), for a deflocculated slurry, the particles are mobile and they can migrate towards the droplet surface with the liquid. Particle packing density in the droplet surface increases as water is removed, leaving an internal void. One side of the granule may collapse inward because of the pressure difference between the internal void and atmosphere. Instead, when the slurry yield stress is sufficiently high, the particles difficulty move, they cannot migrate with water towards the droplet surface and a solid granule is formed (Figure 28 b). The influence of the slurry yield stress on granule morphology is also reported in Figure 29.

The granules obtained from deflocculated slurries present a higher density than that resulting from flocculated suspensions, since the particle packing density in the granule shell is higher than that in the full granules, where particles occupy the total granule volume.

Some examples of granules obtained by Walker et al. are reported in Figure 30.
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Figure 28 Mechanism for the formation of hollow granules, for deflocculated slurries (a) and full granules, for flocculated slurries (b) ⁶⁰

Figure 29 Influence of the slurry yield stress on granule morphology ⁶⁰
The influence of granule morphology on the mechanical properties of sintered bodies has been investigated by several Authors, often obtaining different results, because of the multiplicity of variables, which play an important role on the granules features, and consequently on both the green and sintered microstructures. While Walker and Reed found that the granule morphology had no influence on the strength and on the Weibull modulus of the sintered alumina samples, other Authors reported about the strength variation of sintered bodies due to the changing in spray drying conditions. Hotta et al. observed the decrease in fracture strength of samples containing different types of flaws, and they imputed the origin of that defects to incomplete collapse of dimples in granules or to the persistence, after sintering, of the interstices between undeformable granules. An example of a flaw due to the internal pore of the granules is reported in Figure 31.

Also the nature and amount of the binder play a complex role in the reliability of the final materials, influencing the deformability of granules, but also, sometimes, affecting the homogeneity of the microstructure, if migration of the binder towards the granule surfaces occurs during spray drying (see Figure 32). The compaction of granules is influenced by their hardness and their size distribution. The compaction process, in fact, can be divided in two stages: the rearrangement of the granules, at low pressure, and the deformation at higher pressure. Hard granules easily rearrange, but, if too hard, they are difficult to be deformed giving rise to large intergranular pores in the green body. These pores can be removed during natural sintering, affecting the final properties of the material. As already stated, the granule hardness depends on the particle packing and on the properties of the binder, such as its transition temperature.
1.4.3 Conclusions

In this chapter the interest for developing ZTA composites in the orthopaedic field has been discussed. This composite offers several advantages, allowing the coupling of the good properties of alumina, for instance the hardness, chemical inertia, biocompatibility, and the particular properties of zirconia, such as toughness, avoiding or limiting the drawbacks of the two monolithic materials.

The aim of this study is the development of a zirconia-toughened alumina composite, starting from the elaboration of a composite powder which could be actually used in the production of biomedical devices, matching both the technological requirements, coming from the industrial process, and the operative ones, related to the specific application. All the elaboration steps will be analyzed, in view of a process tailoring that leads to the production of femoral head prostheses.
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References

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